Trace Elements in Soils and Plants

Third Edition

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Preface to the Third Edition

Eight years have passed since the second edition of *Trace Elements in Soil and Plants* appeared. During this period there has been a real explosion in research and public interest related to trace elements in the environment. An incredible number of publications have recently focused on the significance of chemical balance to a safe environment and human health.

I have tried to continue the goal we set for the two earlier editions of this book, which was to provide a brief but informative introduction to the biogeochemistry of trace elements in the soil–plant system. The new edition incorporates up-to-date data from about 400 recent sources and highlights the significance of anthropogenic factors in changing the trace element status in soils and plants. Some of the most destructive impacts of man are changes in the natural cycling of chemical elements, and in particular of trace elements.

New data are especially selected to present knowledge on hot topics, such as (a) assessment of natural/background content of trace elements in soil, (b) bioindication of chemical status of environmental compartments, (c) soil remediation, and (d) hyperaccumulation and hyperextraction of trace metals from soil.

Contemporary legislation related to environmental protection and public health, at national and international levels, is based on data that characterize chemical properties of environmental compartments, especially of our food chain. Thus, quality of the environment and food is now a matter of public concern, and, therefore, a system in metrology in trace analysis has recently been developed at the international level.

As stated previously, the author's intent is to provide a broad but concise background on the subject, and to accomplish this, selectivity of data is necessary. This inevitably leaves the work of many investigators uncited. I regret the many omissions that such an approach has necessitated.

This volume offers a current review of recent soil–plant chain findings and is an excellent text that should be a requirement for all students entering environmental and agricultural professions. The information on the health-related significance of trace elements in foods makes this edition valuable for other readers as well.

The third edition of this book has been written without the second author, my late husband Henryk. The lack of his assistance was a real burden.

Alina Kabata-Pendias
August 2000

The Authors

Alina Kabata-Pendias, Ph.D., D.Sc., Professor Ordinary of Environmental Geochemistry, was head of the Trace Elements Laboratory of the Institute of Soil Science and Plant Cultivation in Pulawy, Poland, for over 30 years. Today, after 50 years at the Institute in Pulawy, Alina Kabata-Pendias holds the title of Professor Emeritus. She is the author of over 290 publications, including three chapters and four books on the occurrence of trace elements in natural and contaminated soil–plant environments. She is also co-editor of 14 volumes on ecological and methodical problems related to trace elements in the environment (published mainly in Polish).

Professor Kabata-Pendias also worked for 30 years at the Geological Survey in Warsaw on the mobility of trace elements and on the alteration of minerals in weathered zones of various geological formations.

She has been a visiting scientist at various scientific centers in several countries and was a Fellow of the Rockefeller Foundation at the U.S. Soil Plant and Nutrition Laboratory in Ithaca, NY.

Professor Kabata-Pendias is a member of international scientific societies and belongs to scientific societies and committees in Poland. She has been active as a member of workshops and advisory boards of various groups of FAO, UNEP, MAB, and SCOPE. She has also served as an invitational reviewer for numerous manuscripts in international journals and is currently serving on the editorial board of *Environmental Geochemistry and Health.*

It is with sadness that we report that Dr. Henryk Pendias (1921–1994), co-author of the first and second editions, has passed away.

He was for 28 years a head of the Department of Petrography, Mineralogy, and Geochemistry of the Geological Survey in Warsaw, Poland. He had been a member of the staff of this institute since 1950. His geochemical studies resulted in over 60 publications, including three books.

The chemistry of various geological formations, the distribution of trace elements in rocks and minerals, and the impact of biogeochemical processes on the mobility of elements in geological environments were the main subjects of his research. He initiated research on the distribution of trace elements in coals of Lower Silesia. He also devoted much time and attention to methodical and analytical studies in geochemistry.

Dr. Pendias attended many national and international scientific meetings. He was a founding member of the Mineralogical Society of Poland and a vice chairman of its Warsaw branch. For many years he was a member of the Geological Society.

THE PERIODIC TABLE OF ELEMENTS

The elements are arranged in order of atomic number, within the groups and subgroups. The symbols given in thin letters indicate the elements not occurring naturally in the environment.

Ia																	0
1 **H**	IIa											IIIa	IVa	Va	VIa	VIIa	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 Tc	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	57 * **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89 ** **Ac**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**									

* lanthanide series	58 **Ce**	59 **Pr**	60 **Nd**	61 Pm	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
** actinide series	90 **Th**	91 **Pa**	92 **U**	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Note: According to an IUPAC recommendation, the main and subgroups should be numbered 1-18.
The subgroup VIIIb has three columns numbered 8, 9 and 10.

LIST OF UNITS, SYMBOLS, AND ABBREVIATIONS

Basic units of the International System (SI) have been guidelines for the units used in this book. Some notable exceptions have been made in order to maintain the necessary links with practical usage.

Unless otherwise specified, the concentration of a trace element in soils and plants is based on the total content by weight of the element in air-dried or oven-dried material.

Units

kg — kilogram; kg = 10^3 g
g — gram = 10^{-3} kg
mg — milligram; mg = 10^{-3} g
μg — microgram; μg = 10^{-3} mg
ng — nanogram; ng = 10^{-3} μg
pg — picogram; pg = 10^{-3} ng
°C — temperature in degrees Celsius
Bq — Becquerel
Ci — Curie
mCi — milliCurie; μCi, microCurie; nCi, nanoCurie; pCi, picoCurie
ha — hectare; ha = 10,000 m^2
L — liter; L = 1 dm^3
mL — milliliter; 10^{-3} L
m^3 — cubic meter; $m^3 = dm^3 \times 10^3$

Symbols

ppm — $\mu g\ g^{-1} = mg\ kg^{-1} = g\ t^{-1}$
ppb — $10^{-3}\ ppm = ng\ g^{-1} = \mu g\ kg^{-1} = mg\ t^{-1}$
M — concentration in terms of moles per liter
mM — millimole; μM, micromole; nM, nanomole
eq — equivalent of an ion is expressed as a ratio of molar weight to the valency of this ion
meq — milliequivalent
N — concentration in terms of milliequivalents per liter
hr — hour

Constants

Eh — electrical potential (volts, millivolts)
pH — minus logarithm, base 10, of H^+ concentration
p — minus logarithm, base 10, of an ion activity
G — free energy (enthalpy) (kcal)

Abbreviations

AAAc — ammonium acetic acid
ADI — acceptable daily intake
ADP — adenosine 5′-(trihydrogen diphosphate)
ATP — adenosine 5′-(tetrahydrogen triphosphate)
AW — ash weight basis of samples
BAC — biological absorption coefficient
B.P. — before the present time (used in expressing geologic time)
DNA — deoxyribonucleic acid
DOC — dissolved organic carbon
DTPA — diethylenetriaminepentaacetic acid
DW — air dried or oven dried (up to 70°C) weight basis of samples; weights in text are DW unless otherwise stated
EDDHA — ethylenediamine-di(*o*-hydroxyphenylacetic acid)
EDTA — ethylenediaminetetraacetic acid
FA — fulvic acid
FW — fresh or wet weight basis of samples (used mainly in relation to plant material)
HA — humic acid
IBA — index of bioaccumulation

OM — organic matter
PTWI — provisional tolerable weekly intake
RDA — recommended daily allowance
REE — rare earth elements
RNA — ribonucleic acid
sp. — species
TEA — triethanolamine
TF — transfer factor

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Appendix
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Acknowledgment

I would like to take this opportunity to thank all the scientists who have worked with me and encouraged me for the past 50 years, since I first began my study of the occurrence and behavior of cobalt in the soil–plant system. There are too many, all over the world, to mention all, but I would especially like to express my appreciation to Dr. Anna S. Knox, Dr. Arun B. Mukherjee, and Prof. Dr. Alexander A. Ponizovsky for readily providing me with relevant publications. I would also like to thank all my colleagues and Prof. Dr. Severyn Kukula, Director of the Institute of Soil Science and Plant Cultivation in Pulawy, for their support during the preparation of the third edition of this book.

Dedicated to the Memory of My Husband
Henryk Pendias,
co-author of the 1st and 2nd editions

CHAPTER 1

The Biosphere

The biosphere, also called the ecosphere, is the natural environment of living things and is the complex biological epidermis of the Earth whose dimensions are not precisely defined. It consists of the surficial part of the lithosphere, a lower part of the atmosphere, and the hydrosphere. Chemical and physical characteristics of the biosphere are determined by these other spheres, which have created relatively constant environments for the existence of living matter in a given ecosystem. The ecosystem is a fundamental environmental system consisting of the community of all living organisms in a given area and having a balanced cycling of elements and energy flow. This is a homeostatic interrelationship between the nonliving (abiotic) environment and the living organisms (biotic environment).

In general, the biosphere consists of three main ecosystems—the land environment, the freshwater environment, and the marine environment. These fundamental ecosystems include several smaller systems of variable dimensions and conditions. A significant part of the ecosystems has already been considerably modified by man, and such modification will continue.

The energy of life is derived from the radiant energy of the sun, which drives the chemical reaction of photosynthesis. The other sources of energy, such as geothermal energy, gravitation, and electric potentials, are of negligible importance in the total energy flow; however, they may determine some conditions of ecosystems.

The beginning of life on Earth, according to one of the existing concepts, is related to silicates and aluminosilicates of chain coordination. Especially some montmorillonite in gel forms exhibited an ability to synthesize proteins. Yushkin and Khlubov[1567] discovered the presence of various amino acids (glutamine, glycine, alanine, histidine, etc.) in montmorillonite found in hydrothermal deposits, enriched in several trace elements, including Be, Mn, Cu, Zn, Pb, Ti, Sr, Ba, F, and REEs. The structural variability of silicate chains and susceptibility to bind with organic compounds due to piezoelectricity are believed to be processes that stimulate the beginning of life.[1450a]

Biochemical processes of producing organic matter in the Earth's environment are dated from the Early Precambrian Period, that is, over 3×10^9 years B.P. (before the present time). The entire process of photosynthesis has been calculated to have developed about 1.5×10^9 years B.P. Since that period, several million kinds of living organisms have developed evolutionarily and have adjusted to their natural environments.

Most mineral nutrients for all life on land are supplied mainly from the soil overlying the surficial lithosphere. The atmosphere is a source of only some of the essential nutrients (N_2, O_2, and CO_2), and the hydrosphere is the main source of water—a basic constituent of all life.

The bulk mass of living matter (above 90%) is composed mainly of organic compounds and water. Organo-mineral compounds and mineral compounds form a relatively small portion of living matter. The bulk of living matter is formed from the chemical elements C, O, H, and N. Such elements as K, P, Ca, Mg, S, Na, and Cl are present in living organisms in smaller and variable amounts. All these elements are readily mobile in the biosphere and are known to form either volatile or easily soluble compounds that are involved in major environmental cycles.

Many elements occur in trace amounts in living matter. Some of these elements are essential for the growth, development, and health of organisms. Usually, the quantitative differences between essential amounts and biological excesses of these elements are very small. Some trace elements seem to be essential to vital processes but their biochemical functions are not yet understood. The essentiality of other trace elements may be discovered in the future.

The chemical composition of living matter has developed and adjusted to the chemistry of environments over long periods of geologic time. However, all organisms, in order to survive in the complex geochemical composition of their surroundings, had to develop mechanisms of active selection of elements involved in vital processes and of rejection of toxic excesses of other elements. These processes are fundamental for homeostasis that is requisite to the existence of each organism.

Although all living organisms, plants in particular, show a natural ability for the selection of chemical elements, they are also highly dependent on the geochemistry of their surroundings. Any environmental factor that has an adverse effect on plants may cause either evolutionary or drastic changes even over short periods of time, involving only a few generations in the life of a plant species. These phenomena have been easily observed in evolving tolerance of populations, especially of microorganisms, to high concentrations of trace elements in either natural geochemical provinces or under man-induced conditions. This evolution of the biosphere is fully described in Williams' statement[1185]: "Evolution through natural selection implies that there must be a drive within biology to readjust the given accidental abundance of the Earth's crust so as to optimize biological chemistry."

Although biological selection of the chemical elements allows plants to control their chemical composition to a certain extent, these controls are somewhat limited with respect to trace elements. Therefore, concentrations of trace elements in plants are often positively correlated with the abundance of these elements in soils and even with the abundances in underlying rocks. This correlation creates several problems for both plants and animals that may be associated either with a deficiency or an excess of trace elements. The questions surrounding how, and how much of, a trace element is taken up by plants from their environments have been very active topics of research in biological circles in recent years. At a time when food production and environmental quality are of major concern to man, a better understanding of the behavior of the trace elements in the soil-plant system seems to be particularly significant.

Biological processes depend on the flow of energy and elements (Figure 1). Sun energy is a fundamental factor that drives all reactions which govern the transfer of elements among the environmental compartments. Global biogeochemical cycles are crucial for the survival of life on Earth in its present form. The major biogeochemical cycles were studied extensively.[949] Each essential element in various forms flows from the nonliving (abiotic) to the living (biotic) components of the biosphere and back to the nonliving again. These cycles vary from one element to another, but each cycle consists of basic phases: gaseous, solution, and sedimentary. Cycles can be considered as having an exchange pool (mobile stage of an element) and a reservoir pool (immobile stage of an element). A reservoir pool is related to a sedimentary phase, including soil.

Trace element cycles are closely associated with major element cycles, but are much less understood. Some recent data on trace element behavior in both the natural environment and that modified by human activities are reviewed by several authors.[922,1137,1155]

Soil is not only a part of the ecosystems, but also occupies a basic role for humans, because the survival of man is tied to the maintenance of its productivity. Soil has very important and complex functions as filter, buffer, storage, and transformation system, protecting the global ecosystem against the effects of pollution. These functions of soil are not unlimited, but are effective as long as soil properties and natural balance are preserved.

CHAPTER 2

The Anthroposphere

I. INTRODUCTION

The role of man in the biosphere has been so important recently that it has become necessary to distinguish the anthroposphere—the sphere of man's settlement and activity. The anthroposphere, however, does not represent a separate sphere, but can be applied to any part of the biosphere that has been changed under an influence of technical civilization.

Man's impact on the biosphere has been very broad and complex, and most often has led to irreversible changes. Primitive man interfered little with relatively stable relationships within his environment. A growing capability of man to alter his surroundings and to control several natural processes is a source of drastic changes altering the balance of fragile natural systems based upon the balanced flow of elements and energy (Figure 1). While geological and biological alterations of the Earth's surface have been very slow, changes introduced and/or stimulated by man have accumulated extremely quickly in recent years. All man-made changes disturb the natural balance of each ecosystem that has been formed evolutionarily over a long period of time. Thus, these changes most often lead to a degradation of the natural human environment. Since the development of agricultural activities, several ecosystems have been altered into artificial agroecosystems. Although man's impact on the biosphere dates back to the Neolithic Period, the problems of the deterioration of ecosystems due to pollution became increasingly acute during the latter decades of the 20th century.

Environmental pollution, especially by chemicals, is one of the most effective factors in the destruction of biosphere components. The most detrimental anthropogenic impact on the biosphere is related to emissions of various acids (e.g., H_2SO_3, H_2SO_4, HF, HNO, HNO_3) and radionuclides. For example, according to Yanshin,[1561] 769 technogenic accidents occurred on the Earth in 1992, of which 4.7% released different pollutants, mainly acids and radionuclides, to the atmosphere.

Among all chemical contaminants, trace elements are believed to be of a specific ecological, biological, or health significance. Cawse[960] emphasized that the interactions between gaseous pollutants and atmospheric trace metals are an important consideration; for example, the aqueous phase oxidation of SO_2 to SO_4^{2-} is catalyzed by Mn, and the formation of HNO_2 aerosol from NO_2 is increased by Cu, Mo, and Zn. Many textbooks have been published on trace elements as pollutants in the biosphere or in particular ecosystems, and all have pointed out the triangular relationships between contents of inorganic trace pollutants in air, soil, and plants.

Energy and mineral consumption by man is the main cause of trace element pollution in the biosphere. An estimation of the global release of trace elements as contaminants into the environment may be based on the established world mineral and energy consumption. A previous estimation of the demand for the elements calculated for the year 2000 (second edition of this book) was overestimated for some metals (e.g., for Fe, Al, Li, U, Hg, and Ta). In most cases, however, the forecast for the year 2000 was close to mining of the elements in the last decade (Table 1). Also, the forecast

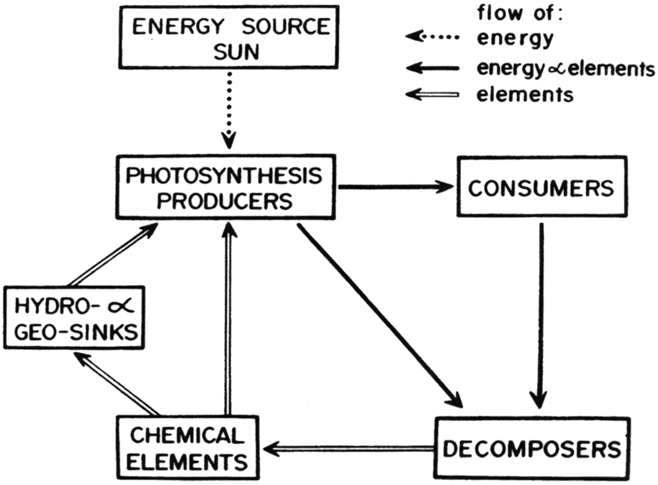

Figure 1 Schematic model of chemical element transport and energy flow in the environment.

for consumption of raw energy materials in the year 2000 was much larger than the production/consumption estimated in 1997 and 1998 (Table 2). It is noteworthy, however, to emphasize that the highest increase has been noticed in crude oil production and hard coal production in the past two decades. Bowen[94] has suggested that when the rate of mining a given element exceeds the natural rate of its cycling by a factor of ten or more, the element must be considered a potential pollutant. Thus, the potentially most hazardous trace metals to the biosphere may be Ag, Au, Cd, Cr, Hg, Mn, Pb, Sb, Sn, Te, W, and Zn. This list does not correspond closely to the list of elements considered to be of great risk to environmental health—Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn.

Present-day soils contain trace elements of various origins. *Lithogenic* elements are those that are directly inherited from the lithosphere (mother material). *Pedogenic* elements are of lithogenic origin also, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes (Chapter 3, Section III). *Anthropogenic* elements are all those deposited into soils as direct or indirect results of man's activities. There have been assumptions that the behavior of trace elements in soils and in consequence their bioavailability differ as to their origin.[381,469] Several recent findings, however, have clearly indicated that regardless of forms of the anthropogenic metals in soils, their phytoavailability is significantly higher than those of pedogenic origin.[1019,1255,1357] Thus, it is most likely that under similar soil conditions, both *lithogenic* and *pedogenic* trace elements will be less mobile and less bioavailable than *anthropogenic* elements (Figure 2).

Trace elements released from anthropogenic sources have entered the environment and have followed normal biogeochemical cycles. The transport, residence time, and fate of the pollutants in a particular ecosystem have been of special environmental concern. The behavior of trace elements in each ecosystem is very complex and therefore has usually been studied separately for air, water, soil, and biota. The urgent environmental problem at the present time is closely associated with pollution in which trace metallic pollutants play a significant role. Ramade[1125] made a lapidary statement on this topic: "Unrecognized, if not deliberately ignored for far too long, the problem of pollution has quite recently become a constant preoccupation of the industrialized nations."

The principal criteria used to estimate trace element threats are: bioaccumulation, toxicity, and persistence. Evaluating environmental persistence in trace element contamination is the most difficult. It is commonly referred to as half-lives of an element in a given environment. Webster et al.[1540] discussed the feasibility of applying half-life criteria and emphasized the need for full consideration of such approaches.

Table 1 World Mining (Tonnes-Megagrams) of the Elements in 1988 and 1997[1357, 1458]

Element	1988	1997	Element	1988	1997
Antimony (18)[a]	81,662	96×10^3 [1992][b]	Molybdenum (16)	108×10^3	136×10^3
Arsenic (21)	46×10^3	37×10^3 [1992]	Nickel (13)	866×10^3	1022×10^3
Barium (9)	3357×10^3	3245×10^3 [1992]	Niobium (25)	19,154	15,749
Beryllium (28)	9832	8452 [1992]	Lead (10)	3285×10^3	2817×10^3
Bismuth (31)	3320	3398 [1992]	Palladium (37)	100 [1984]	112 [1995]
Boron (11)	2995×10^3	2608×10^3 [1992]	Platinum group	—	146 [1995]
Bromine (14)	370×10^3	379×10^3 [1992]	Rhenium	—	31 [1995]
Chromium (7)	4438×10^3	3750×10^3	Mercury (29)	5145	3089
Tin (15)	200×10^3	216×10^3	Rubidium (43)	<1 [1986]	5 [cp]
Zinc (5)	7133×10^3	7036×10^3	Selenium (33)	1600 [1986]	70,000 [cp]
Zirconium (12)	929×10^3	766×10^3 [1992]	Silver (26)	14,559	14,542
Fluorine (6)	4929×10^3	3846×10^3 [1992]	Strontium (17)	86,000 [1976]	157×10^3
Gallium (41)	25 [1984]	145 [cp][c]	Thallium (42)	20 [1979]	14 [cp]
Germanium (36)	100 [1984]	270 [cp]	Tantalum (34)	490	353
Aluminum (2)	$17{,}497 \times 10^3$	$21{,}804 \times 10^3$	Tellurium (38)	100 [1986]	269
Hafnium (40)	27 [1984]	60	Thorium (35)	270 [1977]	13,000 [c.m.][d]
Indium (39)	60 [1984]	145	Titanium (8)	4281×10^3	3472×10^3
Iodine (27)	12,586	15,354	Uranium (19)	60,860	38,840
Cadmium (24)	20,800	19,675	Vanadium (23)	36,000	27,000
Cobalt (22)	43,695	24,800	Tungsten (20)	51,244	30,995
Lithium (30)	4500 [1979]	4043 [1995]	Gold (32)	1797	2222
Manganese (4)	8650×10^3	6699×10^3	Iron (1)	$553{,}463 \times 10^3$	$528{,}981 \times 10^3$
Copper (3)	9356×10^3	$11{,}386 \times 10^3$			

[a] In parentheses ( ) is given an order based on mining quantity in 1988.

[b] In brackets [ ] is given a year of mining other than in headings.

[c] [cp] is capacity of production.

[d] Thorium is given as concentrated monacite, [c.m.].

Table 2 World Demand for Raw Energy Materials

Raw Product	Production (Mt) In 1974	Production (Mt) In 1998[a]
Coal, hard	2227	3975 (2916)[b]
Coal, lignite, brown	842	886
Crude oil	2792	3600
Natural gas[c]	1255	2350[d]

[a] *Source: Mining Magazine*, September 1999.

[b] *Source: Mining Journal, Suppl. Review*, 1999.

[c] In $m^3 \times 10^9$.

[d] Data for 1997.

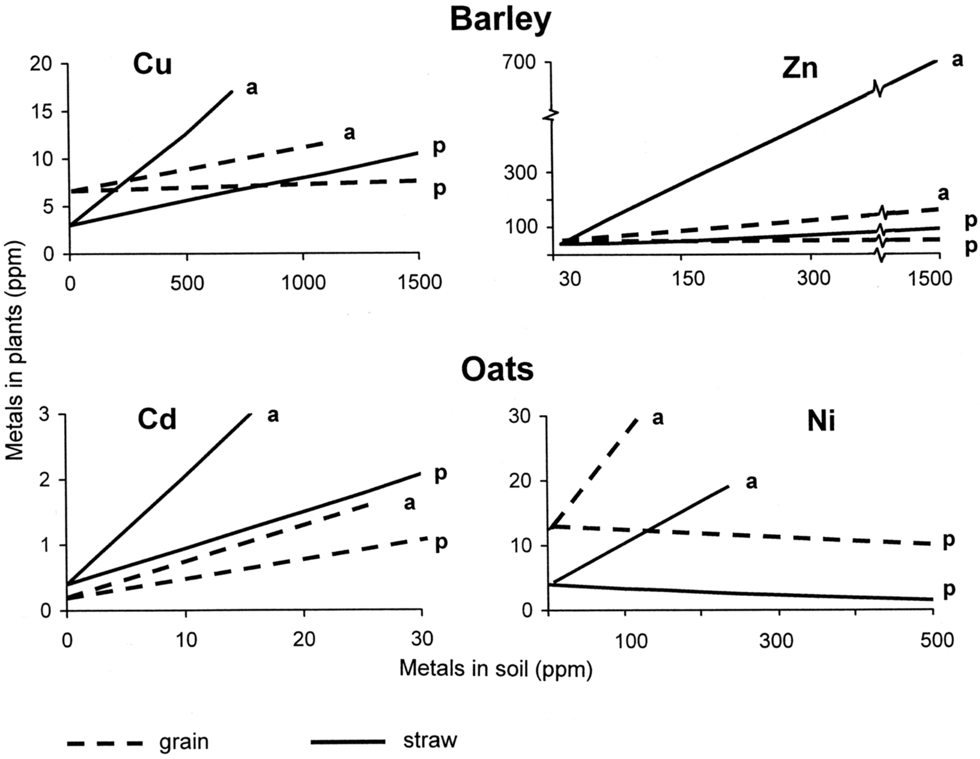

Figure 2 Trace metal uptake by barley and oats as influenced by the metal's origin, presented as multiple linear regression. Sources of metals: (a) anthropogenic, and (p) pedogenic. (Modified from Chlopecka,[1255] and Grupe and Kutze.[1018])

II. AIR POLLUTION

Most air pollution has arisen from the burning of coal and other fossil fuels and from smelting of iron and nonferrous metals. The steady global increase of trace element concentrations in the atmosphere is illustrated in Table 3. Some trace pollutants, most likely Se, Au, Pb, Sn, Cd, Br, and Te, can exceed 1000 times their normal concentration in air. In general, elements that form volatile compounds, or are present at a lower particle radius, may be readily released into the atmosphere from the burning of coal and other industrial processes. Materials released by man's activities are not the only contribution to global air pollution; some natural sources such as eolithic

Table 3 Trace Elements in Air from Different Locations

Element			Shetland	Europe			America		
(ng m^{-3})	South Pole	Greenland	Islands	Norway	West Germany	Japan	North	Central	South
Al	0.32–0.81	240–380	60	32	160–2900	40–10,600	600–2330	760–880	460–15,000
As	0.007	—	0.6	1.9	1.5–53	0.3–120	2–40	—	—
Be	—	—	—	—	0.9–4	5–100	0.1–0.3	—	—
Br	0.38–1.41	14–20	15	4.4	30.5–2500	1.6–150	6–1200	65–460	2–200
Cd	0.015	0.003–0.63	0.8	—	0.5–620	0.5–43	1–41	—	—
Cr	0.003–0.01	0.6–0.8	0.7	0.7	1–140	1.3–167	5–1100	1–2	1–8
Cu	0.03–0.06	—	20	2.5	8–4900	11–200	3–153	70–100	30–180
Fe	0.51–1.19	166–171	90	48	130–5900	47–14,000	829–2000	554–1174	312–9225
I	0.08	—	4	0.6	3–15	6	40–6000	—	—
Mn	0.004–0.02	2.8–4.5	3	3	9–210	5.3–680	60–900	14–16	4–330
Mo	—	—	0.2	—	0.2–3.2	—	1–10	—	—
Ni	—	—	4	1.2	4–120	1–150	120	—	—
Pb	0.19–1.2	15–22	21	—	120–5000	19–1810	45–13,000	0.2–317	11–344
Sb	0.001–0.003	0.9–45	0.4	0.3	2–51	0.13–63	1–55	0.8–15	1–24
Sn	—	—	—	—	1.5–800	—	10–70	—	—
Ti	—	—	10	2.6	22–210	5–690	10–230	—	—
V	0.0006–0.002	0.8–1.4	3	1.9	5–92	1.5–180	4–174	7–200	7–91
Zn	0.002–0.051	18–41	15	10	550–16,000	14–6800	88–741	60–182	25–1358
(pg m^{-3})									
Ce	0.8–4.9	—	100	60	360–14,000	100–18,000	20–13,000	—	—
Co	0.1–1.2	70–150	60	60	390–6790	44–6000	130–2200	250–650	120–360
Cs	—	—	40	20	60–1500	16–1500	70–300	—	—
Eu	0.004–0.02	—	4	—	5–80	7.3–27	10–1700	—	—
Hf	—	40–60	—	—	300	18–590	0.5–290	60–70	40–760
Hg	—	40–80	40	10	170–11,200	1600	70–3800	70–120	70–690
In	0.05	—	20	—	30–360	1200	20–140	—	—
La	0.2–1.4	50–110	200	30	610–3420	53–3000	490–9100	440	290–3400
Sc	0.06–0.21	30–40	15	5	30–700	5–1300	80–3000	150–220	60–3000
Se	4.2–8.2	170–360	500	260	150–11,000	160–21,000	60–30,000	280–1210	50–1530
Sm	0.03–0.09	10–12	10	3	240–420	9.8–320	70–1000	30–80	30–630
Ta	—	10–30	—	—	—	6–100	50–280	20–50	20–150
Tb	—	1–5	—	—	10	—	19–34	8–27	20–120
Th	0.02–0.08	20–40	20	11	30–1000	16–1300	50–1300	10–20	30–1050
U	—	—	—	—	20[a]	—	<500	—	—

[a] Median values for Europe.

From References 94, 381, and 395.

dusts, volcanic eruptions, evaporation from water surfaces, and others should also be taken into account. Buat-Ménard[957] calculated that emissions of trace elements in the Northern Hemisphere are several times higher than in the Southern Hemisphere and are about 80% and 30%, respectively, of anthropogenic origin. A sharp increase in technogenic fluxes of trace elements has occurred in recent times. Pacyna[1112] estimated the anthropogenic emissions of trace elements in Europe. Calculated deposition of atmospheric trace pollutants on the land surface is (average, in g ha^{-1} year^{-1}) 7 As; 0.05 Be; 3 Cd; 20 Cr; 17 Cu; 17 Ni; 156 Pb; 0.5 Se; 38 V; and 88 Zn. These values are fairly similar to those measured at the individual sites in Europe.[1112]

Relatively high atmospheric concentrations in both southern and northern remote regions of the Earth are observed for Se, Sb, Pb, and Cd.[1222] Calculated values of the enrichment index of elements for the atmospheric deposition in Norway are as follows:

- >1000 for As, Cd, and Sb
- >100 for Cu, Ni, Pb, and Zn
- >10 for Cr, Sr, and V

The atmospheric deposition of trace elements, mainly the heavy metals, contributes to contamination of all other components of the biosphere (e.g., waters, soils, and vegetation). This deposition has been widely reviewed, especially by Rühling and Tyler,[669] Folkeson,[238] Jenkis,[1037] and Thomas,[780] and it has been established that mosses and lichens are the most sensitive organisms to atmospheric pollution by trace metals, although sensitivity varies decidedly among species (see Chapter 2, Section V). The trend in atmospheric deposition of trace elements has been evaluated by Berg and Steinnes[1223] using a national moss survey based on 458 samples of the ground-growing moss *Hylocomium splendens* (Table 4). Between 1977 and 1990, the levels of most long-range transported elements

Table 4 Concentration of Trace Elements in Moss (*Hylocomium splendens*) Growing in Norway, Collected in the Period 1990–1955 (ppm)

Element	Average	Range	Element	Average	Range
Ag	0.037	<0.003–0.24	Mn	310	28–2100
Al	380	110–10,000	Mo	0.23	<0.006–11
As	0.23	<0.1–2.8	Nb	0.11	<0.002–0.8
Ba	31	4.8–720	Nd	0.49	0.051–5.1
Be	0.023	<0.0004–0.37	Ni	3.6	0.41–240
Bi	0.033	0.0012–0.8	Pb	8.6	0.88–59
Cd	0.18	<0.005–1.7	Pr	0.13	0.013–1.5
Ce	1.1	0.12–13	Rb	13	1.2–74
Co	0.37	0.047–0.7	Sb	0.15	0.0083–4.3
Cr	2.6	0.21–290	Se	0.39	<0.5–2.9
Cs	0.26	0.019–3.1	Sm	0.1	<0.0007–0.94
Cu	7	2.1–160	Sn	0.25	<0.008–2.5
Dy	0.07	0.0028–0.53	Sr	15	2.8–51
Er	0.037	0.00045–0.29	Tb	0.013	0.00036–0.11
Eu	0.02	0.0023–0.12	Te	0.0052	<0.002–0.089
Fe	660	120–21,000	Th	0.07	0.004–5.1
Ga	1.1	0.14–16	Ti	53	12–310
Ge	1.1	0.24–11	Tl	0.12	0.0022–1.4
Gd	0.095	0.0036–0.89	Tm	0.0048	<0.0001–0.039
Hf	0.0084	<0.003–0.41	U	0.05	0.0028–1.3
Hg	0.075	0.0023–0.48	V	2.8	<0.01–16
Ho	0.013	<0.0009–0.097	W	0.093	<0.002–1.5
La	0.55	0.067–6	Y	0.31	0.038–2.3
Li	0.22	0.027–2.6	Yb	0.032	<0.0003–0.28
Lu	0.0042	<0.0001–0.039	Zn	45	8.8–600
			Zr	0.35	0.057–12

After Berg and Steinnes.[1223] (With kind permission from Elsevier Science and the authors.)

were reduced by more than 50%. Except for Pb, a further reduction in the atmospheric trace element deposition (especially trace metals) was observed in Norway, which can reflect general European trends.

The environmental characteristics of inorganic trace pollutants in air are the following:

1. Wide dispersion and long-distance transport
2. Bioaccumulation, most often affecting the chemical composition of plants without causing easily visible injury
3. Reaction in living tissues by disturbing the metabolic processes and by causing the reduction of sunlight entering plant tissues
4. Resistance to metabolic detoxification, therefore entering the food chain

Indirect effects of air pollutants through the soil are of real importance because of the large-scale sustained exposure of soil to both wet and dry deposition of trace elements. These environmental effects should also be given greater attention.

III. WATER POLLUTION

Trace elements are present in natural waters (ground and surface), and their sources are associated with either natural processes or man's activities. The basic natural processes contributing trace elements to waters are chemical weathering of rocks and soil leaching. Both processes also may be largely controlled by biological and microbiological factors. The anthropogenic sources of trace elements in waters are associated mainly with mining of coal and mineral ores and with manufacturing and municipal waste waters. Water pollution by trace elements is an important factor in both geochemical cycling of these elements and in environmental health. The hydrocycle is the "crossroad" chain of trace element fluxes in each ecosystem and terrestrial ecosystem as well.[1137] Ecological consequences of trace element pollution of waters are difficult to assess because, on the global scale, they are also likely to promote unpredictable geochemical processes.

Most trace elements, especially heavy metals, do not exist in soluble forms for a long time in waters. They are present mainly as suspended colloids or are fixed by organic and mineral substances. Thus, their concentration in bottom sediments or in plankton is most often an adequate indication of water pollution by trace elements. As Dossis and Warren[191] concluded, sediments may be regarded as the ultimate sink for heavy metals that are discharged into the aquatic environment. On the other hand, easily volatile elements such as Br and I can reach higher concentrations in surface waters, from which they can also readily vaporize under favorable climatic conditions. Microbial alkylation of the group of metals including Hg, Se, Te, As, and Sn that occurs mainly in sediments and on suspended particles in waters is also of great importance in their mobility.[359]

Korzh[1369] estimated the global transfer of the elements from oceans *via* the atmosphere on the continents. Yearly deposits of elements, grouped according to amounts, is as follows (major elements are in parenthesis):

t/year × 10^0: Be, In, Eu, Tb, Tm, Lu
t/year × 10^1: Sc, Co, Ge, Nb, Ag, Sn, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Hf, Ta, Re, Au, Hg, Pb
t/year × 10^2: Cr, Mn, Fe, Cu, Ga, Se, Y, Zr, Cd, W, Tl
t/year × 10^3: Al, Ti, V, Ni, Zn, As, Sb, Cs, U
t/year × 10^4: Li, Rb, Mo, I, Ba, (N, P)
t/year × 10^5: B, F, (Si)
t/year × 10^6: Br, Sr, (C)
t/year × 10^7: (Mg, S, K, Ca)
t/year × 10^8: Cl, (Na)

This is clear evidence that the transfer in the water–air–soil chain plays a very significant role in elemental cycling.

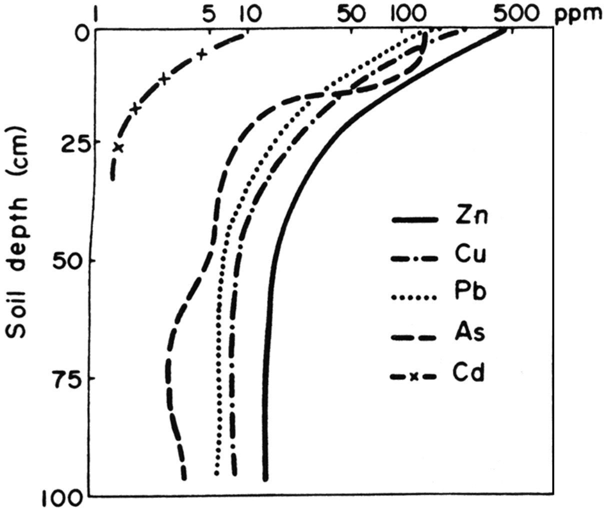

Figure 3 Vertical distribution of Zn, Cu, Pb, and Cd in a profile of the soil sludged during a period of 15 years and the distribution of As in light soil polluted by a metalliferous mine.[297,395]

The contribution of anthropogenic trace pollutants is very high for many sea basins. As Matschullat[1404] calculated, the fluxes of metals to the Baltic Sea from anthropogenic sources of both river flow and atmospheric deposition amount to over 90% of total input of Cd, Hg, and Pb, and about 80% of Cu and Zn.

Both phytoplankton and vascular water plants are known to selectively concentrate trace elements. For example, the highest accumulation by mezoplankton is observed for Cd, Cu, and Zn, while seaweeds take up Cd, Zn, Mn, and Pb more readily.[1512] As a result of this selectivity, concentrations of some trace elements in waters may decrease in some seasons, while other elements may become soluble during the decay of plants. Concentrations of trace elements in both bottom sediments and aquatic plants of streams are known to be a useful tool in biogeochemical exploration and environmental research. Soluble fractions of trace cations are rapidly caught either by clays or organic compounds and deposited in bottom sediments, or they are absorbed by root tissues of aquatic plants. Thus, concentrations of trace metals in these samples of the aquatic compartment reflect geochemical anomalies of the bedrocks as well as different anthropogenic sources of pollutants. The biochemical mapping of Sweden, based on aquatic plants, includes quite a number of trace elements: As, Au, Ba, Cd, Cl, Co, Cr, Cu, Hg, Mo, Nb, Ni, Pb, Rb, Se, Sr, U, V, W, Y, and Zn.[953,1128]

Wastewater used on farmland is generally a source of several trace elements. Therefore, the possibility of contamination should limit this method of wastewater disposal because of the accumulation of hazardous amounts of heavy metals in surface soil (Figure 3).

Several limits are established for concentrations of trace elements in waters. The most crucial are health-related limits for potable waters.[1357] Limits for discharge waters are also of great importance for the total "geochem" balance in the environment.

IV. SOIL

A. Soil Contamination

Soil is a very specific component of the biosphere because it is not only a geochemical sink for contaminants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. However, the most important role of soil is its productivity, which is basic for the survival of humans. Thus, maintenance of the ecological and agricultural functions of soil is the responsibility of mankind.

Two terms—*soil contamination* and *soil pollution*—have been defined differently in various publications. The recent definition given by Knox et al.[1367] refers to soil contamination as soil whose chemical state deviates from the normal composition but does not have a detrimental effect to organisms. Pollution occurs when an element or a substance is present in greater than natural (background) concentrations as a result of human activity and has a net detrimental effect on the environment and its components. The authors stated: "From a plant, animal, and human health perspective, soils are not considered polluted unless a threshold concentration exists that begins to affect biological processes."

Metal pollution of soils is as old as man's ability to smelt and process ores, and has been documented, especially in Greenland's snow and ice.[1241] The metal emission, mainly of Pb, is now observed on local, regional, and global scales, especially throughout Europe. This phenomenon goes back as far as the Bronze Age (2500 B.P.). Any age of cultural development has left metal pollution of the environment, stored mainly in soil, sediment, and ice. Ernst[1294] comprehensively reviewed ancient metal contamination from the Bronze Age to Roman times.

Trace elements originating from various sources may finally reach the surface soil, and their further fate depends on soil chemical and physical properties and especially on their speciation. Although the chemistry of soil contaminants has recently been the subject of many studies, our knowledge of the behavior of polluting trace elements is far from complete. The persistence of contaminants in soil is much longer than in other compartments of the biosphere, and contamination of soil, especially by heavy metals, appears to be virtually permanent. Metals accumulated in soils are depleted slowly by leaching, plant uptake, erosion, or deflation. The first half-life of heavy metals, as calculated by Iimura et al.[336] for soils in lysimetric conditions, varies greatly—for Zn, 70 to 510 years; for Cd, 13 to 1100 years; for Cu, 310 to 1500 years; and for Pb, 740 to 5900 years. From the compilation of data given by Bowen,[94] the following residence time of trace elements in soils of temperate climate can be estimated: for Cd, 75 to 380 years; for Hg, 500 to 1000 years; and for Ag, Cu, Ni, Pb, Se, and Zn, 1000 to 3000 years. In soils of tropical rainforests, the rate of leaching of the elements is much shorter and is calculated at about 40 years. All similar estimations have clearly indicated that the complete removal of metallic contaminants from soils is nearly impossible.

The input–output balance of metals in soils discussed in Chapter 3, Section III.B, shows that trace metal concentrations in surface soil are likely to increase on a global scale, with growing industrial and agricultural activities. There are several indications that the composition of surface soil may be influenced by both local contamination and long-range transport of pollutants. Purves[634] concluded that the extent of soil contamination in the urban environment is now so great that it is possible to identify most soils as urban or rural on the basis of their content of a few trace metals that are known to be general urban contaminants. The annual increment of heavy metals caused by dust fallout in Tokyo is estimated for Cd to be 0.05 ppm and for Pb and Mn to be about 0.5 ppm.[395]

Urban pollution has recently become a subject of many studies. De Mique et al.,[1417a] based on the investigations of pollution in Oslo (Norway) and Madrid (Spain), have distinguished so-called "urban" pollutants: Ba, Cd, Pb, Sb, Ti, Zn, and to a smaller extent Cu. Results of several other investigations have indicated, however, that the pollution of cities is specific and varies with local conditions; for example, in Warsaw (Poland), the relative increase is noticed for Li, Ni, Zn, Cr, Pb, Ba, Sr, and Fe (Figure 4). During the 20 years from 1977 to 1997, a moderate increase in Pb, Cd, and Cu, but not in Zn, was noticed in soils along the streets of Warsaw: Cd from 6.0 to 10.0, Cu from 36 to 45, and Pb from 150 to 190 (average, ppm).[1268] An extreme increase of traffic intensity was also observed in Warsaw at that time. In Novosibirsk (Russia), relative increases were observed for As, Br, Cd, Cu, Hg, Mo, Pb, Zn, and Zr,[1340] and in Minsk (Belorussia) for Cd, Pb, and Cu.[1452] In Siena (Italy), Ba and Pb were the most increased metals, and Ba has been proposed as a tracer for vehicle emissions, in place of Pb.[1423] However, Zn and Pb are the most commonly enriched

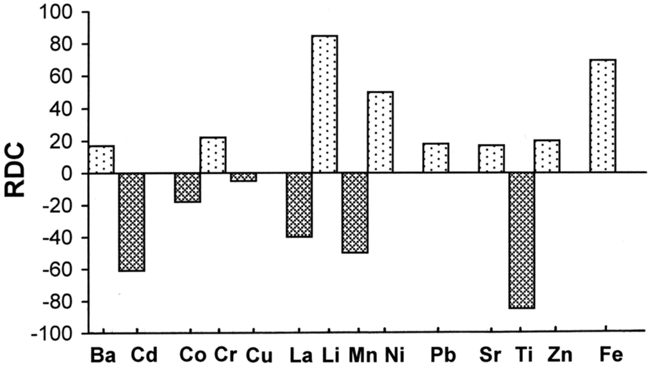

Figure 4 Variation in the content of trace elements in dandelion (*Taraxacum officinale* Web.) leaves collected in Warsaw (1995) and presented as RDC values. (Modified from Kabata-Pendias and Krakowiak[1356]). RDC, Relative Deviation to Constant; RDC = {[AM − RF]/RF} × 100; AM, Metal Contents of sample; RF, Reference Contents of Metals.

metals in the soils of many cities.[1361] Birke and Rauch calculated the geogenic and anthropogenic fractions of the total accumulated metals in soils of the Berlin area.[1227] The relative (in % of total) anthropogenic accumulation is highest for Zn, Hg, Cu, and Cd (60 to 80%), medium for Ni, Pb, and Sn (50 to 60%), and low for Ag and Cr (20 to 30%). The lowest anthropogenic origin, 1%, is given for Zr.

The regional contamination of soils, as reported most commonly, occurs mainly in industrial regions and within centers of large settlements where factories, motor vehicles, and municipal wastes are the most important sources of trace metals. However, due to the long-distance aerial transport of trace pollutants, especially those that form volatile compounds (e.g., As, Se, Sb, and Hg), it has become difficult to estimate the natural background values for some trace elements in soils.

Several methods were developed to calculate background (pristine) contents of trace elements in soils. There is great demand for such data as reference values because entirely natural contents of trace elements do not currently exist. In general, these methods are based either on statistical calculations or on the relation of trace element to various soil parameters and geologic factors. Some of the best known methods are described below:

1. GB—*Geochemical Baseline*: values are calculated as concentration ranges bracketed by the GM/GD^2 to the $GM \times GD^2$. These encompass the central 95% of observed contents (after Tidball and Ebens[1518]).
2. IGD—*Index of Geochemical Distribution*: is calculated as: GM + 2GD. TM soil status: (a) "pristine": $MC/IGD < 1$, and (b) contaminated: $MC/IGD > 1$ (after Kabata-Pendias[1352]).
3. IGL—*Index of Geochemical Load*: is calculated *versus* geochemical background: $\log_2 MC/BC \times 1.5$. TM soil status: (a) "pristine": $IGL < 3$, and (b) contaminated: $IGL > 3$ (after Müller[1438]).
4. IPD—*Index of Pedogenic Distribution*: is based on the comparison of TM distributions in soils: (a) vertical, (b) lateral, and (c) typological (after Baize[1212]).
5. PEF—*Pedochemical Enrichment Factor*: is calculated *versus* Clarke's values of mother rocks and normalized to A1 contents: $[MC/Al_s] : [CC/Al_r]$, TM soil status: (a) "pristine": $PEF < 1$, and (b) contaminated: $PEF > 1$ (after Kabata-Pendias[1349,1350]).
6. FSP—*Factor of Soil Parameters*: is based on the selection of the most significant soil factor that controls TM contents. The content of clay granulometric soil fraction (<0.02 mm) was established as a major soil factor for the evaluation of TM background concentrations within soil textural groups (after Kabata-Pendias and Krakowiak[1355]).
7. SCV—*Spatial Concentration Variability*: is based on geochemical baseline values and allows establishment of observed limits of values at a given distance from the source of pollution (after Gough and Crock[1312]).

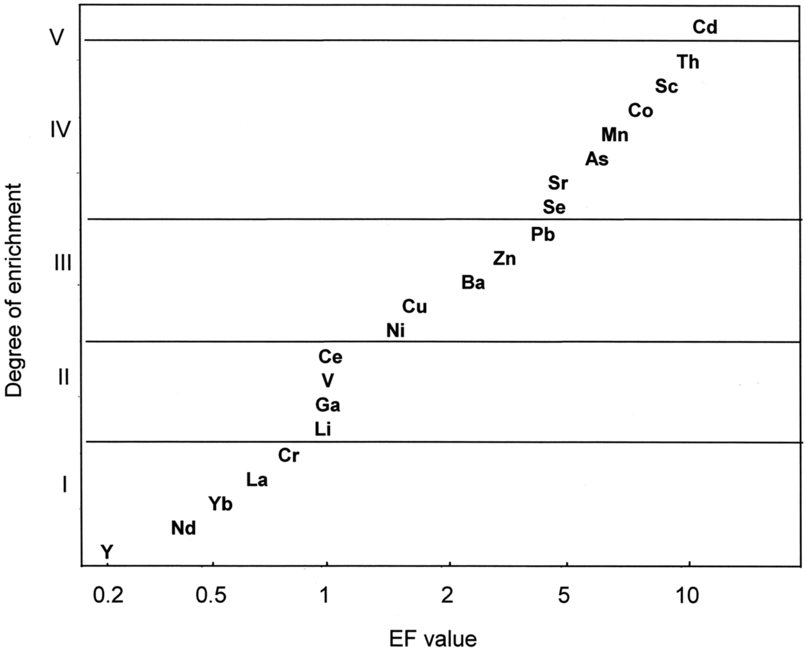

Figure 5 Enrichment factor (EF) values for trace elements in surface sandy soils of Poland as compared with mean concentrations (*Clarke*) in sandstones, and normalized to Al contents. Degree of EF: I—decrease, II—relative stability, III—slight increase, IV—moderate increase, V—strong increase.[1349]

8. GIS and MA—*Geographical Information System* and *Multivariate Analyses*, and also other statistical methods, are used to differentiate anthropogenic from natural anomalies in soils and plant roots (after Zhang Selinus[1572,1573]).

Abbreviations: TM = trace metals, GM = geometric mean, GD = geometric deviation, MC = measured value, BC = geochemical background content of a given element, CC = Clarke's value, SCF = soil clay fraction, Al_s = Al content of soil, and Al_r = Al content of rock.

Very useful are PEF and FSP indices. The first is calculated in relation to trace element contents of mother rocks against so-called "stable" elements (e.g., Al, Ti) (Figure 5), and the second is based on the relation between clay soil fraction and trace element contents. Also, the interpretation of routine survey data based on isoline plots has been used for classifying soil contamination.[1272]

The estimation of critical time when a metal in soil will reach its ecologically critical concentration is a subject of recent studies. As Pačes[1447] calculated for a given agricultural catchment in the Czech Republic, the steady-state concentrations of Cu and Zn in the soils will never overshoot the critical load, while As, Cd, and Pb will reach the norms set for the soils after 4.5, 61, and 980 years, respectively.

Elevated concentrations of trace elements can also be of lithogenic (geogenic) origin. This was reported by Čurlik and Forgač[1267] for some alluvial soils, by Baize[1214] for soils derived from limestones, and by Skiba[1498] for soil of southern Spitsbergen (Sorrkap Land) derived from mica shales. The highest amounts of metals in surface soils derived from mica shales are (ppm): Zn 90, Pb 34, and Cd 0.61.

In addition to aerial sources of trace pollutants, fertilizers, pesticides, and all sewage-derived materials have added to the trace element pool in soils. The mobilization of heavy metals from smelter and mine spoil by transport with seepage waters or by windblown dust may also be an important source of soil contamination in some industrial regions. The variability of trace element concentrations in materials used in agriculture is presented in Table 5. Goodroad,[273] Piotrowska

Table 5 **Agricultural Sources of Trace Element Contamination in Soils (ppm DW)**

Element	Sewage Sludges (70, 249, 593)	Phosphate Fertilizers (55, 94, 306, 381, 399, 701, 744, 755a, 809)	Limestones (20, 25, 249, 532)	Nitrogen Fertilizers (701, 875, 1357, 1362)	Manure (20, 25, 249, 532, 744)	Pesticides (%) (510)
As	2–26	2–1200	0.1–24.0	2–120	3–25 (150)[b]	22–60
B	15–1000	5–115	10	6	0.3–0.6	—
Ba	150–4000	200	120–250	—	270	—
Be	4–13	—	1	—	—	—
Br	20–165	3–5	—	6–716	16–41	20–85
Cd	2–1500	0.1–170	0.04–0.1	0.05–8.5	0.3–0.8	—
Ce	20	20	12	—	—	—
Co	2–260	1–12	0.4–3.0	5–12	0.3–24	—
Cr	20–40,600	66–245[b]	10–15	3–19	5.2–55	—
Cu	50–3300	1–300	2–125	1–15	2–60	12–50
F	2–740	8500–38,000	300	82–212	7	18–45
Ge	1–10	—	0.2	—	19	—
Hg	0.1–55	0.01–1.2	0.05	0.3–3	0.09–0.2 (26)[b]	0.8–42
Mn	60–3900	40–2000	40–1200	—	30–550	—
Mo	1–40	0.1–60	0.1–15	1–7	0.05–3	—
Ni	16–5300	7–38	10–20	7–38	7.8–30	—
Pb	50–3000	7–225	20–1250	2–1450	6.6–15 (3500)[b]	60
Rb	4–95	5	3	2	0.06	—
Sb	—	—	—	2–600	—	—
Sc	0.5–7	7–36	1	—	5	—
Se	2–10	0.5–25	0.08–0.1	—	2.4	—
Sn	40–700	3–19	0.5–4.0	1.4–16	3.8	—
Sr	40–360	25–500	610	100–5420	80	—
Te	—	20–23	—	—	0.2	—
U	—	30–300	—	—	—	—
V	20–400	2–1600	20	—	—	45
Zn	700–49,000	50–1450	10–450	1–42	15–250	1.3–25
Zr	5–90	50	20	6–61	5.5	—

Note: References are in parentheses.

[a] Mainly ammonium sulfate.

[b] Maximum concentration, after Crompton.[1264]

and Wiacek,[620] and Stenstrom and Vahter[755a] reported that long-term use of inorganic phosphate fertilizers adds substantially to the natural levels of Cd, F, and U in soils, while other elements such as As, Cr, Pb, and V do not increase significantly. Effects of sewage sludge applications on soil composition are especially of great environmental concern and have been the subject of many studies and much legislation. Advisory standards and guidelines for safe addition of trace elements in sewage sludge to land is still in the stages of experiment and negotiation; however, several authors have given threshold values for the maximum addition of trace elements in one dose and over a period of time (Table 6). Despite some diversity of opinion, there is general agreement, especially regarding the maximum concentrations of heavy metals in soils. Maximum allowable limits set up for paddy soils in Japan are somewhat different.[395] Cu content was established at 125 ppm (0.1 N HCl soluble) and As was established at 15 ppm (1 N HCl soluble) as critical for rice growth. The hazardous concentration in soils of Cd is limited by allowable Cd in rice, which should not exceed 1 ppm. It should be emphasized, however, that all the allowable limits need to be related not only to the given plant-soil system, but also to ratios between single elements as well as to their total burden in soil.

In several soils, the threshold levels have already been exceeded, either in gardens and orchards or in other locations, by contamination from industrial emissions or heavy and repeated applications of sewage sludges as well as in urban areas and soils near highways. A high heavy metal content of sludges is the most important hindrance to their use in agriculture. Although Purves[634] reported that in practice the concern with using sludges commonly is only their phytotoxicity due to excesses of Zn, Cu, and Ni, their content of Cd in particular, as well as of Pb and Hg, should be of concern as serious health risks. As Andersson and Nilsson[25] have observed, long-term use of sewage sludge increased the soil levels of Zn, Cu, Ni, Cr, Pb, Cd, and Hg. Of these elements, however, only Zn, Cu, Ni, and Cd were increased in cereal grains, and Zn, Cu, Cr, and Pb were increased in cereal straw. Chaney[127] and Sikora et al.[726] recommended higher doses of sewage sludges because of the relatively low availability of heavy metals to plants.

The immobilization of trace metals by sewage sludge is apparently due to the fixation of metals mainly in forms (operational) of oxides (Figure 6). In other soil conditions, however, the effect of sewage sludges can be different, and some trace metals can be mobilized as, for example, complexes with small organic molecules. As Crompton[1264] stated, we can only poorly understand what biotransformations from inorganic metals to organometallic compounds can occur when metal-contaminated sewage sludge is disposed of as fertilizer on agricultural land. The presence of inorganic metals in sewage sludge creates a potential for the formation of organometallic compounds by biosynthetic processes. Thus, an understanding of all factors influencing the phase distribution of metals in soils is a prerequisite to estimating the critical loads of metals and their effect on soil organisms. Beckett et al.[59] concluded that in addition to the commonly monitored levels of Cu, Ni, Zn, Cd, Cr, and Pb during the disposal of sewage sludge on farm land, it may be necessary to monitor levels of Ag, Ba, Co, Sn, As, and Hg and also possibly Mo, Bi, Mn, and Sb, until their likely accumulations in surface soil can be shown to be harmless.

Although trace metal-contaminated soils have gained much attention, the excess of other trace elements, such as B, Br, F, and Se can also be, in some regions, an environmental concern. In many cases, increased concentrations of these elements in surface soils is associated with soil salinity affected by irrigation/drainage practices and processes. Elevated concentrations of these elements may also be related to composition of parent material as well as to the impact of the chemical industry, coal combustion, and leaching from waste landfills.

The behavior and especially the phytoavailability of cations in soils are governed predominantly by their speciation as well as by several soil properties. The speciation and localization of metallic contaminants in soils are related to their chemical forms at the time of impaction. Aerial particles transporting trace metals are most common in mineral forms of oxides, silicates, carbonates, sulfates, and sulfides, and when originated from coal combustion, the glassy structure predominates. Trace metal species entering soils with sewage sludges differ based upon the source and the

Table 6 Maximum Allowable Concentrations (MAC) of Trace Elements in Agricultural Soils Proposed or Given in the Directives in Various Countries, and Different Years (ppm DW)

	Austria[206]	Poland[376a,1352]	Germany[1138]	Russia[1011]	U.K.[959]	U.S.[1113]	Germany[1306]	Euro Comm.[1408]	U.S.[1408]
Element	**1977**	**1977 & 1993[b]**	**1984**	**1986**	**1987**	**1988**	**1992[a]**	**1986**	**1993**
As	50	30	20	2	10	14	—	—	—
B	100	—	25	—	—	—	—	—	—
Be	10	10	—	—	—	—	—	—	—
Cd	5	1–3	3	—	3–15	1.6	1.5	1–3	20
Co	50	50	—	—	—	20	—	—	—
Cr	100	50–80	100	0.05[c]	—	120	100	50–150	1500
Cu	100	30–70	100	23[d]	50	100	60	50–140	750
F	500	—	200	—	—	—	—	—	—
Hg	5	5	2	2.1	—	0.5	1	1–1.5	8
Mo	10	10	—	—	—	4	—	—	—
Ni	100	30–75	50	35	20	32	50	30–75	210
Pb	100	70–150	100	20	500–2000	60	100	50–300	150
Sb	—	10	—	—	—	—	—	—	—
Se	10	10	10	—	—	1.6	—	—	—
V	—	150	—	150	—	—	—	—	—
Zn	300	100–300	300	110	130	220	200	150–300	1400

[a] Limits for soil pH > 6.

[b] Range for very light acid soil and for heavy neutral soil, respectively.

[c] Value given for Cr^{6+} fraction.

[d] Value given for soluble pool of the metal.

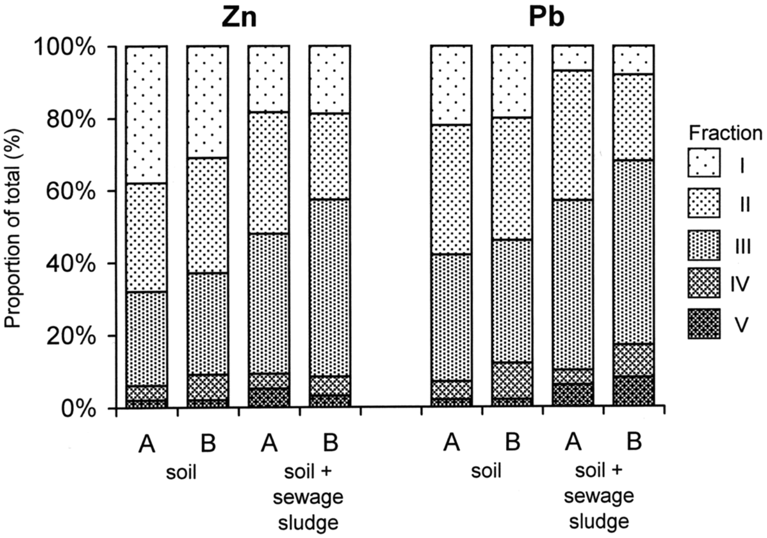

Figure 6 Impact of sewage sludge on fractionation of Zn and Pb in medium sandy soil (A), and loamy soil (B). Fractionation according to Tessier et al.[1162]: I—exchangeable, II—carbonate, III—oxide, IV—organic, V—residual. (Modified from Manko.[1399])

treatment of wastes. The forms associated with sesquioxides and with compounds bound to organic residual fractions usually predominate in sludges of municipal origin. When wastes are mixed with some industrial effluents, however, the speciation of metals greatly differs based upon the discharged forms from factories.

Effects of excessive levels of trace metals on soil properties depend on complex reactions between the trace cations and other components of all soil phases—solid, liquid, and gaseous. These reactions have been broadly studied in recent years, and several principles, mechanisms, and models (including the GEOCHEM computer program) were established and proposed by the authors.[954,1153,1154] The chemical forms governing the mobility and phytoavailability of trace metals and residence times of pollutants in soil layers are the main subjects of mechanistic modeling and calculations. The mobile fraction of trace metals behaves like bivalent cations in soil phases and is controlled by dynamic equilibria between solid and liquid phases. However, the complexity of all possible reactions in natural heterogeneous soil systems needs more data for an appropriate prediction of ecological consequences of the soil pollution with trace metals. The fate of these metals in soils depends upon many soil processes, which can be generalized as follows:

1. Dissolution
2. Sorption
3. Complexation
4. Migration
5. Precipitation
6. Occlusion
7. Diffusion (into minerals)
8. Binding by organic substances
9. Absorption and sorption by microbiota
10. Volatilization

All these processes are governed by several soil properties, of which soil pH and redox potential are known to be the most important parameters. Thus, the solubility of trace metals is often shown as a function of pH affected by the amount and kind of organic matter (Figure 7). Also other soil

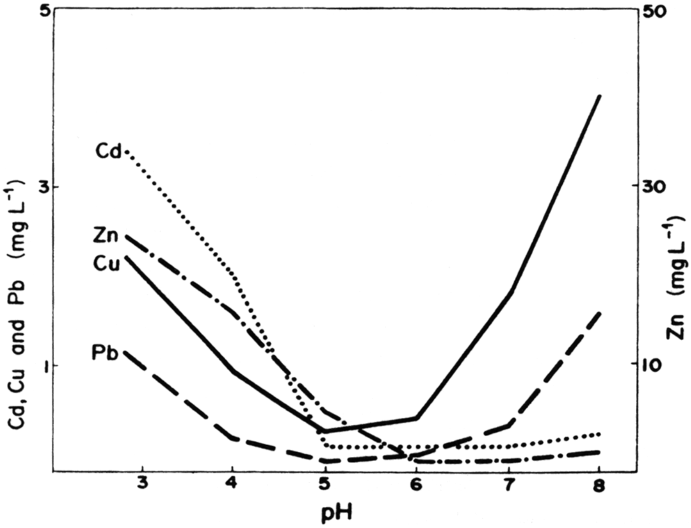

Figure 7 Concentrations of trace metals in equilibrium solutions of sandy gleyic podzol. (Modified from Brümmer and Herms.[956])

factors, such as CEC, carbonates, Fe and Mn hydrous oxides, clay minerals, and fine granulometric fractions are known to play significant roles in the behavior of trace elements. Frequent association of trace element pollution with the acid deposition (mainly SO_2 and NO_x) greatly complicates overall ecological disturbance created by the chemical degradation of soils.

Soil contaminated with heavy metals can produce apparently normal crops that may be unsafe for human or animal consumption. Kloke[398] calculated that if the content of Hg, Cd, and Pb in the soil is not higher than the threshold values (Table 6), it can be expected that the contents of these metals in human diets will not exceed weekly tolerable intakes established by FAO/WHO. Therefore, safe use of sewage sludge must be assessed on the basis of a safe addition of trace metals into soils.

Permissible levels of trace elements, particularly heavy metals, used on farmland can be calculated based on several factors. Thus, permissible levels of trace elements in surface soils differ highly based on local conditions (Table 6). For example, the estimates based on geochemical principles and general hygienic limitations proposed by Goncharuk and Sidorenko[1011] and Niezbizhskaya and Saet[1100] are much lower than those calculated for the protection of vegetation, given by El-Bassam and Tietjen,[206] Kitagishi and Yamane,[395] and Kloke.[398] It is most important, however, to evaluate acceptable application rates in relation to:

1. Initial trace element content of soil
2. Total amount added of one element and of all heavy metals
3. Cumulative total load of heavy metals
4. Heavy metal dose limitation
5. Equivalency of trace element toxicity to plants
6. Threshold values of trace element concentrations in soils
7. Relative ratios between interacting elements
8. Soil characteristics (e.g., pH, free carbonates, organic matter, clay content, and moisture)
9. Input-output balance
10. Plant sensitivity

The most crucial issue is the establishment of MAC values for arable soil and particularly for garden and commercially grown crop soils. MAC values for such soils in Poland are related to soil variables.[1352,1354]

Lewin and Beckett[469] comprehensively reviewed monitoring of heavy metal accumulation in agricultural soils treated with sewage sludge and pointed out that it would be unreasonable to assume, without checks, whether heavy metals in soil will become immobilized with time or not. Williams et al.[1186] carried out a 9-year study on metal mobility in sludged soils. The increased soil acidity and the high percentage availability of metals in sludged soils did not result in an increased metal movement within soil profile.

Different soil types, plant species, and growing conditions contribute to the divergent influences of soil contamination on trace element status in plants. Some authors use a term, "soil resistance to heavy metal contamination," which is related to the critical levels of metallic pollutants that exhibit toxic effects on plants and environments. This term is largely related to the cation exchange capacity (CEC) of soils (see Chapter 3, Section III.C). Usually, the resistance of a nonacid heavy soil with a higher content of organic matter exceeds several times the resistance of a light sandy acid soil.

Contaminated soils display considerable variations in the mechanisms and strength by which metals are retained. A general effect of the contamination is the reduced ability of soils to further metal adsorption.[1415] This is very significant in the assessment of pollutant loading rates and in the understanding of the long-term behavior of trace metals in soils.

Increasing acidification during recent decades has led to ecological disruption observed in many European countries. A steady increase of hydrogen ions in top soils resulting mainly from emitted sulfur and nitrogen dioxides leads to an imbalance of all nutrients, and further, to destruction of natural buffering properties of soils. A common effect of these changes is an increased mobility of all cations. A high rate of trace metal mobility in soils affects the increase of both bioavailability and leaching down soil profiles into water systems. Loamy neutral soils may accumulate a higher amount of trace elements with much less environmental risk. However, a general chemical imbalance of such soils usually results in decreased biological activity, decreased or increased pH, and, as a further consequence, in degradation of organic and mineral sorption complexes.

Contamination of agricultural and forest soils has already become relatively common and is likely to continue. Noticeable, also, is the fact that most often soils become contaminated by several metallic pollutants that are accompanied quite frequently by acid rains (mainly SO_2, NO_x, and HF). Such an association of pollutants in soil greatly complicates their impact on the environment. Trace elements as well as other inorganic and organic pollutants are known to accumulate in surface soils as a result of both contamination from point sources (industrial, urban, and agricultural) and from long-range aerial transport. However, soils and other surficial sediments cannot act as permanent storage for immobile trace elements. The remobilization processes will again transfer these elements into biogeochemical cycles, and as a consequence, will disturb the intricate interrelationship of the flow of elements and energy in the soil-plant-animal system (Figure 1).

The state of our knowledge about the impact of trace inorganic pollutants on soil ecological variables is relatively broad. There is not enough data, however, to attempt to set up definite values for criteria needed to protect soils against the long-term effects of trace element pollution. Some preliminary values have, however, been proposed as guidelines for primary hazard assessments. These guidelines for threshold levels, "trigger concentrations," of trace elements, and particularly trace metals, will differ from place to place to meet the variable ecological conditions of each region or country. They should, however, be based on similar standard methods and experimental procedures for the measurement of the content of each element. A number of observed ecological standards are often used to assess the significance of trace metal levels in soils. These include:

NOEC—No Observed Ecological Consequences
HNOAEC—Highest No Observed Adverse Effect Concentration
LKE—Lowest Known Effect (or Level)
LOEC—Lowest Observed Effect Concentration
PAA—Permissible Annual Application
MAL—Maximum Allowable Loading
MPL—Maximum Permissible Loading

MCA—Maximum Cumulative Amount
RMCL—Recommended Maximum Contaminant Levels
ATL—Action Trigger Level (the concentration above which remedial measures and treatments are necessary)
ELD—Ecosystem Lethal Dose
LOAEC—Lowest Observed Adverse Effect Concentration

Approaches to setting limits for trace elements, MAC, are based on fundamental criteria such as: (1) transfer of trace elements (mainly metals) to various organisms and to man; (2) assessment of the likely harmful effects; (3) estimation of two threshold values, LOAEC and HNOAEC; and (4) evaluation of metal balance (input/output) of metals. Values given in the Second Edition compared to those cited now (Table 6) indicate a tendency for more liberal limits, especially for metals of concern in agriculture practice and food production: Cd, Cr, Cu, Hg, Ni, Pb, and Zn. A comparison of the U.S. (1993) maximum cumulative pollutant loading limits in soils treated with sewage sludge with limits proposed in Austria (1977) for agricultural soils treated with municipal sludge (Table 6) reveals a significant increase in MAC, from about 1.6 times for Hg to 15 times for Cr. The proposed increase for Cd-MAC for $>$ 6 to 20 times is a subject of special concern. As McGrath et al.[1408] stated: "Differences in the philosophy behind environmental protection and in the choices of which organisms to protect explain the different metal limits for sewage sludge which have been adopted in the countries examined."

In addition to general ecological effects, criteria should take into account damaging effects on crops, injury to animals—particularly the hazards associated with the ingestion of soil during grazing—and possible accumulation effects that may occur in the food chain. The possible contamination of human food is an especially urgent problem. To ensure safe quality of the food-chain products, it is useful to standardize the allowable loadings of contaminants (MAL) to agricultural land.

Values for any critical concentration or loading of trace elements that can be established at the present time should be regarded as tentative and approximate assessments that may be changed with improvements in the database and understanding of the significance of the presence of particular elements in particular soils, farming practices, or ecosystems. There is a real need for critical examination of the crucial questions concerning the standards that should be used to establish the criteria for "safe" limits for trace element contents of soils. Several proposals show a general agreement for most individual elements (Table 6), but ultimate accepted values should take into account possible interactions between different trace elements and between trace elements and other components of soils. Data presented in Table 6 are for the total contents of trace elements. Agreement on criteria based on the measurements of the amounts of "available" elements will present further problems because of the difficulty in deciding if "availability" should be measured in biological or chemical terms, and the exact way in which either can be measured.

B. Soil Remediation

As Kobabayashi et al. reported, some of the first actions for soil remediation were in Japan, where an excess of soil Cd was removed by repeated treatment with EDTA solution and lime (the Cd content of the surface soil decreased from 27.9 to 14.4 ppm).[405]

Recently, there has been a virtual explosion of various papers and books on soil remediation. General reviews on this topic are given in several publications; see, for example, Adriano et al.,[1199] Knox et al.,[1367] and Vangronsveld and Cunningham.[1528]

Proposed methods for cleaning soils degraded with metals have been reviewed initially by Rulkens et al.[1472] Five main procedures to clean contaminated soil are described:

1. Removal of contaminants by molecular separation. Extraction and desorption treatments.
2. Removal of particulate contaminants by phase separation. Froth flotation and other extractive treatments.

3. Removal of contaminants by chemical/thermal destruction. *In situ* vapor extraction and other treatments.
4. Removal of contaminants by biodegradation of substances containing trace metals.
5. Removal of contaminants by biological absorption (phytoextraction) or biological mobilization.

Conventional, most commonly used remediation technologies, as described by Saxen et al.[1481] include:

- Soil flushing
- Pneumatic fracturing
- Solidification/stabilization
- Vitrification
- Electrokinetics
- Chemical reduction/oxidation
- Soil washing
- Extravagation, off-site disposal

A large number of techniques have been developed using these procedures, but only a few have been applied successfully in practice. At present, there is extraordinary interest in bioextraction methods using bioremediation, phytomelioration, and phytomining.[1198,1266,1409] It is necessary to emphasize that restoring the soil's original properties may never be achieved, especially using technical methods. However, good restoration of soil properties can give good results when using some of the best technology for a given kind of soil and for the type and concentration of the contaminants. Phytoextraction and phytoremediation using plants that hyperaccumulate trace metals, especially when transgenic plant species can be used, seem very promising. Black[1228] has reviewed economic and practical aspects of phytoremediation, and pointed out environmentally crucial issues such as the potential impact of hyperaccumulator plants on wildlife.

The problem of concern in soil remediation actions is the cost. Phytoremediation techniques are likely to be less costly than those based on conventional technology. However, as McGrath[1410] stated, full costs of plant-based techniques will not be known until mature technology is offered and applied. At present, a real demand for phytoextraction techniques is to increase the yield of plants that hyperaccumulate metals and increase the mobility of metals in soils.

Some experiments using earthworms to clean polluted soils were also conducted.[1486] Effects of this method vary with the specific conditions, and some elements are observed to be more easily taken up by earthworms (e.g., Cd and I) than others (Mn and Cs). The role of metal-resistant bacteria in soils has also been considered. Such bacteria can make plants more tolerant to metal pollution sites.[1387]

Agricultural practices have also been applied to soil remediation by immobilization of trace metals. Most commonly, the uptake of metals by plants is diminished by keeping a neutral soil pH, and by amendments with materials having a high capacity to bind metals in possibly slightly mobile fractions. These are mainly phosphorites, zeolites, montmorillonites, humic organic matter, and some wastes (e.g., fly-ash). The beneficial effects of these treatments are broadly discussed by several authors.[1266,1529] The mechanism by which zeolites reduce labile metal concentrations in soils has been recently discussed by Edwards et al.[1289] The immobilized metals are either retained in the synthetic zeolites or precipitated as metal carbonate or oxide as the soil pH increases. Zeolites have been shown to be resistant to degradation in the soil over a period of 3 months.

Trace metal mobility in soils is known to be related to land use. Usually, metals in forest soils are more easily mobilized (e.g., bioavailable and leached) than metals in agricultural soils. This is directly related to the higher acidity of soils and to a higher presence of low-molecular-weight organic substances in forest soils than in arable ones. This phenomenon will be an environmental concern in the future due to programs of forestation of poor agricultural quality soils, especially in Europe.

A new method recently presented by Mench et al.[1413] is based on the affinity of Fe and Mn oxides (or sulfates) to adsorb and occlude several trace elements from the ambient solution. Application of steel shots containing mainly Fe (over 90%), and oxides of other metals in negligible amounts (below 1%) resulted in immobilization of considerable amounts of trace metals in soil. Steel shots affect the uptake by plants of As, Zn, Cu, Ni, and Pb. The effect in Cd immobilization is apparently less successful.[1414] Also, Al-montmorillonite reveals higher binding properties for Zn than for Cd.[1211] In each case of metal fixed by binding materials, the question arises as to the persistence of this immobilization, under what soil conditions, and in what time frame could it turn into a mobilizing effect.

V. PLANTS

The significant role of plants in both cycling of trace elements and contaminating the food chain has been well illustrated for various ecosystems and published in numerous papers. Plants can accumulate trace elements, especially heavy metals, in or on their tissues due to their great ability to adapt to variable chemical properties of the environment: thus, plants are intermediate reservoirs through which trace elements from soils, and partly from waters and air, move to man and animals. As Tiffin.[789] has concluded, plants may be passive receptors of trace elements (fallout interception or root adsorption), but they also exert control over uptake or rejection of some elements by appropriate physiological reactions.

Using plant chemical status for geochemical prospecting is a very old practice in exploration of metal ores. Some of the first scientists who provided geochemical background information for plant-based prospecting were Vernadsky[1532] and Warren.[848] Recent reviews of biogeochemical prospecting are presented by Dobrovolsky[1280] and Kovalevsky.[1372] The response of plants to the chemistry of the environment is controlled by several external and biochemical factors. Nevertheless, the chemical analysis of plants is a promising tool to study chemical properties and changes in the lithosphere.

Plants reveal a variable, and sometimes specific ability to absorb trace elements from soil. The ratio of an element in plants to its concentration in soil, a so-called Biological Absorption Coefficient (BAC), is widely used for comparing different plants (Figure 23 in Chapter 4). Three general uptake characteristics can be distinguished in plants: accumulation, indication, and exclusion. To a large extent, this depends on the specific ability of plants. A huge difference in metal uptake between plant species, and also between genotypes of a species, has been demonstrated in many studies. Comprehensive information on this is given in recent publications edited by Brooks,[1244] and by Prasad and Hagemeyer.[1459,1460]

The biota reveal the potential to develop a resistance upon anthropogenic loads of trace elements to ecosystems. However, the biodiversity and biological activity of polluted ecosystems are very poor, as commonly observed in the vicinity of industrial plants, and especially metal smelters.

One of the basic environmental problems relates to the quantities of accumulated metals in plant parts used as food. Special attention should also be given to the forms of metals distributed within plant tissues, for the metal forms in plants seem to have a decisive role in metal transfer to other organisms. The chemical quality of plant food is a matter of public concern and is of primary importance in the program of consumer and health protection. In the past decade, several expert committees, especially under joint FAO/WHO programs, have been working on the toxicological evaluation of trace element levels in plant foodstuffs. There are already a number of governmental and international laws on threshold levels of so-called *toxic metals* (mainly Cd, Pb, Hg, and As) in plant food. The calculation of two values—Acceptable Daily Intake (ADI) and Provisional Tolerable Weekly Intake (PTWI)—is presently regarded as the most suitable assessment of health risk due to increased and/or unbalanced trace elements in food and forage plants. Survival studies carried out to establish range and mean concentrations of selected trace elements in crop plants (Table 7) present data for Poland.

Table 7 **Trace Metals in Some Crop Plants of Poland, Geometric Mean (ppm)**[1514]

Plant	Cd	Zn	Pb	Cu	Ni
Cereal grain (6500)[a]	0.06	33.3	0.23	0.44	3.74
Potato tubers[b] (5680)	0.11	19.9	0.33	0.61	4.46
Grass (3760)	0.12	31.6	0.89	0.84	5.51

[a] In parentheses, number of samples collected in the period 1992–1996.

[b] Unpeeled tubers.

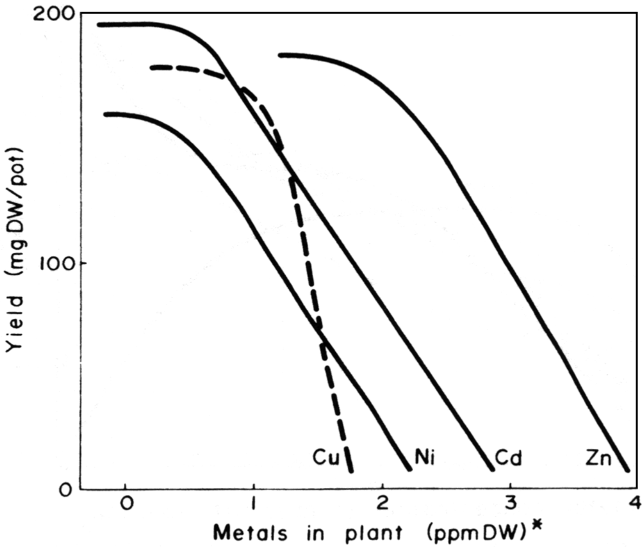

Figure 8 Response of young barley plants to heavy metal concentrations in their tissues. Asterisk indicates concentration of metals is given in powers of ten. (Modified from Beckett et al.[59])

The study of the chemistry of soils and plants in relation to the incidence of geographically distributed diseases is the basis for the discipline of medical geochemistry. It is a relatively new (initiated by Låg in 1980)[1385] but emerging field, needing a better understanding of specific cycling and the pathway of a trace element in a given environment. Plant/metal data given broadly in the literature should be useful for hazard assessment in health and agriculture.

The current database of the U.S. Environmental Protection Agency contains nearly 25,000 records on 21 metals in plants as related to the uptake, accumulation, and translocation by vascular plants. The highest number of records, over 1000, are for the Zea, Phaseolus, and Triticum families.[1439] A high relative proportion of all metal records is for: Cu 18.6%, Zn 17%, Cd 14.4%, and Pb 9%. Below 1% are records for V, Cs, Th, Sb, Pt, Be, Sn, and U. The conclusions of that review indicate that Cd and Hg are considered among the more toxic metals. The most frequently identified metals causing biological/ecological harmful effects are Pb, Cs, As, Cr, Zn, Ni, and Cu. However, these effects were primarily observed in freshwater/wetland habitats rather than in terrestrial habitats.

Several authors have observed that the yield of various crops can be decreased due to metallic pollution (Figure 8). The generalized effects of metal concentrations in nutrient solution on yield and metal content of plants are shown in Figure 9. Most important, however, are the biological and health effects on man and animals caused by metallic pollution in plants. This subject has been reviewed in detail in many textbooks on environmental health.

Each case of plant pollution is unique and should be studied for a specific environment. There is an increasing awareness that results of studies based on simulation-type systems cannot be related

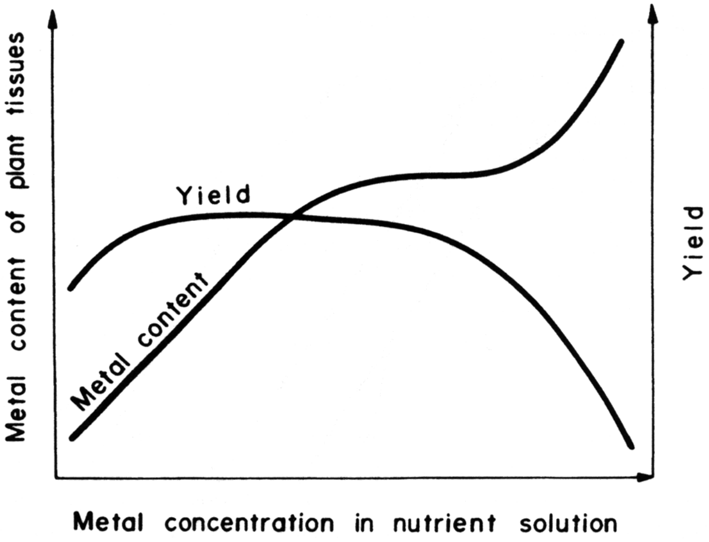

Figure 9 Generalized effects of trace metal concentrations in nutrient solution on yield and metal content of plants.

to those in a natural system. This fact is supported by de Vries and Tiller,[831] who reported a much lower absorption of heavy metals by lettuce and onions grown in a market garden soil than by those grown under greenhouse and miniplot conditions.

Trace pollutants entering plant tissues are active in metabolic processes, but can also be stored as inactive compounds in cells and on the membranes. In each case, however, they may affect the chemical composition of plants without causing easily visible injury. The most common symptoms of phytotoxicity of several trace elements are rather nonspecific and are described in detail in Table 40.

A. Biomonitoring

Plants are good indicators of the health of the soil in which they are growing. Plants also respond directly to the state of air. The tops of all plants are collectors for all air pollutants, and their chemical composition may be a good indicator for contaminated-areas when it is assessed against background values obtained for unpolluted vegetation. Mosses and lichens are known to be the most sensitive indicators of atmospheric pollution.[1037,1135] Several other plants and plant organs are shown to be suitable indicators of pollution of soil and aquatic environments (see Chapter 5, Section VIII). Nettle is highly recommended by Ernst and Leloup[990a] as a better biomonitor for metals, especially for Fe, than the other perennial herbs. A preferred phytoindicator is the common dandelion.[1278,1356,1470] Compared to green plants, mushrooms can concentrate a large amount of several trace metals, and are also good indicators for environmental pollution.[414,635,1008,1056] Mushrooms are known as the most sensitive accumulators of Se, for which concentrations are about a thousand times higher than in green plants (see Figure 23). While Cd can be accumulated to high concentration ratios, Pb seems to be excluded from mushrooms. Cu and Zn levels are higher in mushrooms than in associated vascular plants, but their concentration ratios (against soil) are relatively low.[1008,1045] Moss analyses, however, provide more suitable and reliable techniques for survey of atmospheric metal deposition. Rühling et al.[1135] described a broad program of environmental monitoring in the Nordic countries based on the survey of metals in mosses. These authors showed that the concentrations of metals in mosses (*Hylocomium splendens* and to some extent *Pleurozium schreberi*) give a linear relationship with the bulk metal precipitation (wet and dry deposition) on the log-log graph. The sorption and retention of trace metals by mosses differ, being usually the highest for Pb and Cu and lowest for Cd and Zn.

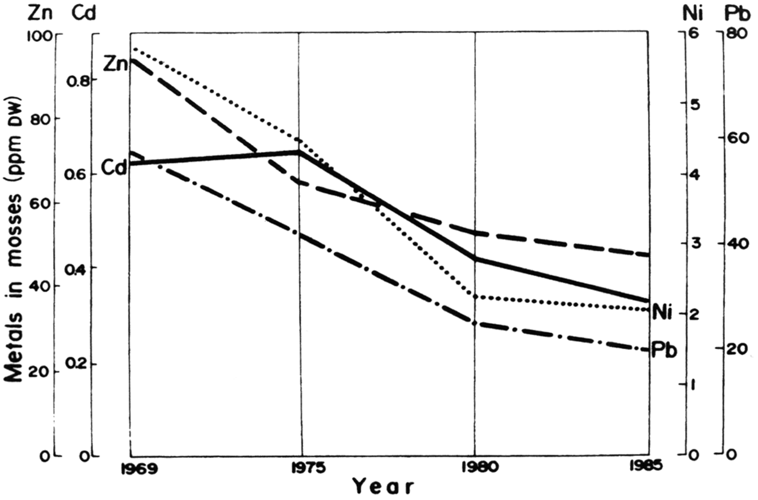

Figure 10 Trends in decreasing Zn, Cd, Ni, and Pb contents in moss species (*Hylocomium splendens* and *Pleurozium schreberi*) in the central part of Sweden during the decades 1960 to 1980.[1135]

Trends observed by Rühling et al.[1135] in decreasing of metal contents of mosses during recent decades (1968–1985) indicate a reduced emission of Zn, Cd, Ni, and Pb (Figure 10). Emission for Cr dropped rapidly during the first period only. The concentrations of As, Cd, Cu, and V in mosses did not change significantly, although there were regional variabilities. Trace metal contents of mosses follow closely the regional pattern of metal distribution in humus soil horizons.[1128]

Since 1977, monitoring has been carried out for 53 chemical elements in moss (*Hylocomium splendens*) collected from 458 sites in Norway.[1223] The last results from 1995 have clearly indicated the decrease of most elements to about 59%. These are mainly trace elements transported over a long distance in the atmosphere: Ag, As, Cd, Bi, Hg, Mo, Pb, Sn, T1, V, and Zn. This is obviously due to highly limited industrial emission in western Europe. The greatest decrease in Pb content of mosses is related to elimination of leaded petrol. The deposition of some metals (e.g., Co, Cu, and Ni) transported from a northeastern direction has not changed during that period. Similar observations of the decreased deposition of trace metallic pollutants are reported for Finland during the period 1985 to 1990,[1381] and for Bulgaria during the period 1986 to 1994.[1278] The trace metal concentrations in pine bark correlate relatively well with contents of lichens and mosses in Finland and in the Kola Peninsula. Some metals, such as Cu, Co, Ni, Fe, and Ti, were much more concentrated in the bark of trees from the Kola Peninsula than that from Finland.[1457] However, the great impact of climatic factors on the deposition of metals on leaf surface and bark must be considered and requires further investigation.[1533]

Trace metal contents of the same species of moss were investigated in Poland in 1994,[1417] and in Alaska in 1995.[1312] Reported concentrations of several trace metals were lower than those found in Norwegian moss. Somewhat similar contents of trace metals are reported for mosses (*Hylocomium splendens* and *Pleurozobium schreberi*) collected in the period 1994 to 1995 from 34 sites in Estonia.[1200] Although there were some sites with elevated levels of metals, the most common concentrations were (in ppm): Cd 0.7–0.8, Co < 0.3, Cu 5–7, Ni 1–1.3, Pb 7.5–10, V < 3, and Zn 40–50. Similar projects were carried out from 1994 to 1996 in the Czech Republic, Ireland, and the U. K.[1239,1301,1469] Samples of mosses were hardly found in the Czech Republic. Ranges of common concentrations of trace metals in mosses were fairly similar to those reported for Finland. Only in the English Midlands region were the highest average contents found for (in ppm): Pb 42, Zn 92, and V 8.

Berries and mushrooms grown in forests are also good in bioassays of pollution. Plants grown in the vicinity of the Ni–Cu smelter complex at Monchesgorsk, Kola Peninsula, Russia, show a linear correlation between the metal content of fruits and their concentration in soil.[1216] Berries (*Vaccinium vitis-ideae* and *Empetrum hermaphroditum*) had up to about 30 ppm Cu and 25 to 40 ppm Ni on soils with 3000 ppm of both metals, whereas the most sensitive mushrooms (*Russula vesca*) contained Ni and Cu at levels of 125 ppm and 133 ppm, respectively. Mushrooms from Japanese forests are also broadly used in bioassays of trace element pollution.[1564]

A broad study on the distribution of trace metals in the forest ecosystem near the city of Serpukhov (120 km southeast of Moscow) was carried out by Zolotareva et al.[1578] The authors observed that Mn is likely to concentrate in leaves, whereas all other metals are distributed variably among the parts of trees and herbs. The ability of plants to uptake elements, expressed as the transfer factor, is similar for trees, grasses, and mosses; the highest values were always for Mn and Zn, and the lowest for Fe and Pb.

Several recent research projects have been carried out on the environmental impact of the past anthropogenic activities. It has been shown that rainwater-fed bogs (ombotrophic *Sphagnum* bogs) can be used as archives of atmospheric dust deposition.[1363] As Shotyk[1488] reported, As, Cu, Pb, and Zn are more abundant in surface and near-surface peat layers compared to deeper parts of the profile. The maximum enrichment factors are approximately 5 times for Cu, 15 times for As, and 30 times for Pb, Sb, and Zn. Variations in the Ti concentrations of peat correspond to changes in soil dust inputs due to soil wind erosion and agricultural development, whereas Pb is an indicator of past mining and smelting activities. The increase in Pb contents in Europe dates back to Roman times, but the highest rates of increase in the enrichment factor are for the Middle Ages as well as for modern times in central Europe.[1363] More than 99.9% of each of Cu^{2+}, Pb^{2+}, and Zn^{2+} is bound to an organic phase, either the solid phase or in solution in peat bog pores. This explains a chemical mechanism by which metal migration in the peat profiles may be significantly retarded.[1487]

Peat-bog records of trace metal accumulation are considered a measure of total net deposition. As Nikolishin et al. described the long-distance aerial distribution of Pb and Zn resulted in an increase in their concentrations in sphagnum peat in the remote area of Siberia during the last half century 1910 to 1970, from below 30 to over 100 ppm AW.[1101]

Tree rings have recently been used to examine past environments. Each ring represents 1 year of growth, thereby preserving evidence of past conditions. Geochemists studied the radial distribution of Zn and Mo in cottonwood from the Summiville mine areas in Colorado, and found increased levels of Cu, Zn, and Mo in tree rings after mining activity.[1364] The interpretation of the chemistry of tree rings, however, is complicated by several processes affecting the incorporation of elements into wood tissue. The spatial distribution of water transport, damage to tree roots, and cation binding capacity in the xylem are some factors that govern tree-ring chemistry. Therefore, additional information on the sites and ways of trace metal deposition in woods is needed for a correct dendroanalytical interpretation of element distribution. As Brackhagen et al.[1242] observed, radial distribution patterns of Cd and Zn in stems of Scots pine trees did not correspond with the known timing of pollution inputs to respective forest stands. However, concentrations of Cd and Zn in stem wood were higher in trees growing on contaminated plots.

CHAPTER 3

Soils and Soil Processes

I. INTRODUCTION

A valid concept of the nature of soil must avoid the common error that soil is simply a mixture of unconsolidated material resulting from the weathering processes of underlying rocks. Soil is a natural body, having both mineral and organic components as well as physical, chemical, and biological properties. Soil properties, therefore, cannot be a simple reflection of the combined properties of all soil components.

Any classification of soils suffers from the disadvantage that it is impossible to relate it to the great complexities of soil genesis and properties. The terms used in defining the soils in different systems seldom are exactly equivalent. The definitions of soil units used in this book are adopted from FAO/UNESCO.[226] Short descriptions of the soil units are presented in Table 8. The names of soils described in this book were taken from the original publications, translated, and the associated soil characteristics were fitted, insofar as possible, into the soil units of the FAO/UNESCO system.

The composition of soils is extremely diverse and, although governed by many different factors, climatic conditions and parent material predominate most commonly. An approximation of soil composition is shown in Figures 11 and 12. Soil is composed of three phases—solid (mineral and organic), liquid, and gaseous—and exhibits properties resulting from the physical and chemical equilibriums of these phases. Moreover, not only the chemical composition of the solid components of soil, but also its mineral structure and the state of dispersion are important factors influencing soil properties.

Although trace elements are minor components of the solid soil phase, they play an important role in soil fertility. A knowledge of the association of trace elements with particular soil phases and their affinity to each soil constituent is the key to a better understanding of the principles governing their behavior in soils. The "normal concentrations" of trace elements in soils are of great interest as background values needed for any assessment of the degree of soil contamination. Recent surveys of trace elements in soils are based on the calculation of geometric means and baselines.[976a,985,1012,1047] The database used in this book, however, allows only the estimation of the concentration ranges and arithmetic means which are presented for several trace elements in the selected soil units (Table 9). These data give the approximate information on possible concentrations of the trace elements in uncontaminated soils.

Two stages are involved in the formation of soil from parent material. The first is the alteration of the primary mineral constituents of the parent rocks by the physical and chemical processes of weathering. The second stage (pedogenesis) results in the formation of a soil profile from the weathered rock material, leading to the development of a mature zonal soil as the end point of the interacting processes. Weathering and pedogenic processes cannot be easily distinguished and separated because they may take place simultaneously at the same sites and most commonly they are closely interrelated. They will be discussed separately, however, in chapter subsections.

Table 8 Soil Units Used in the FAO/UNESCO Soil Map of the World[226]

Name of Unit	Symbol	World Distribution[a]	USDA Equivalent[1103]	Certain Old Names	Predominating Soil-Forming Factor[b]	Short Description of Soils
Fluvisols	J	2.40	Fluvents	Alluvial soils	a	Recent alluvial deposits, little alteration
Gleysols	G	4.73	Aquic suborders	Black earths or hydromorphic soils	c	Soils formed from various materials with hydromorphic properties mainly within the top horizon
Regosols	R	10.10	Orthens, Psamments	—	a	Little altered, unconsolidated parent rock
Arenosols	Q		Psamments (part)	—	a	Soils formed from sand, no diagnostic horizons
Lithosols	I	—	Lithic subgroups	—	a	Shallow soils over hard rock
Rendzinas	E	17.17	Rendolls	Rendzinas	a	Shallow soils over limestones
Rankers	U		Lithic, Haplumbrets	—	a	Shallow soils formed from recent siliceous deposits, little alteration
Andosols	T	0.76	Andepts	Volcanic soils	a	Soils formed from recent volcanic ash
Vertisols	V	2.36	Vertisols	Brown soils	a	Clay, cracking soils
Solonchaks	Z	2.03	Salic great group	—	c	Soils, often formed from recent alluvial deposits, with salt accumulation
Solonetz	S		Natric great group	—	c	Alkali soils with hydromorphic properties (high exchangeable Na content)
Yermosols	Y	8.93	Typic Aridisol	Aridisols	c	Desert soils or other formed under aridic regime
Xerosols	X	6.79	Mollic Aridisol	Grey soils	c	Similar to above, but better development of ochric A horizon
Kastanozems	K		Ustosols	—	b	Soils formed under steppe vegetation
Chernozems	C	—	Borolls (part)	—	a,b	Soils developed under prairie vegetation
Phaeozems	H	3.09	Udolls (part)	Degraded chernozems	b	Similar to K and C soils, but more leached
Greyzems	M	—	Borolls (part)	—	b	Soils formed under forests in cold temperate climate
Cambisols	B	7.02	Inceptisols (part)	Brown soils	c	Highly altered soils, having a cambic B horizon
Luvisols	L	7.00	Alfisols (part)	Lessivage processed	c	Similar to B soils, with clay accumulation and more leached
Podzoluvisols	D	2.00	Glossic, Great group of Alfisols	Grey-podzols	c	Transition soils between L and P soil units

Podzols	P	3.63	Spodosols (part)	—	c	Highly altered profile due to leaching
Planosols	W	0.91	—	Mineral–hydromorphic soils	c	Soils slightly leached due to a slowly permeable horizon
Acrisols	A	7.97	Ultisols (part)	—	c	Strongly leached soils with a clay horizon, transition between L and F soil units
Nitosols	N		Some Ultisols and Alfisols	Red-brown soils	c	Tropical soils transition between A and F soil units
Ferralsols	F	8.11	Oxisols	Oxisols, lateritic soils	c	Soils with sesquioxide rich clay fraction formed under tropical climate
Histosols	O	1.82	Histosols	Peats, mucks, bog soils	b	Organic soils, having H horizon of more than 40 cm
Anthroposols[c]	—	—	—	Hortisols, industrosols, regosols	—	Soils formed under a predominant influence of man's activity
Miscellaneous land units	—	3.18	—	—	—	—

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[a] The distribution of major soils, in percent of world soil area, as given by Dudal.[194]

[b] a, Parent rock; b, vegetation; and c, pedogenic processes stimulated mainly by climate.

[c] Soil unit not given in the FAO/UNESCO system.

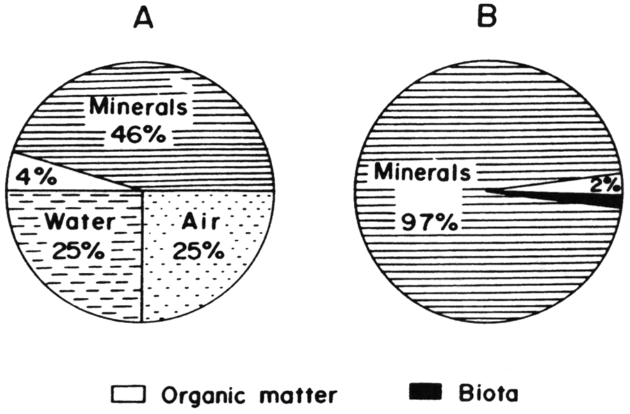

Figure 11 Approximate composition of a representative silty loam surface soil of vertisol soil unit (brown soil). (A) Volume percent of total soils; (B) weight percent of solid phase of soil.

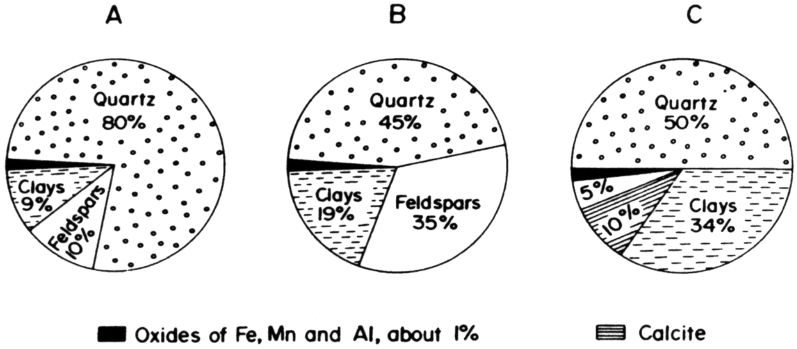

Figure 12 Approximate composition of mineral constituents of surface soils derived from different rocks in a temperate humid climate. (A) Podzoluvisol over sandstone; (B) vertisol over granite; (C) rendzina.

II. WEATHERING PROCESSES

Weathering, the basic soil-forming process, has been extensively studied and reviewed as the complex interactions of the lithosphere, the atmosphere, and the hydrosphere that occur in the biosphere and that are powered by solar energy. Weathering can be chemically described as the processes of dissolution, hydration, hydrolysis, oxidation, reduction, and carbonatization. All of these processes are based on rules of enthalpy and entropy, and they lead to the formation of mineral and chemical components that are relatively stable and equilibrated in the particular soil environments. Biochemical weathering leads to the destruction of parent minerals and to the passing of the elements from the minerals into solutions and suspensions.

Living organisms and their decomposition products play a significant role in weathering. Two types of compounds released by organic matter or organisms are believed to be particularly involved in weathering processes: carbon acid, formed from the CO_2 released during decay of organic matter, and organic chelates. Stevenson[1157] described that most cations released from rocks and minerals during weathering form soluble complexes with natural organic chelates. These processes are comprised of several stages from the first attack on insoluble mineral matter by simple organic chelates excreted by microorganisms to complete saturation of the chelating sites in organic matter, and to the incorporation of the elements into living tissues.

Table 9 Ranges and Means[a] of Total Concentrations of Trace Elements in Surface Soils[b] Calculated on the World Scale (ppm DW)

	Podzols (sandy soils)		Cambisols (silty and loamy soils)		Rendzinas		Kastanozems and Chernozems		Histosols (organic soils)	
Element	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
As	<0.1–30	4.4	1.3–27	8.4	—	—	1.9–23	8.5	<0.1–66.5	9.3
B	1–134	22	<1–128	40	1–210	40	11–92	45	4–100	25
Ba	20–1500	330	19–1500	520	150–1500	520	100–1000	520	10–700	175
Cd	0.01–2.7	0.37	0.08–1.61	0.45	0.38–0.84	0.62	0.18–0.71	0.44	0.19–2.2	0.78
Co	0.1–65	5.5	3–58	10	1–70	12	0.5–50	7.5	0.2–49	4.5
Cr	1.4–530	47	4–1100	51	5–500	83	11–195	77	1–100	12
Cu	1–70	13	4–100	23	6.8–70	23	6.5–140	24	1–113	16
F	<10–1100	130	<10–800	385	<10–840	360	10–1194	550	10–335	220
Hg	0.008–0.7	0.05	0.01–1.1	0.1	0.01–0.5	0.05	0.02–0.53	0.1	0.04–1.11	0.26
I	<0.1–10	2.3	0.3–8.3	1.7	0.3–9.5	3.4	0.3–10.8	2.4	1–10	4
Li	<5–72	22	1.4–130	46	6–105	56	9–175	53	0.01–3.2	1.3
Mn	7–2000	270	45–9200	525	50–7750	445	100–3907	480	7–2200	465
Mo	0.17–3.7	1.3	0.1–7.2	2.8	0.3–7.35	1.5	0.4–6.9	2	0.3–3.2	1.5
Ni	1–110	13	3–110	26	2–450	34	6–61	25	0.2–119	12
Pb	2.3–70	22	1.5–70	28	10–50	26	8–70	23	1.5–176	44
Sc	0.8–30	5	2.4–20	8	<5–15	8	<5–20	10	—	—
Se	0.005–1.32	0.25	0.02–1.9	0.34	0.1–1.4	0.38	0.1–1.2	0.33	0.1–1.5	0.37
Sr	5–1000	87	15–1000	210	15–1000	195	70–500	145	5–300	100
Ti	200–17,000	26,000	500–24,000	3300	400–10,000	4800	700–7000	3500	80–6700	2300
V	10–260	67	15–330	76	10–500	115	25–150	78	6.3–150	18
Zn	3.5–220	45	9–362	60	10–570	100	20–770	65	5–250	50

[a] Ranges of common abundance in topsoils and arithmetic means.

[b] Soil units as given in Table 8.

Greatly simplified, basic weathering processes can be characterized as follows:

1. Dissolution: minerals are soluble in the aquatic phase
2. Hydration: minerals increase their water content
3. Hydrolysis: reaction of minerals with water, producing new ions and/or insoluble components
4. Oxidation: incorporation of the oxygen into the chemical components or increase of the element potential
5. Reduction: reactions that are the reverse of oxidation
6. Carbonatization: alteration of compounds into carbonates due to the incorporation of CO_2

All of these reactions are controlled by chemical equilibria of the particular earth surface environment. The stability of such a system is often illustrated by Eh–pH diagrams for the given geochemical reaction.[256,477] Despite the many questions raised and the difficulties in a practical evaluation of these diagrams, they clearly indicate that both factors—the redox system (Eh) and the buffer capacity (pH)—control physical and chemical properties of the soil. Theoretically, Eh and pH sums represent equilibrium constants, and are estimated to range from 4 (for anaerobic soils) to 17 (for well-aerated soils).[933,989] Redox categories of soil are now expressed in mV units (Eh) and range from >400 mV (aerated) to -300 mV (anaerobic). Soils, however, are not at equilibrium. Especially soil-Eh is extremely variable. Measurements of soil-Eh and soil-pH may explain several thermodynamic processes that occur in the soil systems.[933,1151]

The reactions of trace elements in a particular weathering environment are significantly different. Some generalizations of their properties as described by several authors are presented in Table 10. The mobility of these elements during weathering processes is determined first by the stability of the host minerals and second by the electrochemical properties of the elements. Fe, as the most common cation of variable oxidation stage in the weathering environments, is known to influence the behavior of the associated cations (Table 11).

The pattern of trace element distribution is usually a parameter that is very sensitive to changes of weathering environments. The so-called "chemical nature" of an element reflects mainly its electronegativity parameters and its ionic size. Selected elemental parameters of trace ions given in Table 12 may explain why individual trace elements reveal an affinity for association with major elements in various geochemical environments. The elements with an ionic potential below 3 predominate as free ions, while the elements with an ionic potential between 3 and 12 tend to form hydrolysates or complex ions. Easily mobile elements usually produce smaller hydrate ions in

Table 10 Behavior of Trace Elements in Various Weathering Environments[75,381,599,1130]

Degree of Mobility	Environmental Conditions	Trace Elements
High	Oxidizing and acid	B, Br, and I
	Neutral or alkaline	B, Br, F, I, Li, Mo, Re, Se, U, V, W, and Zn
	Reducing	B, Br, and I
Medium	Oxidizing and acid	Li, Cs, Mo, Ra, Rb, Se, Sr, F, Cd, Hg, Cu, Ag, and Zn
	Mainly acid	Ag, Au, Cd, Co, Cu, Hg, and Ni
	Reducing, with variable potential	As, Ba, Cd, Co, Cr, F, Fe, Ge, Li, Mn, Nb, Sb, Sn, Sr, Tl, U, and V
Low	Oxidizing and acid	Ba, Be, Bi, Cs, Fe, Ga, Ge, La, Li, Rb, Si, Th, Ti, and Y
	Neutral or alkaline	Ba, Be, Bi, Co, Cu, Ge, Hf, Mn, Ni, Pb, Si, Ta, Te, and Zr
Very low	Oxidizing and acid	Al, Au, Cr, Fe, Ga, Os, Pt, Rh, Ru, Sc, Sn, Ta, Te, Th, Ti, Y, and Zr
	Neutral or alkaline	Ag, Al, Au, Cu, Co, Fe, Ga, Ni, Th, Ti, Y, and Zr
	Reducing	Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cu, Cs, Ge, Hg, Li, Mo, Ni, Pb, Re, Se, Te, Th, Ti, U, V, Y, Zn, and Zr

Table 11 Association of Trace Cations with Iron Cations in Neutral or Slightly Acid Aqueous Phase[1122]

Fe Oxidation Stage	Associated Cations
Fe^{2+}	Ti^{3+}, Ti^{4+}, V^{3+}, V^{4+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Pb^{2+}, W^{6+}, U^{4+}
Fe^{3+}	Ti^{4+}, V^{4+}, Cr^{6+}, Mn^{2+}, Mn^{4+}, Co^{2+}, Co^{3+}, Pb^{2+}, Pb^{4+}, W^{6+}, U^{6+}

Table 12 Geochemical Associations and Some Properties of Trace and Major Elements

Major Elements (boldface) and Associated Trace Element	pH of Hydrous Oxide Precipitation	Ionic Radii (Å)	Electronegativity (kcal/g atom)	Ionic Potential (charge/radius)	Diameter of Hydrated Ion in Aqueous Solution (Å)
K^+	—	1.7–1.6	0.8	0.6	3.0
Na^+	—	1.2–1.1	0.9	0.9	4.5
Cs^+	—	2.0–1.9	0.7	0.5	2.5
Rb^+	—	1.8–1.7	0.8	0.6	2.5
Ca^{2+}	—	1.2–1.1	1.0	1.8	6.0
Mg^{2+}	10.5	0.8	1.2	2.5	8.0
Sr^{2+}	—	1.4–1.3	1.0	1.5	5.0
Ba^{2+}	—	1.7–1.5	0.9	1.3	5.0
Pb^{2+}	7.2–8.7	1.6–1.4	1.8	1.9	4.5
Se^{3+}	—	0.8	1.3	3.7	9.0
Fe^{2+}	5.1–5.5	0.9–0.7[a]	1.8	2.6	6.0
Cu^{2+}	5.4–6.9	0.8	2	2.5	6.0
Ge^{4+}	—	0.5	1.8	8.3	—
Mo^{4+}	—	0.7	—	5.5	—
Mn^{2+}	7.9–9.4	1–0.8	1.5	2.0	6.0
Zn^{2+}	5.2–8.3	0.9–0.7	1.8	2.6	6.0
Fe^{3+}	2.2–3.2	0.7–0.6[a]	1.9	4.4	9.0
Co^{2+}	7.2–8.7	0.8–0.7	1.7	2.6	6.0
Cd^{2+}	8.0–9.5	1.03	—	—	—
Ni^{2+}	6.7–8.2	0.8	1.7	2.6	6.0
Cr^{3+}	4.6–5.6	0.7	1.6	4.3	9.0
Mn^{4+}	—	0.6	—	6.5	—
Li^+	—	0.8	1.0	1.2	6.0
Mo^{6+}	—	0.5	1.8	12.0	—
V^{5+}	—	0.5	—	11.0	—
Al^{3+}	3.8–4.8	0.6–0.5[a]	1.5	5.6	9.0
Be^{2+}	—	0.3	1.5	5.7	8.0
Cr^{6+}	—	0.4	—	16.0	—
Ga^{3+}	3.5	0.7–0.6	1.6	4.9	—
La^{3+}	—	1.4–1.3	1.1	2.3	9.0
Sn^{2+}	2.3–3.2	1.3	1.8	1.5	—
Y^{3+}	—	0.9	1.2	3.1	—
Si^{4+}	—	0.4	1.8	12.0	—
Ti^{4+}	1.4–1.6	0.7	1.5	5.8	—
Zr^{4+}	2.0	—	1.4	4.3	11.0

[a] Values given for high and low spin, respectively.

aqueous solutions than do more stable elements; also, the free energy (enthalpy) needed for the formation of their ions seems to be less than the energy required for ion formation of less mobile elements. Nieboer and Richardson[1099] proposed the classification of ions based on their coordination chemistry that describes the formation of ion/ligand complexes (Table 13). This classification gives general information on possible compounds that may be formed in specific environmental conditions.

Table 13 Classification of Ions Based on the Formation of Complexes[1099]

Class	Ions
Oxygen seeking	Cs^+, Li^+, Ba^{2+}, Sr^{2+}, La^{3+}, Gd^{3+}, Lu^{3+}, Y^{3+}, Be^{2+}, Sc^{3+}
Borderline	Cd^{2+}, Sn^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{2+}, V^{2+}, Zn^{2+}, Mn^{2+}, Ti^{2+}, In^{3+}, Ga^{3+}, $Sb^{3+,-}$, $As^{3+,-}$, $Sn^{4+,-}$
Nitrogen/sulfur seeking	Au^+, Ag^+, Cu^+, Tl^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, Bi^{3+}, Ti^{3+}, $Pb^{4+,-}$

Trudgill[1167] described that the amounts of cations solubilized by biological activity and by chelate action are usually much greater than those mobilized by the action of water and hydrolysis alone. The role of microorganisms (bacteria and fungi) and plants is of great importance in solubilizing minerals, and thus, in the input of chemical elements to the soil solution. These processes are known as biological weathering.

III. PEDOGENIC PROCESSES

Several specific reactions, in addition to those involved in weathering, lead to the formation of a particular soil profile. Although there is great diversity in pedogenic processes, they all include the following similar stages:

1. Addition of organic and mineral materials to the soil
2. Losses of these materials from the soil
3. Translocation of these materials within the soil, both vertically and horizontally
4. Transformation of organic and mineral matter in the soil

These processes can be constructive or destructive in soil formation. Six factors that largely control the kind of soil that finally develops are:

1. Climate (temperature, rainfall)
2. Vegetation and other soil biota
3. Parent material (the nature of minerals)
4. Topography (open or closed systems)
5. Time
6. Anthropogenic activity (degradation, contamination, recultivation)

Classification of soil units very commonly is based on the factors predominating in soil-forming processes (Table 8). Pedogenic processes stimulated mainly by climate most commonly predominate, but soils influenced most strongly by parent material or vegetation are quite frequent.

Initially, at early stages of weathering and pedogenic processes, the trace element composition of the soil will be inherited from the parent material. With time, however, the trace element status of soil will become different due to the influence of predominating pedogenic and anthropogenic processes (Table 14). The comparison of trace element concentrations in soils with their concentrations in parent material is commonly used as a factor of their mobility during pedogenic processes. However, the dilution effect of humus in organic-rich soils should be considered in making meaningful judgments on the accumulation or migration of these elements during weathering and soil formation. The fate of trace elements mobilized by dissolution of the host minerals of compounds depends on the properties of their ionic species formed in the soil solution (Tables 10 and 13) and is governed by the chemical system of a soil that can be characterized as follows:

1. Heterogeneous distribution of compounds
2. Seasonal and spatial alterations in major master variables, as pH, Eh
3. Transformation of species: (a) electron transfer reactions, (b) ligand exchange reactions, (c) organometallic reactions, (d) biotransformations

Table 14 Principal Types of Soil-Forming Processes and Trends in the Behavior of Trace Elements

Process	Most Favorable Climatic Zone	Typical Soil Unit[a]	Behavior of Trace Elements in Surface Soil: Accumulation	Behavior of Trace Elements in Surface Soil: Migration
Lack of chemical alteration	Ice-bound or desert	R,Q, and Y	—	—
Podzolization	Cold northern	D and P	Co, Cu, Mn, Ni, Ti, V, and Zr (in illuvial horizon)	B, Ba, Br, Cd, Cr, I, Li, Mn, Rb, Se, Sr, V, and Zr
Aluminization	Cool and humid temperate	B. L, M. W, and A	Co, Mn, Mo, and V (in gleyed horizon)	B, Ba, Br, Cu, I, Se, and Sr
Siallitization	Warm temperate and dry tropical	V and K	B, Ba, Cu, Mn, Se, and Sr	—
Lateritization	Humid tropical	A,F, and N	B, Ba, Cu, Co, Cr, Ni, Sr, Ti, and V	—
Alkalization	Warm with dry seasons	Z,S, and (X)	B, Co, Cr, Cu, Mo, Ni, Se, Zn, and V	—
Hydromorphic formations	Intrazonal soils	—	B, Ba, Co, Cu, I, Mn, Mo, Se, Sr, and U (in organic horizon)	B, Br, Co, Cu, Mn, Ni, U, and V

[a] Symbols of the soil units as given in Table 8.

4. Transfer between phases: (a) adsorption reactions, (b) diffusion-absorptions into solids, (c) diffusion to solution phase (e.g., solubility), (d) formation of solid phase, (e) co-precipitation, (f) coagulation
5. Biouptake and bioaccumulation

Biological, chemical, and physical characteristics of such natural systems as soils have chemical gradients with depth and also have significant seasonal alterations of some major master variables. The lack of accurate *in situ* measurements of these critical chemical parameters as well as the lack of determinations of their distribution and variability at the level of individual soil pores and particles is an important limitation in our understanding of the chemical context of the soil system. Thus, dynamic equilibrium between soil components is governed by various interactions between the soil solid and gaseous phases, biota, and the soil solutions, as is illustrated by the diagram in Figure 13.

Several recent studies of kinetics of reactions in the soil system were conducted, and some principles, mechanisms, and models were described and proposed.[1151,1154] The chemical forms governing the mobility and phytoavailability of trace metals and residence times of trace pollutants in the soil layers have been the main subjects of mechanistic modeling and calculations. Sparks[1151] stated that thermodynamic data can predict only the final state of a system from an initial nonequilibrium mode. However, kinetic data provide valuable insights into the reaction pathways and into the mechanisms of chemical reactions in the complex multi-phase soil system.

A. Dissolution and Mobilization

Chemical reactions leading to solution of each species of ions can be characterized by thermodynamic equations. At each equilibrium state the reaction rates of both directions compensate and keep the composition of the soil phases (solid, liquid, and gaseous) constant.

Chemical equilibria of various soils have been studied and comprehensive mathematical models for the particular soil conditions are presented by Bolt and Bruggenwert.[86] Although many papers have been published on the behavior of trace elements in soils, their chemistry is insufficiently known. The diversity of ionic species of trace elements and their various affinities to complex with inorganic and organic ligands make possible the dissolution of each element over a relatively wide range of pH and Eh. Each element can also be quite readily precipitated and/or adsorbed, even

Table 15 **Trace Elements in Natural Soil Solutions Obtained by Centrifugation from Soils of Various pH Values**[1045]

	Soil Type and Range of pH Values				
Element	**Acid Sandy (2.5–4)**	**Sandy (4–4.5)**	**Silty (5.5–6.5)**	**Loamy (7–7.5)**	**Calcareous (7.5–7.8)**
B	—	—	—	200	800
Cd	107	—	—	—	—
Co	—	—	—	0.5	5
Cu	783	76	20	50	50
Fe	2223	1000	500	200	100
Mn	5965	8000	5000	100	700
Mo	—	—	—	5	3
Pb	5999	—	—	—	—
Zn	7137	1000	5000	100	300

Note: Values are arithmetic means (μgL^{-1}) of 4 to 5 samples.

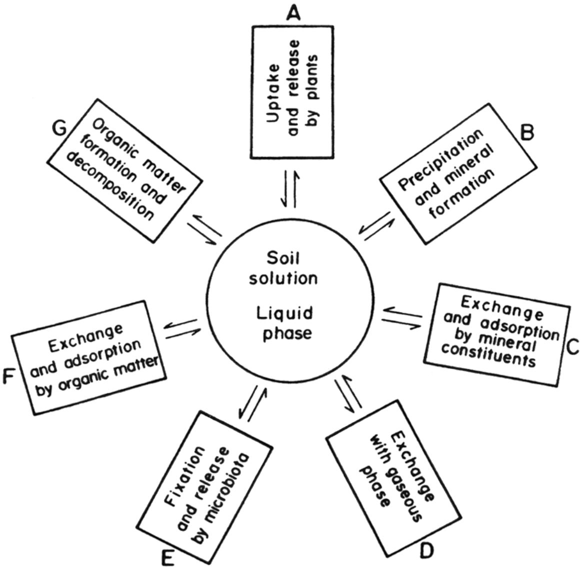

Figure 13 Interactions between soil components and compartments.

under a small change of the equilibrated conditions. In soils, solubility equilibria may change significantly within a few centimeters (even millimeters) at both horizontal and vertical soil gradients. Thus, these equilibria are local and may often be quite different in various sites of the soil. Since the dynamic nature of soil components causes dissolution and precipitation, many of the minerals and amorphic solids may not be in equilibrium under soil conditions.

Many textbooks present stability diagrams for ionic species of trace elements as functions of pH and Eh.[166,256,477] In natural soil conditions, pH ranges most often between 5 and 7, and Eh ranges between 400 and −200 mV, except where there are high reduction states in waterlogged soils. The properties of ionic species of each element vary, and the pH range for precipitation of their hydrous oxides is flexible (Table 12). One can, however, conclude that usually the most mobile fractions of ions occur at a lower range of pH and at a lower redox potential, which is illustrated in Figure 14. It can be anticipated that with increasing pH of the soil substrate, the solubility of most trace cations will decrease. Indeed, the concentration of trace elements is lower in soil solutions of alkaline and neutral soils than in those of light acid soils (Table 15). Sposito[1153] investigated the

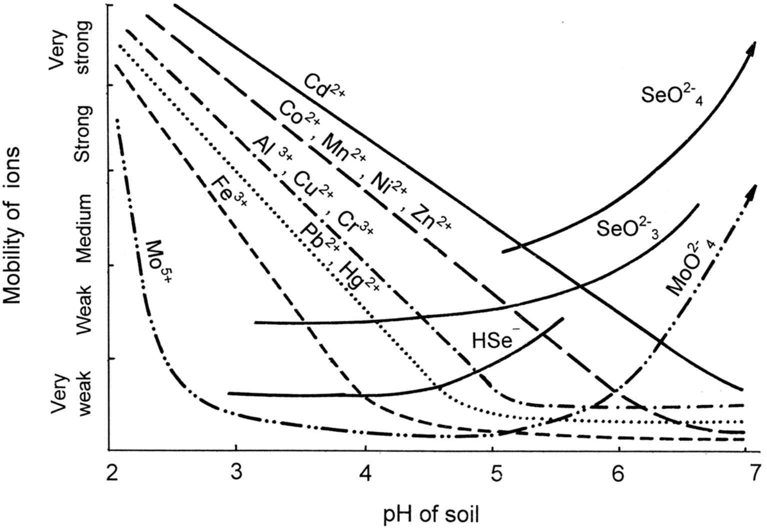

Figure 14 Schematic trends in the mobility of metals as influenced by soil pH. (Data for light mineral soil.)

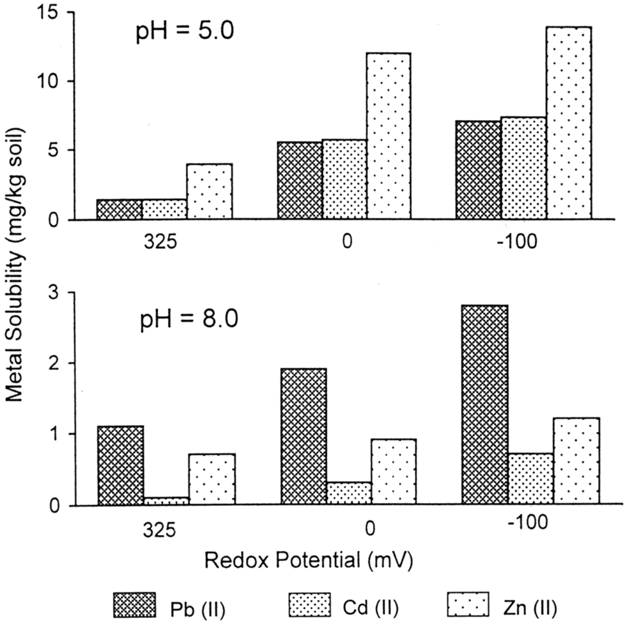

Figure 15 Impact of redox potentials on the solubility of soil trace metals in water at pH 8.0 and 5.0. (With permission from Kluwer Academic Publishers and the authors[1258].)

chemical thermodynamics and its applicability to the soil solution and described possible systems of trace cation exchange.

Most often, the mobility of trace metals, especially of Cd, Cu, Cr, and Zn, increases in poorly aerated (low oxidation stage, Eh < 100 mV) soils. However, increasing Cd solubility with increasing Eh up to >200 mV was also observed.[1425] The effect of redox potential on availability of Cd, Cu, and to a smaller degree Zn, was reported by Gambrell and Patrick.[1304] Also, Chuan et al.[1258] described that acidic and reducing soil conditions are more favorable for trace metal solubilization, and the effect of pH is more significant than that of redox potential (Figure 15).

Smith and Huyck[1501] studied metal mobility under different environmental conditions. Although it is difficult to predict element mobility in surficial environments, the authors referred to the capacity of an element to move within fluids after dissolution. The following conditions and behaviors of trace metals were distinguished:

1. Oxidizing and acid, $pH < 3$: (a) very mobile—Cd, Co, Cu, Ni, and Zn; (b) mobile—Hg, Mn, Re, and V; and (c) somewhat mobile and scarcely mobile—all other metals.
2. Oxidizing in the absence of abundant Fe-rich particulates, $pH > 5$: (a) very mobile—Cd and Zn; (b) mobile—Mo, Re, Se, Sr, Te, and V; and (c) somewhat mobile and scarcely mobile—all other metals.
3. Oxidizing with abundant Fe-rich particulates, $pH > 5$: (a) very mobile—none; (b) mobile—Cd and Zn; and (c) somewhat mobile and scarcely mobile—all other metals.
4. Reducing in the absence of hydrogen sulfide, $pH > 5$: (a) very mobile—none; (b) mobile—Cd, Cu, Fe, Mn, Pb, Sr, and Zn; (c) somewhat mobile and scarcely mobile—all other metals.
5. Reducing with hydrogen sulfide, $pH > 5$: (a) very mobile—none; (b) mobile—Mn and Sr; and (c) scarcely mobile to immobile—all other metals.

It is evident that Fe-rich particulates and hydrogen sulfide are among the abiotic factors most significant in controlling trace metal behavior in the terrestrial environment. Ankley et al.[1202] include the acid-volatile sulfide system in developing the sediment quality criteria (SQC), which clearly refers to a crucial impact of sulfides on the behavior of metals in sediments.

The solubility of trace elements in soil has great significance in their biovailability and their migration. Heavy soils, both neutral and alkaline, provide good storage for trace elements and will supply them to plants at a slow rate. This slow release may, however, cause deficiency effects of certain micronutrients to develop in plants. Light soils, on the other hand, can be a source of easily available trace elements during a relatively short period of time. These soils can also lose their pool of available micronutrients at quite a high rate.

The liquid phase of soil, also called *soil solution*, is composed of water with colloidal suspension and dissolved substances, which can be free salts and ions of these salts.

Some of the first studies of soil solutions conducted by Hodgson et al.[320] indicated that appreciable quantities of trace elements are present as complexes, mainly with organic ligands. Inorganic complexes may, however, also be of importance for the particular element and condition.

Knowledge of the total composition of the soil solution or any nutrient solution is essential for predicting plant uptake of nutrients or plant growth. The uptake of a given ion depends not only on its activity in the solution, but also on the activities of other ions and the relation that exists between solution ions and exchangeable or solid-phase ions. However, the transfer of chemical elements between soil compartments and plants does not necessarily go through the liquid phase. Several direct exchanges at the surface of phases and compartments are possible. Most common and significant interchanges occur between the compartments A and C, D, E, F; B and E, G; C and D, E, F; and E and C, D, F (Figure 13).

The concentrations of trace elements in soil solutions vary considerably among soils and with time. Great fluctuations have been observed under the influence of the following factors:

1. Time
2. Vegetation
3. Microbial activity
4. Waterlogged states
5. Heterogeneity of the solid soil phase

Moreover, methods used for obtaining solutions from soils differ widely; therefore, it is difficult to adequately determine mean concentrations of trace elements. Nevertheless, the range of trace element concentrations, as measured in various soil solutions, is reasonably similar (Table 16).

Table 16 Trace Elements in Natural Soil Solution of Different Soils (μg L^{-1})

	Techniques Used for Obtaining Soil Solution										
	Suction from Soil Paste	Pump off 0.01 N $CaCl_2$ Solution	Centrifugation			Ceramic Plate or Porous Cup Suction			Unspecified Technique		Zero-Tension Lysimeter[b]
Element	(99)	(320)	(375)	(892)	905)	(311)	(342)	(298)	(794)[a]	(1174)	(942)
Al	400	—	—	460	—	—	—	—	—	—	—
As	—	—	—	—	—	—	4–12	—	—	—	—
B	3060	—	67–880	—	—	—	—	—	—	12–33	—
Ba	260	—	—	—	—	—	—	—	—	—	—
Cd	—	—	—	6	—	3–5	5–300	0.2	<0.01–0.2	—	0.2–2.9
Co	60	<0.4–14	0.3–5	3	—	12–87	—	0.3–1	—	0.6–29	—
Cr	10	—	—	0.4	—	0.6–0.7	Trace	—	—	9–29	0.6–7.5
Cu	40	3–18	28–135	37	78	18–27	14–44	0.5–3	<1–3	29–116	1.8–22
Fe	50	—	150–549	16	—	36	—	30–40	<50–1000	—	—
Hg	2.4	—	—	—	—	—	—	—	—	—	—
Li	111	—	—	—	—	—	—	—	—	—	—
Mn	170	—	32–270	243	55	1000–2000	—	25–50	2000–8000	120–7100	—
Mo	730	—	2–8	2	30	—	—	—	—	2.1–3.3	—
Ni	20	—	—	150	—	3–15	20–25	3–8	—	3–21	0.6–5.4
Pb	50	—	—	8	—	5–63	Trace	0.6–2	<2	3–21	4–65
Sr	930	—	—	—	—	—	—	—	—	—	—
Ti	<100	—	—	—	—	—	—	—	—	—	—
V	70	—	—	—	—	—	—	—	—	—	—
Zn	70	21–180	73–270	351	22	190–570	40–17,100	4–25	1–15	88–143	31–470

Note: References are in parentheses.

[a] Data for paddy soils, after flooding for 14 weeks.

[b] Solutions of organic horizons of soils of forest ecosystems in different countries.

Vaselli et al.[1531] measured trace metal concentrations in soil solution by means of zero-tension microlysimeters from two pedological horizons of the Xerochrept forest soil in Tuscany (Italy). Concentrations of these metals varied significantly with time of collection, especially in the solution obtained from the A horizon; for example, range (in μg/L) for Zn was 35–1586, Cu 9–131, Mn 5–200, Ni 1–50, Cr 2–44, Pb 1–17, and Cd <0.1–0.9. Metal contents in solution from the B horizon were most stable and indicated significantly higher amounts of Ni (range 31–92 μg/L) and Cr (range 3–154 μg/L). The authors explained this phenomenon as an effect of weathering of parent material enriched in these metals.

Rainfall, evaporation, and plant transpiration can change trace element concentrations in soil solutions more than tenfold, whereas the observed variations for major ions (Ca, Mg, K, Na, NO_3, and PO_4) are much less. The acidification increases the intensity by which trace metals are mobilized in soils. The concentration of metals in the solution of the very acid soil was 9080 $\mu g\ L^{-1}$ (the sum of Fe, Mn, Zn, Pb, Cu, and Cd), whereas the solution of the same kind of soil, but with neutral range of pH, contained 17 μgL^{-1} of these cations.[1048]

Soluble major ions greatly influence the quantities of soluble trace elements. Solutions of most soils contain an excess of Ca, which in many soils constitutes more than 90% of the total cation concentration. Ca is, therefore, the most important cation in governing the soluble stage of trace elements in soils. There are examples, however, of soils in which complexing trace cations prevent precipitation in the presence of Ca^{2+} and in soil solutions having a relatively high pH level. Thus, higher than normal concentrations of dissolved metal ions in solutions and the ready uptake of trace elements by plants usually are related to the formation of complexes. This possibility is suggested also by the observation that half of the calcium in soil solutions is usually present as an organic complex.[356] The anionic composition of soil solutions is also of importance in controlling the trace element status. Little is known, however, about the relation of trace elements to anionic species in soil solutions.

Differing complexing tendencies of cations to interact with ligands can be explained by the rules of coordination chemistry. It is possible, therefore, to predict that certain cations more readily complex a particular ligand. Thus, some metallic ions such as Be^{2+}, Cr^{3+}, and Co^{3+} will react readily with PO_4^{3-}, CO_3^{2-}, NO_3^-, and organic amines, etc.; the group including Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Sn^{2+} may more easily complex Cl, Br, NO_2, and NH_3, while cations of the chemical nature of Hg^{2+}, Ag^+, and Tl^+ are likely to link with complexes of I, CN, CO, S, P, and As.

In the soil aqueous phase, organic compounds and water are the most abundant ligands; therefore, hydrolysis and organic complexing are the most common reactions in soil solutions. These reactions are pH sensitive and can be correlated with the size and charge of the cations. Higher ionic potentials usually indicate a higher degree of hydration in the solution, thus an easier precipitation. The range in pH for the precipitation of hydrous oxides of some cations (Table 12) illustrates that the order of cation mobility in an aqueous phase under an oxidation regime of soil may decrease as follows: $Mg^{2+} = Ca^{2+} > Ag^+ > Hg^{2+} > Mn^{2+} > Cd^{2+} > Ni^{2+} = Co^{2+} = Pb^{2+} > Be^{2+} > Zn^{2+} = Cu^{2+} > Cr^{3+} > Bi^{3+} > Sn^{4+} > Fe^{3+} > Zr^{4+} > Sb^{3+}$. However, the application of data on heavy metal activity in pure systems to soils can only be informative because of various effects of complex ion formation, solid solution, and coating. Rose et al.[1131] discussed general rules governing the mobility and transport of chemical elements in aqueous solutions of the surficial environment and emphasized that the transition elements with incomplete inner electron shells (e.g., most of trace metals) are slightly soluble and strongly adsorbed by media.

The solubility of trace elements in soils evidently depends on complex formation. However, most of the species of trace elements, especially cations, are but slightly soluble, and only small proportions occur in the aqueous phase. The calculation made by Kabata-Pendias[375] showed that the total content of trace cations generally ranges from 10 to 100 μgL^{-1} in normal soil solutions, while in contaminated soils these values can be much higher. When soluble compounds of trace metals are added to soils, their concentrations in equilibrated solutions increase with increasing doses of added metals. In an experiment conducted by Cottenie et al.,[148] the relative solubility of the added metals at the highest dose rate in light sandy soil was as follows: 39% of 1000 mg Zn/kg, 50% of 5000 mg Cu/kg, 30% of 5120 mg Cd/kg, and 26% of 2695 mg Pb/kg.

Bujtas et al.[1246] studied the solubility rate of metals added with sewage sludge enriched in metals (Cd, Cr, Ni, Pb, and Zn) to soils. The transfer factor, calculated as a ratio of metals in solution of highly contaminated soil to their contents in solution of the control soils, decrease in the following order: Cd 1804 > Ni 604 > Zn 563 > Pb 156 > Cr 4. These results clearly indicate extremely easy solubility of Cd under soil conditions of brown forest soil at pH (KCl) about 5.0. For sandy acid soils, values of the transfer factor were even higher. On the other hand, Csillag et al.[1265] concluded that the transfer of these metals applied to soil in forms of sludges was rather negligible when amounts of added metals corresponded to the official limits.

Sauvé et al.[1478] calculated free metal activity (pCu^{2+} and pPb^{2+}) in the soil solution based on total Cu, pH, and soil organic matter. They concluded that these values improve the prediction for toxic effects on crops and biological activity of soils, and are also appropriate for other metals.

B. Transport and Budget

The balance input-output budget for trace elements is rarely met, even under natural conditions. The anthropogenic part of this imbalance is related both to the increase of deposition rate of elements and to the increase in cation leaching resulting mainly from the soil acidification, and also from other impaired impacts of the land use. The budgets of metals in forest soils have received much attention, especially in Sweden and West Germany.[310,311,815,816,907,941,942,1156]

The transport of dissolved trace elements may take place through the soil solution (diffusion) and also with the moving soil solution (mass flow, leaching). Generally, in soils formed under a cool and humid climate, the leaching of trace elements downward through the profiles is greater than their accumulation, unless there is a high input of these elements into the soils. In warm, dry climates, and also to some extent in humid hot climates, upward translocation of trace elements in the soil profiles is the most common movement. The rates of trace element migration in the profiles are affected by chemical, physical, and biological soil properties, of which the most important are:

1. Eh-pH system
2. CEC and salt content
3. Amount and quality of organic matter
4. Water and temperature
5. Plant species
6. Micro- and mezobiota activities

Although much work has been done on trace element movements within soil profiles, complete knowledge concerning their cycling and balances is still lacking. Theoretical reviews of mechanisms involved in the transport and accumulation of soluble soil components were given by Bolt and Bruggenwert[86] and by Lindsay.[477] The equilibria discussed by these authors are useful not only in illuminating fundamental reactions that are important in weathering and soil formation, but also for use in various fields of agricultural and environmental management. However, the models cannot be used for examining the quality of thermodynamic data obtained from a particular soil without making necessary modifications that take into account the variations of soil properties, and even then, some skepticism may remain.

Several detailed studies based on lysimetric experiments, and other research often using isotopic tracers, have yielded much information on element transport. However, each soil profile with developed horizons has its own characteristic trace element movement.

Impoverishment of soils in trace elements is due mainly to their mobility downward with percolating waters through the profiles of freely drained acid soils and also to trace element uptake by plants. On the other side of the balance is the input of trace elements with atmospheric precipitation and their accumulation in particular soil horizons. In acid soils (e.g., with pH below 6.5), several elements, such as Zn, Mn, Cu, Fe, Co, and B, are easily leached. These elements, however, are likely to form quite stable compounds if the pH of the soil rises above 7. Other elements, such as Mo and Se, are mobilized in alkaline soils, while in acid soils they become almost insoluble.

Trace element budgets have been calculated for various ecosystems (Table 17). Input/output differences show that for the majority of elements, the accumulation rate in the surface soils is positive. Leaching rate of trace metals was found to be higher than atmospheric input only in acid forest soils. Thus, under a forest ecosystem with a high rate of mobility and leaching of metals from the soil, a decrease of these cations is observed, even under a relatively high input to the soil. Such a case is described by Mayer and Schultz[1088] for the forest ecosystems in West Germany. The flux balance for acidified forest soils has indicated the depletion of most metals, with the exception of Pb. The losses of metals from the topsoil at pH 2.9 were as follows (in g ha^{-1} $year^{-1}$): Mn ± 0; Cr −2; Cd −12; Co −55; Cu −68; Zn −221; Al −43,300, while a gain was noticed only for Pb (+324). The rate of metal leaching from the forest soil at pH 4.3 was much lower, and the gain of more metals (e.g., Cr, Cu, and Pb) was observed.[1088] Similar data are presented by Tyler et al.[1172] for metal leaching from forest soils in Sweden. The calculations of Cd budget for soils of two European countries (Table 18) show that the input of this metal originating both from the point source of pollution and from long-range transport is about equal to the nonpoint source of pollution related to farm management practices. In industrial regions with increased emission of metals, aerial dust and precipitation are the most significant sources of trace metals. It was estimated, however, that at the global scale the input of most metals is higher from industrial sources than from the application of chemicals and wastes in farming.[957,1135] Countries with a high rate of technogenic fluxes of metals are also likely to receive a high deposition rate of these elements.[1112] Kovda[1054] made the general assessment of recent soil pollution and calculated the technogenous deposition of trace metals on land to range from 1 to 100 g ha^{-1} $year^{-1}$. In soils with a low rate of leaching, the continuous accumulation of trace metals is most likely (Table 17).

Bergkvist et al.[942] reviewed recent literature on trace metal fluxes in forest ecosystems with an emphasis on metal budgets in both forest ecosystems and forest soils. Their final conclusions can be summarized as follows:

1. The rate of both soil acidification and metal leaching depends greatly on the soil type and vegetation type.
2. Spruce and beech stands show a higher metal leaching rate than birch stands and open grass-dominated areas with the same parent mineral soils.
3. The potential loss of metals (and of base cations) is greater from a brown forest soil than from a leached podzol.
4. In general, forest topsoils accumulate Cu and Pb and lose Zn, Cd, and Ni. Cr is rather in balance, especially in less acidic soils.
5. Losses of Zn from forest soils usually are not compensated by weathering rate, thus a deficiency of this metal can be expected, in particular under increased soil acidification by acid rain.
6. The organic topsoil (litter and mor layers) is the most significant sink for metals, especially for Cu, Pb, and Cr; but when organic compounds mobilize these metals, they are likely to precipitate in the upper B horizon.
7. The relationship between the pH and the total concentrations of Zn, Cd, and Ni is very close although nonlinear; a drastic change in the metal solubility in the mineral soil (or horizon) occurs in the pH range of 4.0–4.5.

C. Sorption and Adsorption

Soils are considered as sinks for trace elements; therefore, they play an important role in environmental cycling of these elements. They have a great ability to fix many species of trace ions. The term “sorption” used in this chapter refers to all phenomena at the solid-solution boundary,

Table 17 Metal Budgets of Soils of Different Ecosystems (g ha^{-1} year^{-1})

Ecosystem, Locality, and Experiment	Element	Total Atmospheric Deposition	Output	Annual Budget
Deciduous forest, Tennessee, U.S.[823]	Cd	21	7	14
Acid light loam (stream water)	Pb	286	6	280
	Zn	538	149	389
Agricultural land, Denmark[304] (drainage water)	Cd	3	0.3	2.7
	Pb	260	0.3	259.7
	Zn	250	120	130
Pine forest, Schwarzwald, Germany[907]	Be	0.3	5.6	−5.3
Brown podzol (seepage water)	Cd	4.5	1.4	3.1
	Co	5.6	4.3	1.3
	Cu	18	7	11
	Ni	34	17	17
	Mn	70	430	−360
	Pb	110	6	104
	Zn	210	76	134
	Fe	300	2000	−1700
Birch and spruce forest, Solling Mountains, Germany[310]	Bi	0.4	0.2	0.2
	Hg	0.4	0.2	0.2
Brown acid silty loam (seepage water)	Tl	1.2	0.3	0.9
	Sb	3	0.3	2.7
	Cd	13	9	4
	Ni	15	14	1
	Cr	22	2	20
	Mn	200	6300	−6100
	Cu	224	108	116
	Zn	3900	1900	2000
	Fe	1600	1900	−300
Field plots, Pulawy, Poland[1045,1047]	B[a]	71	40	31
Podzolic light loam (seepage water)	Cd	5	3	2
	Cu	39	25	14
	Mn	181	90	91
	Pb	200	40	160
	Zn	540	180	360
Spruce forest, Hässleholm, Southern Sweden[815,816]	Cd	2	5	−3
	Cr	8	10	−2
Podzolic forest soil (lysimeter)	Ni	10	9	1
	V	12	28	−16
	Cu	20	29	−9
	Pb	150	81	69
	Zn	180	270	−90
	Fe	2000	13,000	−11,000
Spruce forest, Gårdsjön, Sweden[940]	Cd	3.2	4.2	−1
Sandy shallow soil (lysimeter)	Cr	3	8.3	−5.3
	Cu	9	4.8	4.2
	Ni	5.7	21.3	−16
	Pb	77	2	75
	Mn	90	690	−600
	Zn	331	461	−130
	Fe	1500	1400	100
Oak forest, Sichote-Alinija, East Siberia, Russia[988]	Cd	29	0.4	28.6
Stream and seepage waters	Cu	136	15	121
	Mn	214	23	191
	Zn	1098	80	1018
	Pb	4708	33	4675
	Fe	3860	244	3616

(*Continued*)

Table 17 (Continued)

Ecosystem, Locality, and Experiment	Element	Total Atmospheric Deposition	Output	Annual Budget
Forest, Czech Republic[109,957a,1376]	B[a]	1480;4000		
	Be	4.5	58	
	Cu	40;50		
	Mo	70;100		
	Zn	500		
	Mn	1000;2480		
	Fe	840;2000		

[a] The only data for nonmetallic elements.

Table 18 Budgets of Cadmium in Agricultural Soils of Poland and Germany[1046] (g ha^{-1} $year^{-1}$)

	Poland	Germany
Input		
Fertilizers	1–2.5	1–6
Slurry	2.5	—
Sludges	1.5	$<$1–25
Harvest residues (recycling)	3	0.3–8
Atmospheric input	2.5–4	3–8
Total input	10.5–13.5	4.3–47
Output		
With crops	3	1–5
With seepage water	3	1–2
Total output	6	2–7
Balance (net gain)	4.5–7.5	1.3–40

including the following intermolecular interactions:

1. Van der Waals' forces
2. Ion-dipole forces
3. Hydrophobic and hydrogen bondings
4. Charge transfer
5. Ion and ligand exchanges
6. Chemisorption
7. Magnetic bonding

Every soil component is active and affects soil solution ion concentration either by precipitation-dissolution reactions or by ionic interactions with phase surfaces.

Soil components involved in sorption of trace elements are:

1. Oxides (hydrous, amorphic), mainly of iron and manganese and, to a much lesser extent, aluminum and silicon
2. Organic matter and biota
3. Carbonates, phosphates, sulfides, and basic salts
4. Clays

Of all these components, clay minerals, hydrated metal oxides, and organic matter are considered to be the most important group in contributing to and competing for the sorption of trace elements. Blume and Brümmer[947] described bonding capacity of the main soil components; organic matter fixes very strongly Cr^{3+}, Fe^{3+}, Pb, and Hg, fixes fairly Cd, Ni, and Co, and fixes slightly Mn and Zn; clay minerals fix very strongly only Fe^{3+}, fix relatively slightly Cd, Co, and Ni, while the other trace metals are bound rather fairly; oxides (sesquioxides) fix very strongly Cr^{3+}, Hg, and Pb, and fix relatively strongly all other metals.

Sorption mechanisms can be based on the valency forces and the process is called "chemisorption." If van der Waals' forces are involved in sorption, the process is called "physisorption." Both sorptions play an important role in the fixation of uncharged complexes. Each trace cation can be sorbed specifically and nonspecifically, as was shown for Cd by Tiller et al.[796] Pickering[1118] described that cation movement in soils and in weathering substrates can be retarded by a range of interface forces which can be subdivided into categories such as:

1. Electrostatic attraction (surface exchange)—ion exchangeable species
2. Weakly adsorbed—attractive forces less well-defined—cations displaceable by reagents such as acetic acid or acidic buffer solutions
3. Specifically adsorbed—a chemisorption process in which formal bonding between cation and substrate is strong; sorbate release can require matrix destruction

The term "adsorption" is commonly used for the processes of sorption of chemical elements from solutions by soil particles. Adsorption is thus the kinetic reaction based on thermodynamic equilibrium rules. The forces involved in the adsorption of ionic species at charged surfaces are electrostatic and can be explained by Coulomb's law of attraction between unlike charges and repulsion between like charges. At metal equilibrium concentrations, the adsorption by soil particles can be described by either the Langmuir or the Freundlich equations for adsorption isoterms.[86]

Surface charges in soil materials caused primarily by ionic substitutions are exhibited mainly by colloids. White and Zelazny[1183] broadly discussed soil characteristics responsible for charge properties of soil colloids governing all processes of cation exchange, cation selectivity, and ion adsorption. At a low pH, a positively charged surface prevails; while at a high pH, a negatively charged surface develops. The colloids of the majority of soils, therefore, carry negative charges and can be electroneutralized by cations present in the surrounding solutions. In the presence of an excess of cations, the process of exchanging the cations for others maintains the electroneutrality of the system. Thus, the cations adsorbed by the solid phase can be replaced by other cations, most often by H ions. An increase in stability of adsorbed metals may result from dehydration and recrystallization processes that occur on the surface of the colloids, especially in alkaline soils.

Variable conditions in soil aeration are known as a significant factor in the precipitation of metals. Bloomfield[946a] recently carried out a laboratory study of the effect of bacterial sulfate reduction on the accumulation of trace metals in anaerobic sediments. He found that Mo, V, U, Cu, Ni, Zn, Cd, Pb, Co, and to a certain extent Mn were precipitated with FeS during anaerobic incubation. Reoxidation of the sulfidic residue caused the pH to decrease and Zn, Cd, Pb, Co, and Mn were largely redissolved. Cu and Ni were also mobilized, but Cu was largely fixed by organic matter, as was Ni to a lesser extent. The relatively small amounts of Mo, V, and U that dissolved when the suspensions were first aerated were rapidly immobilized as the pH decreased.

The ability of the solid soil phase to exchange cations, the so-called CEC, is one of the most important soil properties governing the cycling of trace elements in the soil. The excess amount of adsorbed cations compared to the amount in solution is interpreted as the buffering capacity of soils, while adsorption capacity defines the amount of ions needed to occupy all adsorption sites per unit of mass.

The CEC of different soils varies widely both in quantity and quality and can range from 1 to 100 meq/100 g of soils.* Surface properties of soil particulates are the most important factors in defining the capacity for adsorption of microcations. Although total adsorption processes cannot be related simply to CEC phenomena, the adsorbed amounts of cations are in accordance with the CEC. Usually, the solid soil phase with a large surface area also shows a high CEC value and high adsorption and buffer capacities (Table 19).

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* CEC of most soils does not exceed a value of 30.

Table 19 Surface and Sorption Properties of Some Soil Minerals[227,287,373a,575,638,699,763,809,833,835,901]

Mineral	Total Surface Area ($m^2\ g^{-1}$)	Cation Exchange Capacity (meq 100 g^{-1})	Total Sorption of Microcations (μM g^{-1})	Sorption of Cations (meq 100 g^{-1})			
				Cd^{2+}	Mn^{2+}	Zn^{2+}	Hg^{2+}
Kaolinite	7–30	3–22	30–70	3.1	3.5	3.4	0.46
Halloysite	30	3–57	—	—	—	—	—
Montmorillonite	700–800	80–150	390–460	60–86	72–116	88–108	0.4–2.2
Illite	65–100	20–50	65–95	—	—	—	—
Chlorite	25–40	10–40	—	—	—	—	—
Vermiculite	700–800	100–150	—	98	92	98	9.7
Gibbsite	25–58	—	—	—	—	—	—
Goethite	41–81	—	51–300	—	—	—	—
Manganese oxides	32–300	150	200–1000	—	—	—	—
Imogolite	900–1500	30–135	—	—	—	—	—
Zeolites	720–880	—	—	—	—	—	—
Allophane	145–900	5–50	—	—	—	—	—
Palygorskite	5–30	—	—	—	—	—	—
Sepiolite	20–45	—	—	—	—	—	—
Muscovite	—	15	—	—	—	—	—
Plagioclase	—	7	—	0.47	0.26	1.2	0.14
Quartz	—	7	—	—	—	—	—

The affinity of cations for adsorption (e.g., for anionic exchange sites) is closely related to ionic potential (charge/radius). In some systems the metal ions (Zn, Cd, Mn) occupy nearly the same percentages of the CEC of various minerals.[763] Some cations, however, may have a higher replacing power than others and can be selectively fixed by the sorbing sites. As Abd-Elfattah and Wada[2] stated, the selectivity of adsorption reveals a possible formation of the coordination complexes of heavy metals with deprotonated OH and COOH groups as ligands. This specific sorption is well-illustrated by heavy metals having high affinities for organic matter and the surface of oxides, with replacing power over alkali and alkaline earth metals. This phenomenon has great importance in the nutrient supply to plants and in soil contamination.

D. Speciation

Trace metals enter the soil layers by a number of pathways, including aerial deposition and by leaching or decomposition of the above-ground parts of plants; by the utilization of wastes and by pesticide and fertilizer application; and by river waters and dredged sediment disposal. The speciation and localization of trace elements in soils are related to their chemistry inherited from parent materials as well as at the time of impaction (see Chapter 2, Section IV.A). Atomic properties also have a significant role in the cation speciation resulting from the formation of ion/ligand complexes (Table 13).

As soils consist of heterogeneous mixtures of different organic and organo-mineral substances, clay minerals, oxides of Fe, Al, and Mn, and other solid components as well as a variety of soluble substances, the binding mechanisms for trace metals in soils are manifold and vary with the composition of soils and their physical properties. Thus, a metal may form different species according to whether it is bound to various soil compounds, reacting surfaces, and external or internal binding sites with different bonding energy. In order to assess the speciation or binding forms of trace metals in solid materials, different analytical procedures involving successive extractions have been developed. Considerable controversy has developed over selective extraction methods to determine the amounts of trace metals associated with various soil phases. Despite all the limitations of these methods, some of them have been broadly used.

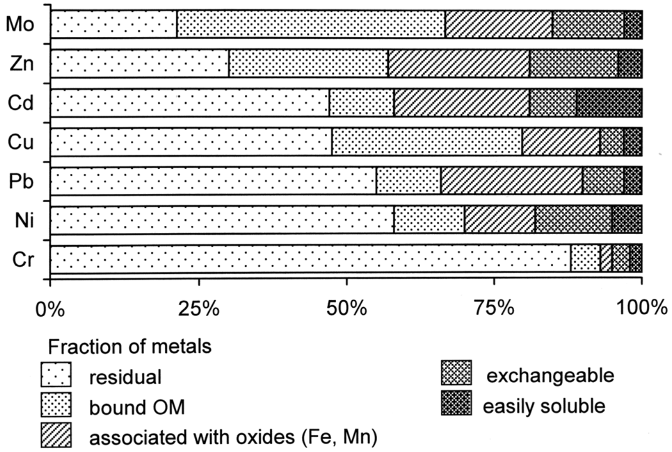

Figure 16 Fractionation of trace metals in soils (in percent of total content). Data for Mo are for the chernozem, and all other metals for the podzolic loamy sand.[1350]

Lorenz et al.,[1392] however, have stated that the free ionic concentration in soil solution did not better predict concentrations of Cd and Zn in plants than their total concentration in soil solution, which suggests that analysis of Cd and Zn speciation is of little practical importance when their bioavailability is assessed. Tessier et al.[1162] were among the first to develop the procedure of sequential extraction to determine the speciation of a particular trace metal in soils. Several other kinetic fractionation methods have been developed, and all procedures are based on the assumption that the following species of metals exist in soils:

1. Water soluble (e.g., in soil solution)
2. Exchangeable
3. Organically bound
4. Occluded in Fe and Mn oxides
5. Definite compounds (e.g., metal carbonates, phosphates, sulfides)
6. Structurally bound in silicates (residual fraction)

Depending on the variability in physico-chemical characteristics of metals, their affinity to soil components governs their fractionation (Figure 16). Rule[1471] broadly reviewed recent literature on phase distribution of trace metals in soils, and concluded that the highest proportions of most metals are found either in residual or in Fe-Mn oxide fractions in both natural and contaminated soils. A high association with exchangeable fraction was observed only for Cd in a few soils. Cd and Zn were also abundant as carbonate fraction in some soils. The association of metals with organic matter was generally lowest for Cd and Ni. Herbert[1327] found that Cu, Pb, Ni, and Zn are bound primarily to cation exchange sites and organic matter in the reference soil, while in the polluted soils, metal partitioning is dominated by the Fe oxide fractions, despite the high organic matter content.

The soluble plus exchangeable fraction characterizes the mobile species of metals in soils. The other metal fractions are more or less immobile. The mobilization of metals from these fractions, or transformation of mobile to immobile metal species is often a slow process which is strongly controlled by reaction kinetics.[955] However, a relatively rapid transformation of metals applied in oxide forms to more mobile carbonate species was also observed.[1357]

Recent results of several studies presented information on the speciation of trace metals in soils.[918,954,992,985,1137] The distribution patterns of metal species in soils vary widely. For example, in ground water of the forest podzol 58% of the total Cd occurred as Co_3-fixed form, and 38% in

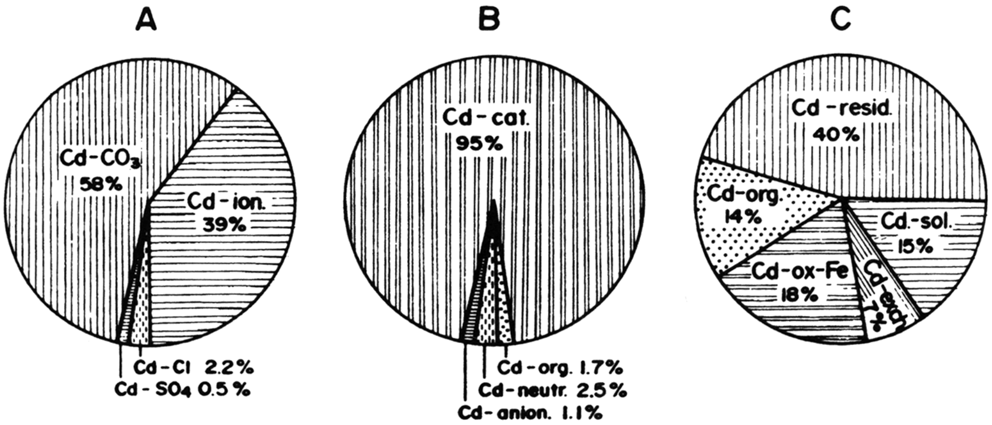

Figure 17 Relative distribution of Cd species in soils as determined by different methods: (A) in ground water of forest podzol, by GEOCHEM method,[992] (B) in solution of soil amended with sewage sludge, by ion exchange procedure,[918] (C) in light loamy soil, by sequential extraction.[985]

mobile ionic forms (Figure 17A). In the solution of soil amended with sewage sludge, 95% of the total Cd was present in free cationic form and only 1.7% was associated with organic matter (Figure 17B). In light loamy soils, 40% of the total Cd was associated with minerals as residual fraction, 18% was bound to hydrous oxides (mainly Fe oxides), 14% was held by organic matter, and only 15% was easily mobile as water-soluble fraction (Figure 17C).

It is still an open question if, and under which conditions, definite trace metal compounds like carbonates, phosphates, silicates, and others exist in soils. It seems more likely that these metals are bound in soil minerals, e.g., Fe and Mn oxides, carbonates, and clay minerals, by isomorphic substitution or by fixation at free structural places. The adsorption capacity of some soil components for cations can be very high and, therefore, a considerable quantity of trace metals can be bound by adsorption, before the formation of a definite metal compound takes place. Some metals (Cd, Co, Cr, Cu, Pb, Zn), however, are known to form discrete solid phases under specific soil conditions, when they occur in elevated concentrations, and due to diagenetic processes or pollution. Several mineral structures such as $Cu_2(OH)_2CO_3$, $Pb_3(PO_4)_2$, $Pb_5(PO_4)_3Cl$, $Zn_3(OH)_6(CO_3)_2$, $Zn_3(PO_4)_2 \cdot H_2O$, and $ZnSiO_4$ were identified in soils.[1024,1038] The adsorption-desorption processes can be described by the Freundlich isotherm and calculated with the help of geochemical models like GEOCHEM, proposed by Sposito and Mattigod.[1154] Although the most important factors that govern these processes are carbonate content (HCO_3^-), CEC, and the Eh-pH system, the adsorption capacity of organic matter can be of great importance. It has been indicated by the findings of Fic,[992] who showed a much higher adsorption of Cd, Cr, Cu, and Zn in the acid (pH 2.7) upper horizon of the forest podzol with a high organic carbon content (5.8%) than in the calcareous parent material (pH 8.0).

CHAPTER 4

Soil Constituents

I. INTRODUCTION

Quantitatively, trace elements are negligible chemical constituents of soils, but are essential as micronutrients for plants. The first publications on trace elements were devoted to plant nutrition problems. Further, it was recognized that the behavior of trace elements in the soil differs widely for both the element and the soil and that these differences should be understood better for the prediction and effective management of the trace element status of soils. Although trace elements are mainly inherited from the parent rocks, their distribution within the soil profiles and their partitioning between the soil components reflect various pedogenic processes as well as the impact of external factors (e.g., agricultural practices, pollution).

Trace element associations with the particular soil phase and soil component appear to be fundamental in defining their behavior. The trace element composition of soils is relatively well-established (Figure 18), although there are still diversities in analytical results, especially in the measurements of very small quantities. Currently, there is also a great deal of work on the distribution of these elements among soil components. One must realize, however, that present-day techniques for soil fractionation are quite drastic and cannot provide very comparative and representative results. Knowledge of the behavior and reactions of separate soil components with trace elements, although fundamental, should not be related directly to overall soil properties, and great caution is needed in using several theoretical models for predicting the behavior of trace elements in soils.

II. TRACE ELEMENTS

Based on results of numerous studies, investigations, and observations, the main soil parameters governing processes of sorption and desorption of trace elements can be presented as follows:

1. pH and Eh values
2. Fine granulometric fraction (<0.02 mm)
3. Organic matter
4. Oxides and hydroxides, mainly Fe, Mn, and Al
5. Microorganisms

Several soil variables control trace element contents and behavior in soil. A factor of soil parameters was established by Kabata-Pendias and Krakowiak[1356] based on the calculation of correlation coefficient matrices for metals and some soil parameters such as: pH, clay fraction content, cation exchange capacity, organic matter content, and Fe content. For about a thousand

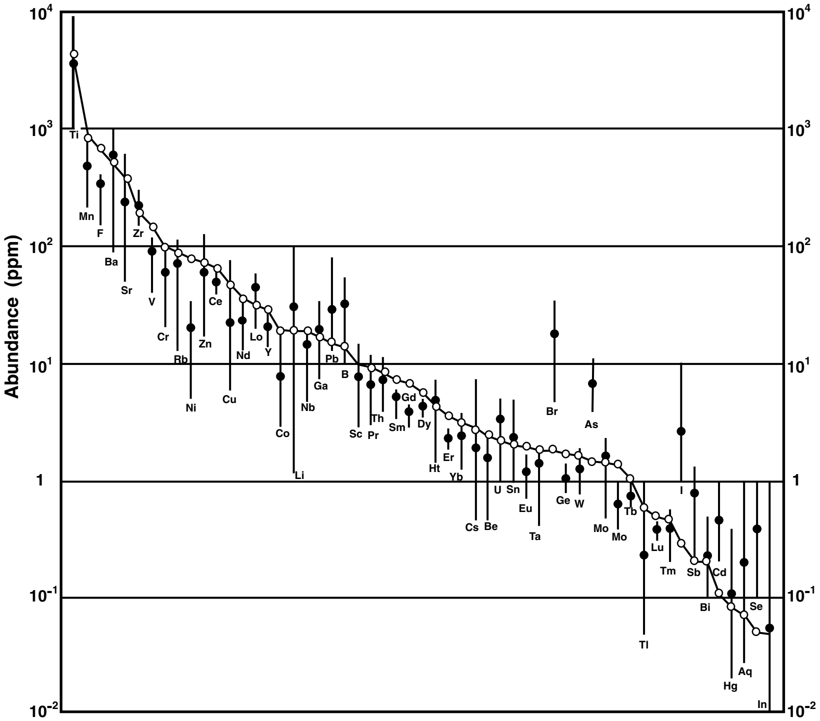

Figure 18 Trace elements in soils compared to their abundance in the lithosphere. Open circles mean content in the lithosphere; black circles mean content in topsoils; vertical lines mean values commonly found in topsoils.

Table 20 Arithmetic (A) and Geometric (G) Mean Contents of Trace Metals (ppm) and Iron (%) in Soils of Various Textural Groups in Poland[1357]

	Light Sandy (N = 552)		Medium Loamy (N = 168)		Heavy Loamy (N = 100)	
Metal	**A**	**G**	**A**	**G**	**A**	**G**
Cd	0.29	0.22	0.35	0.31	0.86	0.51
Cu	10.4	7.2	13.2	11.8	20.3	18.5
Cr	8.0	7.0	15.3	14.6	25.6	24.3
Mn	254	205	399	368	640	574
Ni	5.5	4.8	11.8	10.9	23.4	21.5
Pb	14.2	12.6	17.7	16.4	25.2	20.9
Zn	41.7	32.5	59.7	51.5	91.0	79.5
Fe (%)	0.6	0.5	1.2	1.1	2.0	1.9
Be	0.30	0.26	0.55	0.49	0.79	0.73
Co	3.5	2.8	6.0	5.4	9.1	8.5
La	8.4	7.6	14.7	14.2	19.2	18.4
Li	4.8	4.0	9.6	8.5	17.3	15.4
Mo	1.1	0.2	1.4	0.3	2.0	0.4
Sr	11	10	20	17	30	24

soil samples, the strongest linear positive correlation was obtained for the metals and fine soil granulometric fraction. This relation varies, however, for given metals, and is nicely illustrated by increasing mean content of trace metals in soils with increasing content of clay fraction (Table 20). The highest relative explanation index (60 to 75%) was calculated for Zn, Fe, Ni, and Cr, whereas the lowest explanation (10 to 30%) was for Cd, Pb, Cu, and Mn (Figure 19). A similar trend in

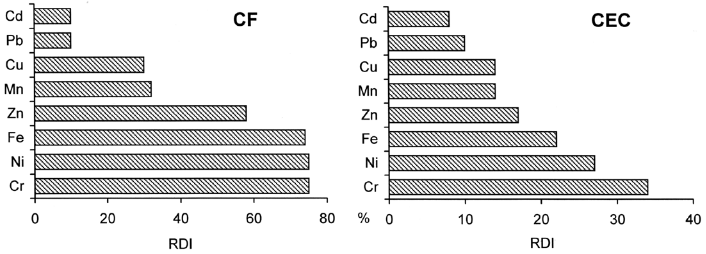

Figure 19 Relative explanation index (RDI) of statistically significant relationship between trace metals and content of clay fraction, <0.02 mm (CF), and cation exchange capacity (CEC) in mineral soils at the 99% confidence level.

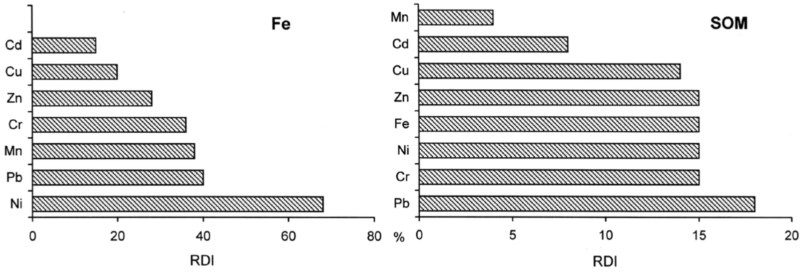

Figure 20 Relative explanation index (RDI) of statistically significant relationship between trace metals and Fe content, and organic matter (SOM) of mineral soils at the 99% confidence level.

correlation of metal contents with cation exchange capacity of soil was observed but at much smaller relative explanation. A high explanation (>60%) was obtained for Ni *vs.* Fe in soils, while this relation was very low (<20%) for Cd and Cu (Figure 20). Soil organic matter influences the distribution of most metals, but only at about 15% of the relative explanation. The smallest relationship with organic matter (<10%) was observed for Cd and Mn. Due to the strongest association of trace metals with clay soil fraction, the calculated range of metals based on the content of soil clay fraction gives acceptable values for the estimation of background contents of metals (see Chapter 2, Section IV. A). The positive correlation of trace metals (Co, Cu, Ni, Pb, and Zn) with clay content of soils is, according to Lee et al.,[1386] responsible for increasing their levels in the B soil horizons where clay is translocated from the A soil horizon. Elpatevsky et al.[1290] and Gao et al.,[1305] on the other hand, stated that the main factor of heavy metal migration is dissolved organic matter (DOM). Based on *in situ* determination of partitioning coefficients (K_p values), Janssen et al.[1345] concluded that, in Duth soils, pH and amorphous Fe content were the most influential factors in the partitioning of metals. However, clay content, Al content, and CEC were also significant. Kutilek[1383] distinguishes three basic types of physical mechanisms of pollutant flow on the pedon scale: (1) flow in interpedal pores, (2) fingering mainly due to instability on the wetting front, and (3) irregularities in hydrophilicity.

III. MINERALS

The mineral constituents of soils inherited from the parent rocks have been exposed for various periods of time to weathering and pedogenic processes. The soil mineral system, which is not necessarily in equilibrium with the soil solution, is complicated by the processes of degradation and neoformation of minerals, as well as by mineral reactions with organic compounds.

The common primary minerals in soils inherited from the parent material can be arranged in two parallel series, according to their susceptibility to weathering processes: (1) series of felsic minerals; plagioclases (Na $\approx$ Ca) $>$ K-feldspar $>$ muscovite $>$ quartz, and (2) series of mafic minerals; olivine $>$ pyroxenes $>$ amphiboles $>$ biotite. These series are based on broad generalizations, and many exceptions may occur in particular soil environments. The primary minerals occurring in some soils are mostly of a larger dimension and are not involved in sorption processes. They are, however, considered to be the source of certain micronutrient elements.

The approximate composition of mineral constituents of surface soils presented in Figure 12 shows that quartz is the most common mineral in the soils, constituting 50 to more than 90% of the solid soil phase. Even in geochemical conditions favorable for the leaching of silicates, quartz remains as a basic soil mineral. Feldspars are of low relative resistance to weathering in soil environments and their alteration usually provides materials for clay mineral formation. Carbonates (calcite, dolomite) and metal oxides are usually accessory minerals in soils of humid climatic zones, while in soils of arid climatic zones they may be significant soil constituents.

The size and shape of mineral particles determine their ratio of surface to volume and mass, and this ratio determines their physical and chemical properties. Therefore, the grain-size composition of soils is considered to be one of the most important factors in soil characteristics and is included in the systems of soil evaluation and classification.

Sorption properties of the mineral part of soil material are associated principally with the clay and silt-size fractions. These fractions are mixtures of several aluminosilicate clay minerals with lesser amounts of quartz, feldspars, and various oxides and hydroxides. In certain soils, carbonate and phosphate minerals are present, and in others, such minerals as sulfides and sulfates may occur.

A. Clay Minerals and Other Aluminosilicates

The boundaries of the mineral group described as “clay minerals” are not well defined, and they tend to enlarge with increasing knowledge. Thus, the division of minerals in this chapter does not relate to any classification system. The common clay minerals in soils can be subdivided into five groups:

1. Kaolinite
2. Montmorillonite, often referred to as smectites
3. Illite
4. Chlorite
5. Vermiculite

Each group includes many compositional and structural varieties; however, they are all 1:1 or 2:1 layer-type aluminosilicates. The structure and chemistry of soil clay minerals have been extensively described in many monographs.[49,281] The surface properties of minerals (area and presence of an electrical charge) seem to be fundamental for the buffer and sink properties of soils.

Clay minerals may contain negligible amounts of trace elements as structural components, but their sorption capacities to trace elements play the most important role. The affinity of trace ions for the clay surface has been examined by many investigators; and while many aspects have been clarified, still much remains to be learned about the adsorption processes.

Although clay mineral samples vary in chemical composition and in their nature, some general surface properties can be given for each mineral group (Table 19) that are responsible for values of the specific surface area of soil materials (Table 21). The capacity values (CEC) vary with the type of clay in the following sequence: montmorillonite, vermiculite $>$ illite, chlorite $>$ kaolinite $>$ halloysite. The ability of the clays to bind the metal ions is correlated with their CEC, and usually the greater the CEC, the greater the amount of cation adsorbed.

Table 21 Surface Area of Various Soils

Kind of Soil	Surface Area (m^2 g^{-1}) (5)	Surface Area (m^2 g^{-1}) (182)
Clays and loams	150–250	22–269
Silty loams	120–200	24–117
Sandy loams and loamy sands	10–40	4–67
Rendzinas	—	17–167

Note: References are given in parentheses.

The minerals of the montmorillonite group can expand and contract in response to charge and size of the absorbed cation between the clay platelets. Thus, their sorption capacity will differ when saturated with different cations. The microcations sorbed by montmorillonite are also easily released into the liquid phase and, therefore, can be an important pool of micronutrient supply to plants growing in particular soil conditions.

The bonding processes for absorbed microcations, although carefully studied, remain controversial.[2,227,356] It has been well-demonstrated, however, that equilibrium and pH values are the most basic qualities in the reactions of sorption and release of microcations by clay minerals.

The chemical nature of transition metals adsorbed on clay minerals has recently been the subject of great interest. Clays containing exchangeable transition metal cations (mainly Cu, Fe, and Co) are known to act as electron or proton acceptors, thus they can be activators in transformations, decomposition, and polymerization of the adsorbed organic species.

Relatively little is known about the adsorption of metal ions on amorphous alumina and silica gels. The mechanisms of coprecipitation and mobilization of certain trace cations with alumina or silica gels may play a significant role in their behavior in the particular soil, especially in those of the tropical climate zone. There are suggestions that metal ions (mainly Cu^{2+}) can substitute for aluminum in the mineral structures, while soluble silicic acid promotes adsorption of Co, Ni, and Zn by clays.[517,793]

The strong adsorption of divalent trace cations (Cu, Pb, Zn, Ni, Co, Cd, and Sr) by freshly precipitated alumina gel is suggested by Kinniburgh et al.[392] to play a role in determining the availability to plants and the movement of some of these cations through the soil.

Some aluminosilicates are known to occur in soils as phyllosilicates (palygorskite, attapulgite, sepiolite) and as zeolites. They all have alternative 2:1-type open structures and are associated with the clay minerals. They can be inherited from parent materials, but can also be of pedogenic origin.[901] Most often, these minerals were found in neutral or alkaline soil series, especially in the presence of salts (e.g., solonetz, solonchaks, andosols, rendzinas). Some of them are more acid resistant than others in the soil environment. However, the detection of these minerals, especially zeolites, can be questioned due to possible destruction during chemical pretreatments of soil material.

Zeolites exhibit capacities to fix gases, vapors, and liquids, and they are known to be active in the sorption of Ba, Br, F, I, and also Mn and Sr. Barrer[49] has illustrated a high affinity of zeolites to sorb and to complex trace elements, particularly heavy metals and radionuclides.

Amorphous aluminosilicates occurring in soils are often described as allophane and imogolite. Allophanes are present in many soils, and the investigators pointed out their importance in the formation and transformation of noncrystalline clay materials and opaline silica.[833] Both allophane and imogolite make sequences of various types and are formed mainly in the soils developed under a warm humid climate. Allophanes are more stable in acid soils, and imologite is more stable in neutral and alkaline soils. Very often they occur as "gel films" that coat soil particles. The effect of these inorganic coatings may be diverse, both increasing and decreasing trace element sorption; they may also reduce the biological availability of occluded trace elements.[356]

All of these mineral constituents have relatively high CEC values and a great affinity to react with soil organic compounds. Under normal soil conditions, they are important trace element sinks.

B. Oxides and Hydroxides

Several oxide minerals, such as silicon oxides, titanium oxides, aluminum oxides, and hydroxides occur in soils. However, in relation to trace element behavior, the most important are Fe and Mn oxides. Al hydroxides can adsorb a variety of trace elements and in some soils the role of these oxides can be more important than that of Fe oxides in retaining certain trace elements. As Norrish[570] has stated, however, there is little direct evidence to support this view.

Oxides and hydroxides of Fe and Mn are relatively common constituents in soils and, having a high pigment power (mainly Fe oxides), determine the color of many soils. Fe and Mn oxides are present in soils in various mineral forms as well as in crystalline, microcrystalline, and amorphous oxides or hydroxides. Their structure and chemical properties are well-described by Hem,[313] Jenne,[356] McKenzie[524,526] and Schwertmann and Taylor.[699]

Although several minerals of the Fe oxides have been detected in soils, goethite is claimed to be the most frequently occurring form. Norrish[570] reported that simple oxides and hydroxides of manganese do not occur in soils and that the most common mineral forms are lithiophorite and birnessite. Chukhrov et al.,[140] on the other hand, have identified vernadite—a simple hydrous oxide of Mn—as the most frequent form in the majority of soils.

These oxides are exposed to reduction and chelation solubility and oxidation-precipitation reactions, in which microbiological processes play an important role. Redox processes, in particular, in marsh soils result in the formation of concretions with dominating Fe and Mn accumulation.[1025] Different nodules of Fe and Mn are known to originate from both chemical and microbial processes; also, the formation of some crystalline minerals is known to be affected by microorganisms. The most common Fe-oxidizing bacteria (*Thiobacillium*) and Mn-oxidizing bacteria (*Metallogenium*) are able to tolerate high concentrations of several heavy metals (Zn, Ni, Cu, Co, and Mn). Thus, they are also involved in trace metal cycling in soils.

Fe and Mn oxides occur in soils as coatings on soil particles, as fillings in cracks and veins, and as concretions or nodules. Norrish[570] and Hiller et al.,[1025] using the electron microprobe analyzer, indicated that many trace elements in soils are concentrated along the deposited oxides in soil material. Fe and Mn oxides have a high sorption capacity, particularly for trace elements, of which large amounts can be accumulated in nodules and at Fe- and Mn-rich points (Table 22). The mechanisms of sorption involve the isomorphic substitution of divalent or trivalent cations for Fe and Mn ions, the cation exchange reactions, and the oxidation effects at the surface of the oxide precipitates. Brümmer et al.[955] studied reaction kinetics of the sorption of trace metals by goethite and stated that these processes involve: (1) adsorption of metals on external surfaces, (2) solid-state diffusion of metals, and (3) metal binding and fixation at positions inside the mineral particles. Variable charges at the surfaces (mainly of Fe oxides) also promote the adsorption of anions. A high sorption capacity of Fe oxides for phosphates, molybdates, and selenites is most widely observed and is highly pH dependent, being lower at high pH values.[638] The amount of a particular ion that is adsorbed depends mainly on the pH of the equilibrium solution. The maximum adsorption values for various ions on Fe oxides range between pH 4 and 5.[699] The adsorption of some metals (Cd, Ni, and Cu) is significantly enhanced in the presence of humic substances.[1057]

Some investigators give the order of preferential sorption of metals by goethite as Cu $>$ Zn $>$ Co $>$ Pb $>$ Mn,[699] while others have presented metal ion affinities for the oxide surface in the following orders: Cu $>$ Pb $>$ Zn $>$ Co $>$ Cd,[240] and Pb $>$ Zn $>$ Cd $>$ Tl.[252] However, the extrapolation of these results to all soils is difficult. Apparently, hydrous oxides of Fe and Mn are the most important compounds in the sorption of trace metallic pollutants, and they exhibit diverse affinities to cations having approximately the same physical dimensions as Mn^{2+}, Mn^{3+}, Fe^{2+}, and Fe^{3+}; they are Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{4+}, and Ag^{+}.

Table 22 Trace Elements in Iron and Manganese Oxides (DW Basis)

	Iron—Minerals and Concentrations			Concretions of Surface Marsh Soils			Manganese Minerals and Concretions					
								Manganese Nodules			Manganese Minerals	
Element	Fe-rich Soil Nodules (977)[c]	Fe-rich Points of Surface Soils (570)	Goethites (570, 881)	Fe-Si-rich	Fe-Mn-rich (1025)	Ti-Fe-rich	Mn-rich Points of Surface Soils (570)	(94)	(524)	(977)[c]	From Soils[a] (525)	From Deposits[b] (837)
%												
Fe	40.1	7.97–29.65	51.7–61.9	6–28	2–15	18–29	3.92–17.69	0.016	—	2.3	0.65–4.6	0.1–4.5
Mn	3.4	0.07–1.52	0.26–0.5	5	16–40	0.3–5.5	5.5–13.6	16	0.36–7.2	50.3	47.4–59.9	28–61
Ti	0.13	—	—	—	—	31–39	—	—	—	0.02	—	—
ppm												
Ba	890–1790	—	—	—	—	—	5730–28,640	2000	140–2300	—	32,000–54,000	110,000–128,000
Cd	—	—	—	20–430	90–520	70–740	—	8	—	—	—	—
Ce	—	—	—	—	—	—	—	720	—	—	—	—
Co	300	400–700	80[d]	40–830	70–390	100–110	5400–24,400	3000	82–380	—	4500–12,000	140–12,000
Cr	—	—	1000[d]	—	—	—	—	14	30–120	—	—	—
Cu	100	40–720	800	50–980	80–450	150–1110	390–960	2600	—	200	—	130–12,600
I	—	—	—	—	—	—	—	120–900	—	800	—	—
Li	—	—	—	—	—	—	—	—	—	—	300–700	2–5340
Mo	—	—	850	—	—	—	—	410	—	—	—	—
Ni	100	260–630	170[d]	40–680	80–680	40–640	860–4870	4900	39–67	600	1000–3400	120–10,900
Pb	—	460–1390	—	130–5690	120–11,910	160–2720	2600–20,400	870	34–100	—	—	—
V	400	—	17,000	—	—	—	—	440	88–110	100	—	—
Zn	400	720–2570	17,300–23,500	50–1790	350–1800	30–1580	320–5540	710	30–33	3500	—	50–3800

Note: References are in parentheses.

[a] Identified minerals: lithiophonite, birnessite, and hollandite.

[b] Identified minerals: psilomelane, cryptomelane, lithiophonite, and pyrolusite.

[c] Mean contents.

[d] In magnetite separated from soils (ignited weight).

C. Carbonates

Carbonates present in soils are often in metastable and polymorphic varieties and thus sensitive to drainage conditions. Carbonates are common constituents in the soils where evapo-transpiration potential exceeds the rainfall. On the other hand, in soils with a high rate of percolating water, carbonates are easily dissolved and leached out. Nevertheless, Ca is usually the predominating cation in solutions of almost all soils.

Calcite is the most widespread and relatively mobile form of Ca carbonates present in soils; it is usually greatly dispersed and has a major influence on the pH of soils and therefore on trace element behavior.

Trace elements may coprecipitate with carbonates, being incorporated in their structure, or may be sorbed by oxides (mainly Fe and Mn) that were precipitated onto the carbonates or other soil particles. Metallic ions may also influence processes of carbonate precipitations.[356] The greatest affinity for reaction with carbonates has been observed for Co, Cd, Cu, Fe, Mn, Ni, Pb, Sr, U, and Zn. However, a wide variety of the elements under various geochemical environments may substitute for Ca in different proportions in nodular calcites. As Vochten and Geyes[828] observed, the secondary calcite crystals show a remarkably high content of Sr and Co—up to 1000 ppm concentrations. Carbonates can be the dominant trace element sink in a particular soil, but the most important mechanisms for regulating the trace element behavior by carbonates are related to variation of the soil pH. For example, $CdCO_3$, $Cu_2(OH)_2CO_3$, and $Zn_5(OH)_6(CO_3)_2$ are likely to occur in neutral or alkaline soils polluted with these metals.[1038,1046]

D. Phosphates

Crystalline forms of phosphate minerals rarely occur in soils; however, many varieties of metastable and metamorphous phosphates are of importance in pedogenic processes. There are few data on the occurrence of Ca phosphates (apatite and hydroapatite) or other phosphates in soils. Rather, it has been suggested that an intimate mixture of Ca, Fe, and Al phosphates predominates in soils.[356]

Several of the rock phosphates contain a large amount of trace elements, of which F, and at times Cd, are highly concentrated (Table 23). Some substitutions for Ca by trace elements are known to occur in natural apatites; they are, however, of little importance in soils. Also, many trace elements (Ba, Bi, Cu, Li, Mn, Pb, Re, Sr, Th, U, and Zn) can be incorporated, together with Fe^{3+}, and Al^{3+}, in hydrated phosphates.[809] Norrish[570] reported extremely high concentrations of lead (1 to 35% PbO) in the phosphate concentrates occurring in ferralsols (lateritic podzolic soils). At the range from neutral to alkaline reaction a possible formation of Pb phosphates in Pb-polluted soils is reported.[1038,1046] Phosphates of Zn may also precipitate in such soil conditions (see Chapter 3, Section III.D).

E. Sulfides, Sulfates, and Chlorides

Sulfides, sulfates, and chlorides are negligible compounds in soils that developed in a humid climate, but in soils of arid climatic zones they can be the dominant controls of the behavior of trace elements. The metallic ions (mainly Fe^{2+}, Mn^{2+}, Hg^{2+}, and Cu^{2+}) may form relatively stable sulfides of acidic or neutral reducing potential in flooded soils. Several other heavy metals (Cd, Co, Ni, Sn, Ti, and Zn) can also be easily coprecipitated with iron sulfides.[356,828]

The precipitation of metallic ions as sulfides is an important mechanism for regulating the solution concentration of both S^{2-} and metallic cations. Sulfides of heavy metals may be transformed into more soluble oxidized sulfates when flooded soil becomes drained and aerated.

Pyrite is the most common mineral of Fe sulfides in soils and other geochemical environments. Some other heavy metals which readily form sulfides may also be, as is Fe, remarkably related to microbial S cycling in soils, as was recently described by Trudinger and Swaine.[809]

Table 23 Trace Elements in Phosphorites and Phosphate Fertilizers (ppm)

Element	Phosphorites (98, 809, 1418, 1558)	Phosphate Fertilizers (381, 554, 1362)
Ag	—	0.8–3
As	0.4–188	2–1200
B	3–50	5–115
Ba	1–1000	200
Be	<0.5–10	—
Br	—	10–500
Cd	0.01–>100	7–170
Ce	9–100	20
Co	0.6–12	1–12
Cr	2–1600	66–600
Cu	0.6–394	1–300
F	<31,000	8500–38,000
Hg	0.2–1000	0.01–0.12
I	0.2–280	—
La	7–130	60–100
Li	1–10	—
Mn	1–10,000	40–2000
Mo	0.03–138	0.1–60
Nb	—	20–570
Ni	0.2–1000	7–32
Pb	1–1000	7–225
Rb	—	90–200
Sb	0.2–10	—
Se	1–10	0.5–25
Sn	0.2–15	3–19
Sr	1000–2000	25–500
Ti	100–3000	—
U	8–1300	10–800
V	20–5000	2–180
Y	—	30–180
Yb	—	8–14
Zn	4–345	50–1450
Zr	10–800	50–1560

Note: References are given in parentheses.

Sulfides of heavy metals are not common in soils, especially in soils with good drainage. Sulfates of metals, mainly of Fe (jarosite), but also of Al (alunites) and Ca (gypsum, anhydrite), are likely to occur under oxidizing soil conditions. They are readily soluble and therefore are greatly involved in soil equilibrium processes. Sulfates of heavy metals are also readily available to plants, and their occurrence in soils has practical importance in agriculture.[673] Chlorides as the most soluble salts occur only in soils of arid or semiarid climatic zones. Chlorides' affinity for forming easily soluble complexes with Cd is of environmental concern.

IV. ORGANISMS IN SOILS

Living organisms, often referred to as the soil biota, composed of fauna and flora of various dimensions (macro-, mezo-, and microbiota), occur abundantly in soils. At the microbiota level, the boundary between plant and animal cells becomes blurred. The importance of living organisms as reflected in biological activity of soils has been discussed in many textbooks.[187,651,856,898]

Several species of biota are known to be useful indicators of soil pollution. However, growth, reproduction, and metabolic activities of biota are sensitive to other soil variables as well as to the concentrations of trace pollutants. The Eh-pH system and organic matter content are especially important. Humic substances are known to have both beneficial and deleterious effects on biota caused by binding or mobilization of metals. It was observed that increased trace element levels have an adverse effect on the natural regulation of the soil biota.[982]

A. Microorganisms

The abundance of microorganisms in topsoils varies with soil and climatic conditions and may reach as much as 20% of the total biota of a soil system. There is no easy way of knowing with certainty the biomass of microorganisms because this quantity can be determined only indirectly. The maximum weight of soil biota given by Richards[651] for a hypothetical grassland soil corresponds to 7 t ha^{-1} of microbiota (bacteria and fungi) and to 1.3 t ha^{-1} of mezobiota. Kovalskiy et al.[422] calculated that the biomass of bacteria and fungi present in the plow zone of soil (20 cm depth) ranges from 0.4 to 1.1 t ha^{-1}. The biomass of bacteria varies significantly during the growing season, and may increase about three times from spring to fall.[421]

Microorganisms are very important ecologically because they are the producing, consuming, and transporting members of the soil ecosystem and therefore are involved in the flow of energy and in the cycling of chemical elements. Thus, the microbiota is responsible for many different processes, from mobilization to accumulation of chemical elements, in soils. Although microorganisms are sensitive to both deficiencies and excesses of trace elements, they can adapt to high concentrations of these elements in their environment.

The role of microorganisms in geochemical cycling of the major elements is relatively well-understood on the global level. The biogeochemical cycling of trace elements has received much less attention. With the recognition that microbial transformations of compounds of these elements can result in some problems of soil fertility as well as in the formation of some environmental pollution or detoxication processes, the importance of microbiota in cycling of trace elements, especially heavy metals, has been more extensively studied. Processes of microbial methylation can occur in oxic and anoxic soil conditions, and can highly influence the behavior of some trace elements. Several elements, such as As, Hg, Se, Te, Tl, Pb, and In, are known to be biologically methylated in soils.[1201] Abiotic processes of methylation can also occur in a soil.

The basic microbial phenomena in cycling processes in the soil environment are:

1. Transport of an element into or out of a cell
2. Charge alteration of an element
3. Interaction of an element with organic compounds to become a functional part of the system
4. Complexing an element by organic acids and other compounds produced by microorganisms
5. Microbial accumulation or mobilization of an element
6. Microbial detoxication of poisoned soil at a site
7. Microbial methylation of an element

The most important microbial function in soil, however, is the degradation of plant and animal residues. It has become apparent that the quantity of trace elements needed or harmful for growth of microorganisms also influences the biological activity of soils.

All available evidence indicates that a low concentration of trace elements stimulates bacterial growth in soil, but a higher content is harmful, being usually most toxic to the bacteria that fix free N and to nitrifying bacteria.[505,812] Of the 19 trace elements studied by Liang and Tabatabai,[471] all inhibited mineral N production in soils. At the concentrations of 5 $\mu M\ g^{-1}$ of soil, the most toxic

Table 24 Toxic Effects of Trace Metals on Microbial Activities in Soils[982]

Metal Concentration in Soils (ppm DW)	Inhibited Process	Reported Sometimes	Reported Always
≤10	Soil respiration	Cd, Hg, Ni, Zn	
	N-mineralization	Hg	
	Nitrification	Hg	
≤100	Soil respiration	Cd, Cu, Pb	Hg
	N-mineralization	Cd, Cu, Ni, Pb	Hg
	Nitrification	Cd, Cu, Ni, Zn	Hg
≤1000	Soil respiration		Cd, Cr, Cu, Ni, Zn
	N-mineralization		Cr,[a] Cu, Ni, Zn
	Nitrification		Cd, Cr,[a] Cu, Ni
≤10,000	Soil respiration		Pb
	N-mineralization		Cd,[b] Pb
	Nitrification		Pb, Zn

[a] Concentration given for about 500 ppm.

[b] Concentration given for about 3000 ppm.

elements were Ag^+ and Hg^+, while the least toxic were Co^{2+}, As^{3+}, Se^{4+}, and W^{6+}. Heavy metals especially are known for their toxicity to microbiota, with fungi and actinomycetes having the most resistance. Reduction of microbial growth and enzymatic activity is often reported for soils contaminated by heavy metals.[88,733,814] Elevated metal concentrations are responsible for commonly observed decreases in symbiotic and nonsymbiotic N_2-fixation.[1089] Doelman[982] summarized reported effects of different concentrations of trace metals on microbial activities in soils. Data presented indicate that Cd, Hg, Ni, and Zn are toxic at lower levels than the other metals (Table 24). Atmospherically borne metals, most often associated with H_2SO_4 and HNO_3, cause significant damage to soil organisms. These effects are related either to direct toxic impact of trace metals and to lowering of pH, or to general deterioration of the habitat quality. Bengtsson and Torstensson[939] reviewed several studies on the inhibition of soil respiration and of turnover of carbon and nutrients in metal-polluted soils. Mathur et al.[515] showed that the effect of a naturally high Cu content of histosols is most suppressive on levels of accumulated enzyme activities involved in the degradation of the major components of organic debris in soils. A low rate of decomposition of vegetation having a high concentration of Pb and Zn is apparently due to the same processes in nature.[877]

Suppression and/or stimulation of biosynthesis of microorganisms by heavy metals depends on the nature of the organisms, the kind of metal, and the pH of soils. Even within one species, the range of required or inhibitory concentrations of a given metal varies significantly.[421]

Based on data presented in the monograph by Weinberg,[856] it may be generalized that the highest concentration of Fe, Mn, and Zn required by various microorganisms (fungi, bacteria, bacilla, and actinomycetes) was around X00 $\mu M\ L^{-1}$. The inhibitory concentrations of these elements on vegetative growth and secondary metabolism of microorganisms have also been established at the above range.

Microorganisms take up trace elements, several of which play important metabolic functions.[344,614,467] It has been shown by Kokke,[407] however, that cells of microorganisms may show quite variable affinities for radionuclides that are necessarily related to their biological function (Table 25).

Heavy metals are known to be the most toxic elements, especially to fungi. Somers[746] reported that the fungicidal action of trace cations is due primarily to the formation of an un-ionized complex with surface groups (e.g., phosphate, carboxyl, and sulfhydryl). This author showed that there is a relationship between the toxic concentration of the metal ion and its electronegativity value. The order of toxicity of aqueous solutions of nitrates and sulfates against conidia of *Alternaria*

Table 25 **Radionuclide Uptake by the Yeast *Candida humicola* as a Function of Time**[407]

Radionuclide	Initial Concentration in Growth Media (μM L^{-1})	Time of Growth (days) 1	2	4	8	16
		% of Initial Concentration				
^{89}Ce	40	93	95	98	99	99
^{55}Fe	40	68	83	95	95	95
^{65}Zn	64	60	60	60	75	99
^{89}Sr	40	18	18	18	37	99
^{131}I	20	16	18	25	—	25
^{106}Ru	40	15	30	45	60	75
^{60}Co	40	3	5	5	18	77
^{63}Nd	40	3	3	3	5	12
^{137}Cs	40	1	2	2	3	5

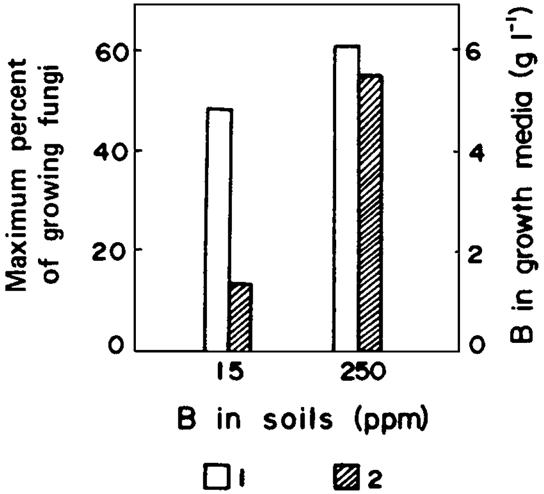

Figure 21 Tolerance of Actinomycetes from soils with various B contents to B concentrations in the growth media. (1) Growing fungi, in percent of total number; (2) maximum tolerable concentration of B in solution.[464]

tenuis was given by Somers[746] as follows:

$$\text{Os} > \text{Hg} > \text{Ag} > \text{Ru} > \text{Pb} \approx \text{Cr} > \text{P} > \text{Ce} > \text{Cu} > \text{Ni} =$$
$$\text{Be} = \text{Y} > \text{Mn} = \text{Tl} > \text{Zn} > \text{Li} > \text{Sr}$$

In soil systems, Hg, Cd, and As seemed to be the most harmful to ammonification processes, while Cu greatly reduced phosphate mineralization rates.[762,813]

Microorganisms can adapt to high concentrations of trace elements. This has been well-illustrated by Aristovskaya[35] and Letunova[464] for several elements such as Fe, Mn, Mo, Se, and B (Figure 21). This adaptation is also well-shown in various microbiogeochemical processes described in detail by Babich and Stotzky,[41] Gadd and Griffiths,[251] Kowalskiy,[419] and Zajic.[898] The sensitivity of microorganisms (mainly fungi) to different concentrations of trace elements has often been used in the determination of the availability of micronutrients such as Fe, Cu, Zn, and Mo.[531,572]

Since trace metals are toxic to microorganisms even at relatively low concentrations, they have evolved efficient mechanisms to detoxify the metals. Chakrabarty[961] and Silver[1150] described a variety of reactions that reduce the toxicity associated with entry of the metal inside the cell. Most common reactions depend on processes of oxidation, reduction, and alkylation.[1106] Other reactions of bacterial resistance to metals are (1) energy-dependent processes of the efflux of the metal from the cell and (2) precipitation of the metal at cell surfaces. Metal-microbe interactions evolved resistance mainly against such metals as Ag, Cd, Cr, Cu, Fe, Hg, Pb, Ni, and Zn. The resistance of microorganisms to other trace elements was also observed, but the mechanisms involved are not yet understood.[1150] Processes of alkylation and dealkylation control to a great extent the toxicity and behavioral properties of some trace elements. Microbial methylation under environmental conditions was observed for As, Hg, Se, Sn, and Te. On a chemical basis, however, one would expect Au, Bi, Pb, Pd, Pt, Sb, and Tl to have a potential capability for forming methylated compounds.[935] Indeed, some forms of Pb and other metals are known to undergo methylation under the soil conditions. Beijer and Jernelöv[935] stated that whether the methylation is a biological or a purely chemical reaction is still under debate, and that it is still unclear if organic Pb^{2+} may be methylated. Also Craig and Rapsomanikis[970] focused attention on the identification of chemical methylating agents known to be present in the environment which are suitable substances for the methylation of metals. Recent studies of Chau et al.[965] indicated that transmethylation reactions between organometals and metal ions occur in aqueous solutions in both biotic and abiotic systems. Results of these studies suggest that, for example, alkyllead or methyltin compounds could be potential methylating agents for the formation of other methylmetals. Thus, alkylation processes in soils are not solely of a bacteriological origin.

The physicochemical relationship between bacteria and mineral surfaces leads to diverse effects of dissolution and secondary precipitation of trace metal ions, including changes in their valence and/or conversion into organometallic compounds. A biological oxidation and reduction of Fe and Mn, for example, is one of the most important factors governing the solubility, and thus, the bioavailability, of these metals in soils. Many bacterial species are implicated in the transformation of trace element compounds, including even neoformation of certain Fe and Mn minerals.[140] This effect, however may also at times be an indirect effect. Bacteria also play the most important role in gley formation, which affects the mobility of metals in soils.[81] The mobilitation of metals on a large scale is of geochemical significance since it may lead to ore formation (e.g., Cu, U). Such processes are the results of the growth of acidiphilic and/or chemolithotrophic bacteria that derive their energy from the oxidation of reduced (or partially reduced) sulfur compounds and metal salts.[961]

A complex balance of trace elements required for microbial activity is of importance in soil productivity. The quantities of specific trace elements available to soil microorganisms can be the critical determinant in the establishment of a disease condition of certain plants. The trace element competition between plants and microorganisms is apparent in various reports, and it may react in different ways. Microbially induced decreases in the availability of trace elements result from a considerably high accumulation of certain elements by microbiota and also from the biological oxidation of compounds of these elements. Microbiological increases of availability, on the other hand, are caused by microorganisms capable of reducing certain compounds (principally, Mn and Fe) and also by their variable bioaccumulation of trace elements (Table 26). Highly elevated levels of trace elements, particularly of As, Cd, Cu, Cr, Hg, Pb, and Sb, are known to reduce the growth and decomposing capacity of soil microbes.[963] Effects of these processes are observed in reduced capability to decompose organic pollutants (e.g., pesticides, oil) and organic debris in soils. Negative impact of these metals on the decomposition of organic matter, on the mineralization of N and P compounds, and on the activity of N fixation is commonly reported (Table 24). However, it is not easy to predict microbial consequences of soil pollution with metals because of variable reduction in the activity of one species, with increasing tolerance in other species.[1150]

Soil fumigation or steaming and many fungicides kill the fungi and therefore may interfere with the ability of plants to absorb micronutrients. The mechanisms of these phenomena are not yet fully understood; however, they may be related to an imbalance of soil microorganisms and

Table 26 Bioaccumulation of Cu, Mo, and V by Microbiomass in Topsoils at Various Seasons[421]

	Cu		Mo		V	
Data on Soil	**Soil (ppm)**	**Biomass (kg h^{-1})**	**Soil (ppm)**	**Biomass (kg h^{-1})**	**Soil (ppm)**	**Biomass (kg h^{-1})**
Low content of elements	48	0.004 (Sp)	6	0.0013 (Sp)	66	0.002 (Sp)
		0.006 (Sm)		0.002 (Sm)		0.003 (Sm)
		0.028 (Fl)		0.009 (Fl)		0.013 (Fl)
High content of elements	270	0.60 (Sp)	72	0.075 (Sp)	840	0.124 (Sp)
		0.25 (Sm)		0.031 (Sm)		0.052 (Sm)
		0.22 (Fl)		0.029 (Fl)		0.049 (Fl)
Control soil (chernozem)	73	0.019 (Sp)	10	0.005 (Sp)	148	0.005 (Sp)
		0.069 (Sm)		0.017 (Sm)		0.019 (Sm)
		0.059 (Fl)		0.013 (Fl)		0.015 (Fl)

Note: Sp, spring; Sm, summer; Fl, fall.

Table 27 Trace Elements in the Biomass of *Bacillus megaterium* Growing in Different Media[1061] (ppm DW)

	Growth Medium[a]	
Element	**Soil Rich in Cu, Mo, V**	**Soil Poor in Cu, Mo, V**
Ag	<0.14–3.6	<0.14–<0.51
Ba	46–368	<24–112
Be	<0.3–4.2	<0.3–2.1
Co	<0.3–14	<0.6–8
Cr	0.8–27	<0.5–17
Cu	10–98	4.5–39
Mo	3.4–21	1.2–6.2
Ni	<0.2–16	<0.7–12
Pb	<1.3–38	<0.8–<8.7
Sr	2.3–55	1.7–7
V	4.3–28	3.2–15

[a] Growth medium was agar-agar with added soil extracts.

their participation in the transport of ions into or within biological systems. As Martin[510a] reported, variable effects in plants of B, Cu, Li, Mn, and Zn toxicities or deficiencies of Cu, Mn, and Zn were found following soil fumigation.

Gadd and Griffiths[251] concluded that two main types of metal uptake by microorganisms can occur; the first involves nonspecific binding of the cation to cell surfaces, slime layers, extracellular matrices, etc., while the second involves metabolic-dependent intracellular uptake. The polygalacturonic acid, a common constituent of the outer slime layer of bacterial cells, can complex several trace metals.

The adsorption of trace elements by microorganisms differs widely, as is shown in Tables 25, 26, and 27. Although the mass of microbiota in soils has been calculated to be in the range of 0.X–X t ha^{-1}, the greatest amounts of metals fixed by microorganisms are the following (g ha^{-1}): Ni, 350; Cu, 310; Zn, 250; Co, 150; Mo, 148; and Pb, 8.4, which corresponds to 0.002 to 0.216% of their total abundance in the 20-cm topsoil level of 1 ha.[422,465]

Calculations made by Kovalskiy et al.[422] and Letunova and Gribovskaya[465] indicated that at the annual rate, the total biocycling of about 11 generations of microbiota may, on the average, involve the following amounts of trace metals (kg ha^{-1}): Ni, 147; Zn, 104; Cu, 78; and Co, 28. Trace elements fixed by microbiomass may be much higher than these values for soils that increase their levels, as has been shown by Krasinskaya and Letunova.[426]

Microbioaccumulation of trace elements may be of great importance both in the cycling of trace elements in soil and in their availability to plants. Fungi and actinomycetes are the most resistant microorganisms to high concentrations of heavy metals, while nitrifying and rhizosphere microorganisms are the most sensitive.

Various waste waters, as well as slurries used for soil irrigation and amendment, can be sources of microbial and other pathogenic organisms of a serious health hazard to humans and animals. This problem has been recently reviewed by Kristensen and Bonde.[429] Bacterial leaching of heavy metals from sewage sludges is, however, a practical application of the biotransformation of the forms of chemical elements.[694,1106]

More than 80% of microorganisms are believed to be adsorbed to soil organic matter and clay minerals.[884] Therefore, comparisons of results obtained for pure cultures of microorganisms may differ from those naturally occurring in soils.

The rhizosphere flora plays a special role in the bioactivity of soils and the availability of nutrients. Although effects of mycorrhizas have been almost always ascribed to an increased phosphate uptake, some observations indicate that they may also influence micronutrient supply. As Lambert et al.,[456] Woldendorp,[884] and Turnau[1524] reported, Zn, Cu, and Sr are the chief elements supplied to plants by a given type of mycorrhiza. Some negative effects occurring in rhizospheres may be observed when anaerobiosis around the root surface due to a high oxygen demand of microflora leads to the formation of ferrous iron compounds which are taken up by plants to concentrations that cause the physiological disorder known as Fe toxicity.[807]

B. Invertebrates

Any species of soil fauna (mezo- and macrobiota) participating in the trophic chain may reflect chemical composition of the soil. Lumbricid earthworms seem to be of the greatest importance as indicator species in the terrestrial ecosystems. Earthworms may constitute up to 80% of the total biomass of the soil fauna, and because of their relatively large biomass, provide a significant food source for many species of several predators (e.g., birds, small mammals). Ma[1079] showed that the accumulation of trace metals in mole tissues reflects the bioavailability of these metals to earthworms. Metals accumulated in both small earth mammals and earthworms do not consistently reflect the metal contents of soils (Table 28). In most cases, however, their accumulation in earthworms can be relatively well-predicted (Table 29). Ma[1078] emphasized that in the ecosystems where earthworms comprise a large proportion of the soil fauna biomass, the bioaccumulation of metals, as high as up to 3500 ppm Zn (DW), can be potentially hazardous to predatory animals. Findings of Ma[1078] indicate that only Cd and Zn are significantly enriched in the worms. However, under specific soil conditions, as for example high acidity, low Ca content, or low CEC value, other trace metals can also be easily taken up by earthworms. Based on laboratory and field observations, Ma[1077] gave the following order of increasing concentration factors of metals in worms in various soils:

$$\mathrm{Cr} < \mathrm{Mn} \leq \mathrm{Fe} < \mathrm{Ni} < \mathrm{Pb} \leq \mathrm{Zn} < \mathrm{Cd}$$

Ma et al.[1080] reported that *Lumbricus rubellus* easily accumulated Cd, Zn, and Pb from acid soils. However, Cu was the exception, and its uptake by earthworms was not influenced by the soil pH. Thus, the demonstrated influence of soil factors on element concentrations in earthworms is related to the effect of soil properties on metal availability to organisms in the terrestrial ecosystems. Roth-Holzapfel[1130a] analyzed species of invertebrates of the spruce forest ecosystem in central Europe. She found that mainly essential elements (e.g., Cu and Zn) were accumulated in primary consumer groups. A concentration of other trace elements with increasing trophic levels was not confirmed, with the exception of Ni and Cd, which are highly mobile in environmental compartments. Similar results are reported by Edwards et al.[1288] on *Eisenia fetida* used for metal accumulation bioassay. They concluded, based on the earthworm bioassay for Cu and Hg, that many factors hampered quantitative determination of the degree of soil metal availability to these biota.

Table 28 Metals in Surface Soils and Earthworms (ppm DW)

Metal	Soil	Earthworms	Ratio, Worms/Soil	Ref.
Cd	2	15	7.5	339
	4	4	1	339
	1.6	11.1	6.9	264
	0.9	14.4	16	264
	1.1	18	16	160
	0.6	12	20	160
	0.1	2.7	27	160
	4.1	10.3[a]	27.6	179
	0.16	6[c]	37.2	1104a
Cu	20	13	0.65	339
	252	11	0.04	339
	335	11	0.03	339
	52	28	0.53	160
	26	18	0.69	160
	9	5	0.55	160
	11	8.5[c]	0.78	1104a
Hg	3.8	1.29[b]	0.33	111
	0.1	0.04[b]	0.40	111
	0.32	0.31[c]	0.97	1104a
Mn	1330	82	0.06	339
	226	28	0.12	339
	164	27	0.16	339
	214	63[c]	0.04	1104a
Ni	26	31	1.19	264
	18	29	1.61	264
	12	32	2.66	264
Pb	1314	3592	2.73	339
	629	9	0.01	339
	700	331	0.47	264
	94	101	1.04	264
	170	62	0.36	160
	20	9	0.45	160
	870	109[a]	0.12	160
Zn	138	739	5.35	339
	992	676	0.68	339
	219	670	3.05	264
	49	400	8.16	264
	275	2000	7.27	160
	40	900	22.50	160
	81	662[a]	8.17	179
	76	256[c]	3.4	1104a

Note: Element concentrations expressed on dry weight basis. Organisms analyzed are *Lumbricus rubellus* or *L. terrestris*, except as indicated.

[a] Other Invertebrata.

[b] FW basis.

[c] *Denolrobaena octahedra*.

In soils highly contaminated by trace elements, mezo- and macrobiota are decreased, their metabolism is inhibited, and finally all organisms may vanish.

V. ORGANIC MATTER

The association of metals with organic matter is described by Weber[1182] as follows: "Metals are enriched relatively to average concentrations in the Earth's crust in a variety of organic-rich environmental materials including: petroleum, asphalt, coal, soils, shales, aquatic sediments, and

Table 29 Effects of Increasing Concentrations of Metals in Soils on Their Accumulation in Earthworms[1079] (ppm DW)

Metal	Soil	*Lumbricus* Species	Concentration Factor[a]
Cd	0.1	19 (8)[b]	190
	6.0	79 (69)	13
	9.2	114 (57)	12
Cu	7	20 (17)	2.8
	25	28 (21)	1.1
	40	28 (23)	0.7
Pb	24	12 (41)	0.5
	115	25 (41)	0.2
	135	25 (20)	0.1
Zn	35	730 (837)	20
	737	1474 (1525)	2
	1015	1789 (1164)	1.7

[a] Ratio worms to soil.

[b] Values predicted by Ma are in parentheses.[1079]

peat." Meyer[1091] concluded that the biomass has also affected the Earth's surface chemistry, because the photosynthetic generation of free oxygen and carbon compounds contributes significantly to the diversity of redox potentials in both sedimentary and igneous-related processes of selection of metals at the source, during transport, and at the site of ore deposition. On the other hand, Rösler and Beuge[1133] pointed out that the often discussed role of trace elements bound to organic substances is of much less importance in their behavior during the metamorphism than has been anticipated. Metamorphic processes of organic sediments involve the fractionation of trace elements with a general trend: (1) Hg, U, and J in peats, (2) Sr and F in lignite, (3) Pb, Cu, and Zn in hard coal, and (4) Mn and Cr in graphite.[1133]

Organic substances play a prominent role in biochemical weathering and thus in geochemical cycling of trace elements. Stevenson[1157] discussed evidence both for and against their involvement in weathering processes. It seems more likely that humic and fulvic acids exhibit an activity of the same order as simple organic compounds in metal ion mobilization from soil minerals. The solubilization and transport of some metals, such as Au, Hg, and U, mediated by humic substances are cited by several authors.[299,1157,1163]

Organic matter of soils consists of a mixture of plant and animal products in various stages of decomposition and of substances that were synthesized chemically and biologically. This complex material, greatly simplified, can be divided into humic and nonhumic substances. Organic matter is widely distributed in soils, miscellaneous deposits, and natural waters. The amount of organic carbon in the earth as humus (50×10^{11} t) has been calculated to exceed that which occurs in living organisms (7×10^{11} t).[201]

The major portion of the organic matter in most soils results from biological decay of the biota residues. The end products of this degradation are humic substances, organic acids of low-molecular and high-molecular weights, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons, and lignin fragments. In addition, the excretion products of roots, composed of a wide variety of simple organic acids, are present in soils. It should be mentioned, however, that the composition and properties of organic matter are dependent on climatic conditions, soil types, and agricultural practices. In soil contaminated with trace metals, and in particular with Cu, over the long term, there can be expected an increase in organic matter content by reducing organic matter decomposition.[390,1478] Similar effects have also been observed with other trace metals. This is of considerable importance in predicting the long-term environmental effects of the trace metal pollution.

The most stable compounds in soils are humic substances partitioned into the fractions of humic acid, fulvic acid, and humin, which are similar in structure, but differ in their reactions. Humic substances are of a coiled polymer chain structure and contain a relatively large number of functional groups (CO_2, OH, C=C, COOH, SH, CO_2H) having a great affinity for interacting with metal ions. Owing to a particular combination of different groups (mainly, OH and SH), humic substances are able to form complexes with certain cations. Some trace anions, such as B, I, and Se, are also well-known to be organically bound in soils. Humic substances are also easily adsorbed by clay and oxide particles in soil and water environments, and these responses are highly dependent on trace cations.[779,799] Laxen[1057] emphasized a role of humic substances in the adsorption of Cd, Cu, Ni, and possibly Pb onto Fe hydrous oxides. The adsorption/coprecipitation of these metals by Fe oxides is enhanced in the presence of humics (see Chapter 4, Section III.B.). Estimated CEC values of humic substances vary from 200 to 500 meq 100 g^{-1}, being higher for humic acids and lower for fulvic acids. General properties of humic substances are:

1. Fulvic acids (fulvates)—have a low degree of polymerization, high acidity and mobility; occur mainly in poor acid soils of a low biological activity
2. Humic acids (humates)—have spherocolloidal polymerization, medium acidity and mobility; occur in weak acid and neutral soils of high biological activity
3. Humins—are products of aging of humates and fulvates, have a high degree of polymerization and low acidity; occur in all soils

Interactions between humic substances and metals have been described as ion exchange, surface sorption, chelation, coagulation, and peptization. It should be emphasized that the existence of a particular site for each cation is not easy to prove because the metal may be bound to two or more ligands from different molecules. All reactions between organic matter and cations lead to the formation of water-soluble and/or water-insoluble complexes. Organic matter and some decomposition products can act as reducing agents and assist in mobilizing some elements. Compounds acting as a reducing agent form complex ions with a number of cations, and also form a few sparingly soluble species. Trudgill[1167] reported that humic matter in laboratory studies reduces a variety of metal ions such as: V^{5+} to V^{4+}, Hg^{2+} to Hg^0, Fe^{3+} to Fe^{2+}, Cr^{6+} to Cr^{3+}, and U^{6+}, to U^{4+}.

Sholkovitz and Copland[720] studied the complexing and chelation of trace elements with organic ligands in natural waters. Their studies led to the conclusion that solubilities of humic acid complexes with Fe, Cu, Ni, Cd, Cu, and Mn are the reverse of those predicted from inorganic solubility considerations. The complexing of these ions with humic substances led to the solubilization at high pH (range 3 to 9.5) and precipitation at low pH (range 3 to 1). Weber[1182] described that: “Many metals in natural waters have solubilities much higher than expected from calculations based on the inorganic ions of the medium. This enhanced solubility is predominantly due to their complexation, adsorption on, and reduction by humic material.”

Organic matter is of importance in the transportation (and subsequent leaching) and accumulation of metallic ions known to be present in soils and waters as chelates of various stability and in supplying these ions to plant roots. The ion exchange equilibrium has been extensively studied for determining the stability constant of metallo-organic matter complexes in soils. The values of stability constants determined by several authors described the ability of humic acids to form complexes with metals (Table 30). Metal-fulvic acid complexes with lower stability constants usually are more readily soluble and thus more available to plant roots. The evaluation of several experiments, however, elucidates that organic matter in soils has a relatively low influence on the uptake of trace metals by plants.[1375] It is still controversial and needs further examination, and perhaps study of the separated fraction of organic matter, with special emphasis on dissolved organic compounds in soils.

The highest stability-constant values were reported by Takamatsu and Yoshida[771] for Cu^{2+}, Pb^{2+}, and Cd^{2+} complexed with humic acid at pH 5, and by Kitagishi and Yamane[395] for Cu^{2+}, Zn^{2+},

Table 30 Stability Constants Expressed as Log K of Metal Fulvic and Humic Acid Complexes at Various pH Levels of the Media

	pH 3		pH 3.5	pH 5				pH 7
Cation	FA (a)	HA (d)	FA (b)	FA (a)	FA (b)	HA (c)	HA (d)	HA (d)
Cu^{2+}	3.3	6.8	5.8	4.0	8.7	8.7	12.6	12.3
Ni^{2+}	3.2	5.4	3.5	4.2	4.1	—	7.6	9.6
Co^{2+}	2.8	—	2.2	4.1	3.7	—	—	—
Pb^{2+}	2.7	—	3.1	4.0	6.2	8.3	—	—
Zn^{2+}	2.3	5.1	1.7	3.6	2.3	—	7.2	10.3
Mn^{2+}	2.1	0	1.5	3.7	3.8	—	0	5.6
Cd^{2+}	—	5.3	—	—	—	6.3	5.5	8.9
Fe^{2+}	—	5.4	5.1	—	5.8	—	6.4	4.8
Ca^{2+}	2.7	0	2.0	3.4	2.9	—	0	6.5
Mg^{2+}	1.9	0	1.2	2.2	2.1	—	0	5.5
Fe^{3+}	6.1[a]	11.4	—	—	—	—	8.5	6.6
Al^{3+}	3.7[b]	—	—	—	—	—	—	—

Note: References are as follows: a, 692; b, 571; c, 771; and d, 395.

[a] Determined at pH 1.7.

[b] Determined at pH 2.4.

Table 31 Effect of pH on Sorption of Metals on Humic Acid[1007]

	Percentage of Initial Metal Concentration[a]		
Metal	pH 2.4	pH 3.7	pH 5.8
Hg	99	98	98
Fe	81	96	100
Pb	19	80	96
Cu	12	59	97
Al	7	86	100
Ni	5	6	61
Cr	0	70	100
Cd	0	7	77
Zn	0	8	64
Co	0	2	45
Mn	0	3	13

[a] Initial metal content was 0.5 × 10^{-4} mol of each metal in 100 mL of solution.

Ni^{2+}, and Cd^{2+} at pH 7. Andrzejewski and Rosikiewicz[28] observed that Mn^{2+}, Co^{2+}, and Ni^{2+} complexes with humic acids were partly soluble, while those of Cu^{2+}, Fe^{2+}, and Cr^{3+} were insoluble. Augustyn and Urbaniak[40] also stated that the higher retention by humic acid was of Fe^{2+}, Cu^{2+}, and Zn^{2+} as compared to other metallic ions. Fe^{3+} and Al^{3+}, however, form the most stable complexes with fulvic acid which greatly interfere with the crystallization of aluminum hydroxide polymorphs.[406]

The stability of metal complexes with fulvic and humic acids increases, in many cases, with increasing pH from 3 to 7 (Table 30). Findings presented by Gamble[1007] confirmed a significant effect of pH on the sorption of metals on humic acid (Table 31). This is best illustrated for Pb, as studied extensively by Hildebrand and Blume.[319] The binding of Fe^{2+} and Fe^{3+} by fulvic acid in solution below pH 5.0 is very strong and, apparently, cannot be exchanged easily by other metals. A relatively high value of the stability constants of Ca^{2+} suggests that this metal can compete with Zn^{2+} and Mn^{2+} in ion exchange processes. Most likely, however, several heavy metals such as Hg, Fe, Cu, Cr, and Pb will readily form stable organic complexes with fulvic acid and, most probably, also with other organic compounds.

Table 32 Trace Elements in Soil Organic Matter and in Clay Fraction (ppm DW)[756]

Surface Soil	Element	Content of Clay Fraction (<1 μm) Total	Organic Matter	Humic Acid	Fulvic Acid
Chernozem	Cu	90	33.0	3.6	29.4
	Zn	116	41.5	3.4	38.1
	Mn	1110	262	Trace	254
	Mo	5	1.7	0.8	0.9
Podzol	Cu	44	17.9	1.2	16.7
	Zn	80	44.7	15.6	29.1
	Mn	1830	307	44	267
	Mo	3	0.7	0.2	0.5

Analyses of fractionated organic acids from soils by Stepanova[756] confirm the greater affinity of fulvic acids for heavy metals (Table 32). Mickievich et al.[537] also reported a much higher concentration mainly of Cu, Pb, and Ti in fulvic acid than was found in humic acid. Heavy metals in soils tend to accumulate in the organic substances, and the lower the metal content, the higher the energy linkage of the metallo-organic groups.[908]

The commonly used value of the stability constant of a complex can be defined as an equilibrium constant of a reaction that forms a soluble complex or chelate. In order to include information about the behavior of insoluble complexes, the value of the stability index has been proposed by Cottenie et al.[148] This index describes the ratio of a given metal fixed with organic substances to its amount in inorganic fractions. The stability index for pure humic and fulvic acids shows that heavy metals (Cu, Zn, Pb, Mn) form complexes several times more readily with humic acid than with fulvic acid, and that the highest proportion of Cu is fixed with humic acid over the range of pH 4 to 5, while with fulvic acid the range of pH is limited to 6 to 7. Both acids often show a higher affinity for Cu and Pb than for Fe and Mn. These findings agree with those reported by Van Dijk,[820] Stevenson and Ardakani,[757] Förstner and Müller,[242] Pauli,[601] Vlasov and Mikhaylova,[825] and Schnitzer and Khan[692] and indicate that the order of the stability constants of metallo-organic complexes, although quite variable depending on pH and other properties of the medium, can be presented in the following sequence: U > Hg > Sn > Pb > Cu > Ni > Co > Fe > Cd > Zn > Mn > Sr.

Gamble[1007] emphasized, however, that because of a great number of variables in the natural system of soil organic polymers, the existence of an equilibrium function must be measured instead of an equilibrium constant. His data, obtained from the calculation based on weighted average equilibrium function theory, show the following order of metal affinity to sorption on humic acids, at pH 3.7:

$$\mathrm{Hg > Fe > Pb > Cr > Cu > Zn > Cd > Mn > Co}$$

Schnitzer and Kerndorff[690] recently established the order of the affinity of metal ions to form water-insoluble complexes with fulvic acid. Although this order depends on the pH of the medium, it may be presented as follows:

$$\mathrm{Fe = Cr = Al > Pb = Cu > Hg > Zn = Ni = Co = Cd = Mn}$$

Despite the diversity in these orders calculated for various experimental conditions, there is general similarity in the estimation of two groups of metals, strongly and slightly fixed by organic polymers in soils.

The sorption capacity of humic acids increases with increasing acidity. Varshal et al.[1530] determined amounts of sorbed metals by humic acids at pH 5 to 6, and gave the following values (in mg/kg of humic acids): Cd 9, Au 16, Sr 17.5, Cu 18, Y 19, Os 24, Yb 28, Cs 29.3, Ce 31, and Pb 120.

The solubility of fulvic acid-metal complexes is strongly controlled by the ratio of FA:metal; therefore, when this ratio is lower than 2, the formation of water-insoluble complexes is favored. There is diversity, however, in the interpretation of metal ion binding by peat because, as Bloom and McBride[80] reported, peat and humic acids are likely to bind, at an acid pH, most divalent cations (Mn, Fe, Co, Ni, and Zn) as hydrated ions. The exception is the Cu^{2+} ion coordinating with functional oxygens of the peat which results in strongly immobilized Cu^{2+} binding.

The index of organic affinities of trace elements in various coal samples was calculated by Gluskoter et al.[269] These authors distinguished three groups of elements:

1. With the highest organic affinity—Ge, Be, B, Br, and Sb
2. With medium organic affinity—Co, Ni, Cu, Cr, Se
3. With the lowest affinity, but occurring in all organic fractions—Cd, Mn, Mo, Fe, Zn, and As

Histosols, soils formed from decomposed plant material, play a specific role in the distribution of trace elements in the biosphere. The elements which are easily taken up by plants and are likely to be fixed by organic matter of histosols appeared to be concentrated in peat soils. Lieth and Markert[1063] compared chemical composition of the peat bog with the nearby mineral soil, and emphasized the variable pattern of the element distribution. They concluded that Cd and Pb are more abundant in the peat than in the mineral soil, apparently due to aerial deposition. The affinity of humic substances to accumulate trace cations has great importance in their geochemistry. The so-called "geochemical enrichment" factors of humic acid that was extracted from peat can reach a value of 10,000 from very low concentrations of cations in natural waters.[299,691] Trace elements migrating as anions (V and Mo) are reduced by humic acids and fixed in the cationic forms (VO^{2+}, MoO_4^{2+}). Metals complexed by fulvic acid presumably are more available to plant roots and soil biota than are those accumulated by humic acid which can form both water-soluble and water-insoluble complexes with metal ions and hydrous oxides.

Cottenie et al.[148] calculated that the humic acid of a soil containing 4% humus may bind 4500 kg Pb, 17,929 kg Fe, 1517 kg Cu, 1015 kg Zn, and 913 kg Mn per hectare. The ability of humic acid to complex with metals was also calculated by Ovcharenko et al.[587] and expressed in grams per kilogram of humic acid, as follows: Cu, 3.3; Zn, 3.3; Co, 3.2; Fe, 3.0, and Mn, 2.6. Sapek[681] showed that the ability of humic acids to fix cations differs widely, and that those isolated from the A_o horizon of podzolic soil have about two times lower sorption capacity to metals than those extracted from the B_h horizon of the same soil. In his experiment, the heavy metal content of air-dry humic acid reached more than 29%. All of these values were determined under laboratory conditions; in a natural soil system, these proportions would be appreciably smaller. In general, however, it can be expected that up to 50% of total trace element content is fixed by organic matter in mineral soils. These figures, however, can vary significantly.[756]

Owing to the relatively insoluble complexes of humic acids with heavy metals, especially in an acid medium, these complexes can be considered to be organic storage for heavy metals in soils. The organic matter may act as an important regulator of the mobility of trace elements in soils; however, in the majority of mineral soils, organic matter does not exceed 2% of total soil weight; therefore, it cannot be of the greatest importance in overall controls of trace element behavior in soils. The environmental role of humic substances has been summarized by the Dahlem Group of Experts[1030] as follows: "Humic substances appear to exert a stabilizing effect on environmental processes, for example by assimilation and subsequent slow release of chemical compounds, they act as a reservoir of trace nutrients and contaminants. Chemical partition of chemicals into humic substances results in a 'buffering' of the environmental mobility of chemicals. Their function, however, as scavengers of pollutants is limited and can be overtaxed. Care should be taken not to overload the system and to prevent long-term damage which may not be apparent until remedial action becomes difficult and perhaps impossible."

A high organic matter content of soil has a complex influence on the behavior of trace elements. The deficiency symptoms of plants grown on drained peatland or moorland (histosols) may be the result of a strong retention of Cu, Zn, Mo, and Mn by the insoluble humic acid.[135] A strong fixation of Cu in soils rich in humus is the most common and may result in a high Mo-to-Cu ratio in forage that is toxic to cattle. Applying organic matter to soil, however, raises the number of microorganisms that can reduce several cations, mainly Fe and Mn, and, in consequence, increase their availability. Increased organic matter content in Pb-amended plots is due to an enhanced preservation of stable humus, perhaps because of newly formed Pb-organic complexes with humic and fulvic acids which are protected from microbial attack.[903] However, there is also evidence that Pb complexes with low-molecular-weight humic substances were mobilized in the soil solution. On the other hand, some organic compounds present in root exudates and in humus can oxidize and therefore immobilize cupric compounds in soil.[81,189]

Simple organic compounds, such as certain amino acids, hydroxy acids, and also phosphoric acids naturally occurring in soils, are effective as chelating agents for trace elements. Cation chelation is an important factor in soil formation processes, as well as in nutrient supply to plant roots. The solubility of metal complexes depends on both the binding strength and the mobility of the complex thus formed, which is determined mainly by the size of the organic group involved. Strong binding of metal to a low-molecular-weight organic substance will appreciably increase its mobility in soil (Figure 22). Organic acids of leaf litter are known to be active in the mobilization of heavy metals in soils. An extract of pine needles dissolved more metals than an extract of oak leaves; in both cases, however, Cu and Zn were more readily complexed than were Co, Ni, and Cd. [87,374] Despite a high mobilization of heavy metals, forest soil litter is also well-known as an

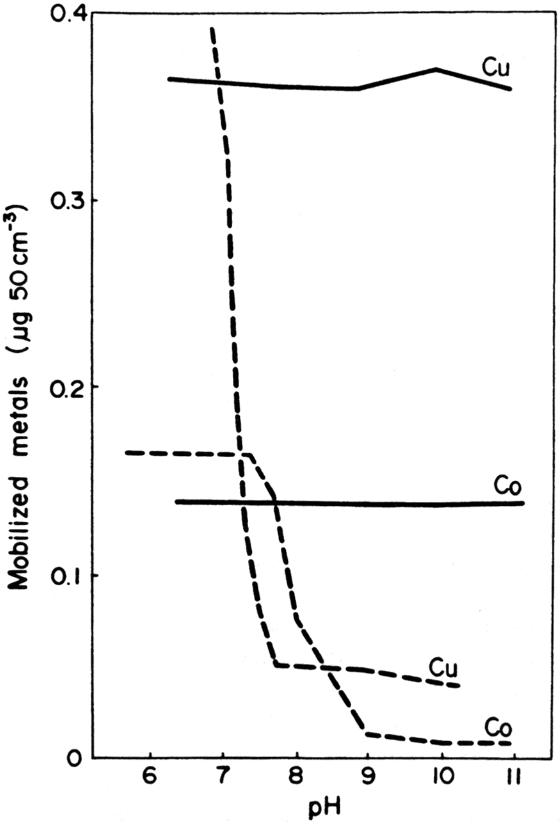

Figure 22 The effect of pH on the solubility of Co and Cu mobilized by aerobically decomposing alfalfa. Solid lines, complexed metals; broken lines, control solution of $CuCl_2$ or $CoCl_2$ alone.[81]

important sink of heavy metal and radionuclide pollutants, as reported by Pavlotskaya,[602,603] Van Hook et al.,[823] and Schnitzer and Khan.[692] The ability of simple organic acids to solubilize heavy metals may be of importance in their cycling. Rashid[642] calculated that each gram of amino acids occurring in the sediments may mobilize 4 to 440 mg of various metals, showing the highest affinity to Ni and Co and the lowest to Mn.

Several chelating agents are at present used in diagnostic extraction for available micronutrients in soils (see Norvell,[571] Mengel and Kirkby,[531] and Lindsay[477]). Of those commonly used are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), which have been used for many years for determining plant-available trace elements in soils. Although the results differ when compared with other soil extractants and with uptake by plants, they are applied in many testing methods, and the ranges for critical levels are given for some micronutrients such as Cu, Zn, Mn, and Fe. The DTPA soil test has also been developed to assess pollution by heavy metals of soils.[143] Soluble chelates of some trace metals, mainly Mn and Zn (i.e., Mn-EDTA; Na_2Zn-EDTA), are also effective as fertilizers. Pickering[1118] summarized data showing the ability of synthetic chelating agents (EDTA and Na-citrate) to displace metal ions from soil components. Both agents easily mobilized metals (Zn, Cd, Cu, and Pb) fixed by kaolinite, illite, and montmorillonite. The mobilizing effect was moderate or very small when those metals were retained to the following substrates: $Fe(OH)_3$ gel, MnOOH, $CaCO_3$, and humic acid.

CHAPTER 5

Trace Elements in Plants

I. INTRODUCTION

The trace element metabolism of plants has been extensively studied and the basic information on many topics is available in monographs on plant physiology or plant nutrition. The metabolic fate and role of each trace element in plants can be characterized in relation to some basic processes such as:

1. Uptake (absorption), and transport within a plant
2. Enzymatic processes
3. Concentrations and forms of occurrence
4. Deficiency and toxicity
5. Ion competition and interaction

These topics are relatively well-understood for certain micronutrients, but further investigations are needed for many other trace elements. The reaction of plants to chemical stresses that are caused by both deficiencies and excesses of trace elements cannot be defined exactly because plants have developed during their evolution and course of life (ontogeny and phylogeny) several biochemical mechanisms that have resulted in adaptation to and tolerance of new or chemically imbalanced environments. Therefore, plant responses to trace elements in the soil and ambient air should always be investigated for the particular soil–plant system.

Plants reveal various tendencies in the uptake of trace elements. Three general uptake characteristics can be distinguished: accumulation, indication, and exclusion. To a large extent, this depends on the specific ability of plants and huge differences in metal uptake between plant species. Also, between genotypes of a species, great variabilities have been demonstrated in many studies. The most common plants tested recently for phytoremediation have been listed by Felix et al.[1298]: *Alyssum murale, Thlaspi caerulescens, Nicotiana tabacum, Zea mays, Brassica juncea*, and *Salix viminalis*. The ability of several agricultural crop plant species, such as mustard, radish, turnip, rape, and amaranth, to accumulate higher amounts of some metals (Cd, Cr, Cu, Ni, and Zn) has been investigated as well.[1492]

Plants able to take up metals above established background concentrations and more than other species from the same soils are called *hyperaccumulators.* These are mainly populations of species found in soils rich in metals either due to geochemical parameters or due to pollution. Hyperaccumulators usually have a low biomass because they use more energy in the mechanisms necessary to adapt to the high metal concentrations in the tissues. There are a number of studies on hyperaccumulators because of their specific physiologic processes and practical aspects. Plants that highly accumulate metals are promising in phytoremediation programs (see Chapter 2, Section IV.B). This has been a highlighted topic at several recent conferences, and has been widely reviewed in recent publications and books.[1244,1459]

A number of various plants are known as medicinal herbs and have been used for a very long time (possibly since Neanderthal man) to cure illness. Although a curative agent is mainly associated with organic compounds such as glycosides or alkaloids, trace elements can have additional impact. Most medicinal plants belong to a kind of weed that can accumulate a greater amount of trace elements than other plants. A good example is dandelion, often used in herb medicine and also as a nutritional plant. However, when dandelion grows in a polluted environment, it is known to take up, from both aerial and soil sources, many more trace metals than other plants.[1356] Thus, trace element content in those plants should be of special concern.

Hyperaccumulators are plants and/or genotypes that accumulate metals above certain concentrations in leaves. As Greger[1316] presented, based on a literature review, hyperaccumulators should contain trace metals in leaves above the following levels (in ppm):

>100 — Cd
>1000 — Co, Cu, Ni, Pb
>10,000 — Mn, Zn

In polluted regions, however, some plants (not hyperaccumulators) may concentrate metals at those levels. Therefore, increased levels of a given metal in a hyperaccumulating plant must be related to their contents in other plants grown in the same environment.[1356]

The chemical composition of plants reflects, in general, the elemental composition of the growth media. The extent to which this relation exists, however, is highly variable and is governed by many different factors. The common concentrations of trace elements in plants growing on various, but nonpolluted, soils show quite a large variation for each element.

A large variety of possible ligands for metals exist in plants, especially in xylem and phloem. Thus, metal ions form complexes with small and macromolecular substances, mainly organic. Inorganic ligands, however, are also very important complexants for metals. Depending on the size and physical and chemical characteristics, metals can form with ligands in plants either easily transported or strongly bound forms, and complexes. Both are of great metabolic importance because they control the transport of nutrients within the plant organs, and also protect the plant against an excess, especially of trace metals.[1456,1459]

It is observed with some regularity that sea plants contain more Al, As, Br, Cl, I, Sr, V, and Fe (on a dry matter basis) than terrestrial plants.[1333a] This is thought to be a general rule in chemical element distribution among sea and terrestrial plants that has also been emphasized by Dobrovolsky,[1280] who calculated the variable abundance of trace elements that are involved in biogeochemical cycling in different climatic zones of the globe. There is an increase of over tenfold when comparing element cycling in a tundra zone with that in a tropical forest.

II. ABSORPTION

The main sources of trace elements in plants are their growth media, for example, nutrient solutions or soils. One of the most important factors that determines the biological availability of a trace element is its binding to soil constituents. In general, plants readily take up the species of trace elements that are dissolved in the soil solutions in either ionic or chelated and complexed forms. Much has been written on the absorption of trace elements from solutions by Moore,[548] Loneragan,[489] Mengel and Kirkby,[531] Wild and Jones,[1184] and others, and this absorption can be summarized as follows:

1. It usually operates at very low concentrations in solutions.
2. It largely depends on the concentrations in the solution, especially at low ranges.
3. The rate depends strongly on the occurrence of H^+ and other ions.
4. The intensity varies with plant species and stage of development.

5. The processes are sensitive to some properties of the soil environment such as temperature, aeration, and redox potential.
6. It may be selective for a particular ion.
7. The accumulation of some ions can take place against a concentration gradient.
8. Mycorrhizae play an important role in cycling between external media and roots.

Generalizations of plant processes operative in the absorption of trace elements rest on the evidence for one or a few of the elements, and most often can represent some approximation to processes acting in a natural plant-soil system. Absorption by roots is the main pathway of trace elements to plants; however, the ability of other tissues to readily absorb some nutrients, including trace elements, has also been observed.

In general, the uptake of trace elements by plants is affected, in addition to plant-specific ability, by soils factors, of which the most significant are pH, Eh, water regime, clay content, organic matter content, cation exchange capacity, nutrient balance, and concentration of other trace elements. Also, climatic conditions are shown to influence the rate of trace metal uptake, which may be partly an indirect impact due to the water flow phenomenon. Generally, a higher ambient temperature influences a greater uptake of trace elements by plants.

Plant ability to take up chemical elements from growth media is evaluated by a ratio of element concentration in plants to element concentration in soils and is called: Biological Absorption Coefficient (BAC), Index of Bioaccumulation (IBA), or Transfer Factors (TF). Some elements are more susceptible to phytoavailability than others (see Figure 23). There is, however, great variability among plants, which is indicated by the data of Bini et al.[1226] for four tree species (*Populus nigra* L., *Platanus orientalis* L., *Laurus nobilis* L., *Pinus picea* L). Ranges of BAC values of these trees varied from 209 to 2000 for Cu, and from 10 to 100 for Ni.

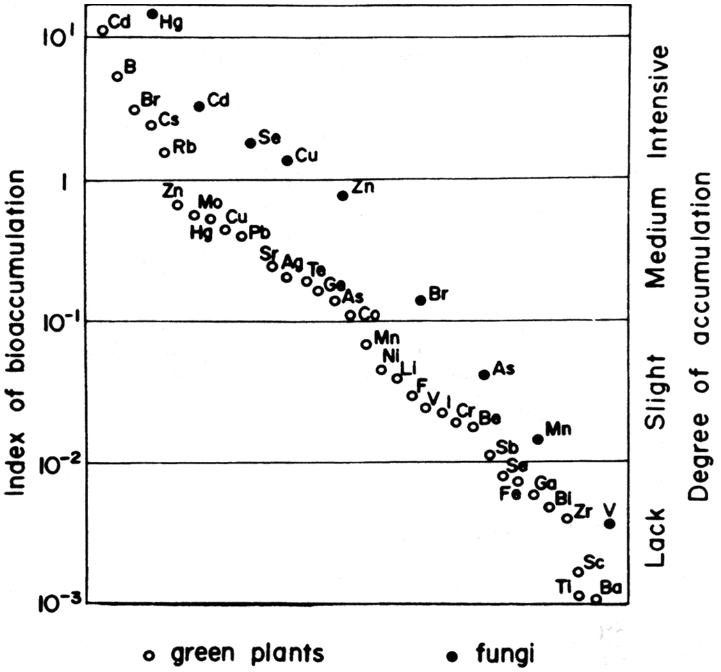

Figure 23 Bioaccumulation of trace elements by plants from soils. Index of bioaccumulation (BAC, IBA) was calculated as the ratio of trace elements in plants to their concentration in soils. The calculation is based on data for different plants and soils. Values for fungi are based on data from Byrne and Ravnik.[117]

A. Root Uptake

The absorption of trace elements by roots can be both passive (nonmetabolic) and active (metabolic), but there are some disagreements reported in the literature concerning which method is involved in certain elements. Despite controversies, in each case the rate of trace element uptake will positively correlate with its available pool at the root surface.

Passive uptake is the diffusion of ions from the external solution into the root endodermis. Active uptake requires metabolic energy and takes place against a chemical gradient. Several data support the suggestion that, at the concentration generally present in soil solutions, the absorption of trace elements by plant roots is controlled by metabolic processes within roots.[489,548,788] The ion activity in the solution is believed to be one of the significant factors that influence plant uptake of ions. Presumably, this is an important factor when the uptake is active, but may not be important when the uptake is passive.

Mechanisms of uptake differ, depending on the given element. Pb and Ni are preferably absorbed passively, while Cu, Mo, and Zn are preferably absorbed actively. When biological and structural properties of root cells are altered, however, all elements are taken up passively. This is the case when concentrations of elements pass over a threshold value for a physiological barrier.

Much evidence indicates that roots exhibit great activity in the mobilization of trace elements that are bound by various soil constituents. Roots and associated microorganisms are known to produce various organic compounds which are very effective in releasing the trace elements from firmly fixed species in soil. The trace elements most readily available to plants are, in general, those that are adsorbed on clay minerals (especially, montmorillonite and illite), while those fixed by oxides and bound onto microorganisms are much less readily available. The depletion of trace elements in solution from the root-soil interface reflects a higher rate of their uptake by roots than mass-flow and diffusion mechanisms in certain soils.[531,638] The mechanisms of uptake of trace elements by roots involve several processes:

1. Cation exchange by roots
2. Transport inside cells by chelating agents or other carriers
3. Rhizosphere effects

Ions and other materials released from roots to rooting media control nutrient uptake by roots. Root exudates of plants are composed mainly of amino acids (e.g., aspartic, glutamic, prolinic) and vary with plant species (and varieties), microorganism association, and conditions of plant growth. Cation oxidation states around roots are believed to be of great importance in these processes. Changes in the pH of the root ambient solution may play an especially significant role in the rate of availability of certain trace elements.[241] Root exudates (e.g., phytosiderophore 2′-deoxymugineic acid) of metal-deficient cereal plants (e.g., Zn, Fe) are especially effective in mobilizing these metals from various precipitations within the root media.[1004a] The exudates released from roots of graminaceous species are of great importance since they are also active in mobilizing other trace metals from soils.

Specific physical and chemical properties of rhizospheres controlled by root exudates and microflora govern processes of the absorption of chemical elements. Apparently, the significant role played by low-molecular-weight organic acids (e.g., oxalic, acetic, fumaric, citric, tartaric) is dissolution and/or complexation processes that mobilize slightly soluble forms of trace elements.[1262,1380]

Roots can also act as a "barrier" in the uptake or transport of trace elements. Otte et al.[1107] described interesting properties of roots of the plants growing in marsh (e.g., *Spartica anglica*). The Fe-plaque formed on the roots consists mainly of Fe (hydro) oxides with a large capacity to adsorb metals. Above certain threshold concentrations, the Fe-plaque becomes saturated with the trace metal, and the root is confronted with higher metal contents exceeding that of the surrounding medium.

Chaney et al.[128] believed that the reduction step is obligatory in root uptake of Fe. The reduction of other metals such as Mn, Cu, Sn, or Hg in the uptake step apparently has not been clearly observed. Rice roots, on the other hand, exhibit a peculiar mechanism to absorb Si and Se in the form of oxides.[395]

The ability of different plants to absorb trace elements varies greatly; when compared on a large scale, however, the index of their accumulating ability illustrates some general trends. Some elements such as Cd, B, Br, Cs, and Rb are extremely easily taken up, while Ba, Ti, Zr, Sc, Bi, Ga and, to an extent, Fe and Se, are but slightly available to plants (Figure 23). This trend, however, will differ a great deal for particular soil-plant systems. Marked differences in the metal uptake between both plant species and varieties open up new aspects for plant breeding programs for the biodepletion in metal transport to the food chain.

Fungi are nongreen plants with quite a diverse mechanism of nutrient uptake, and they have a specific affinity for some trace elements. They may accumulate Hg and also other elements such as Cd, Se, Cu, and Zn to high levels (Figure 23). Concentrations of several trace elements in plants from a pine forest in Japan indicate that there is a preferable uptake by mushrooms of such elements as Cd, Zn, Cu, Cs, and Rb.[1564,1565] Concentrations of these elements were one order of magnitude higher than those in plants growing in the same forest. Concentrations of Ca and Sr in mushrooms, on the other hand, were lower than those in plants.

B. Foliar Uptake

The bioavailability of trace elements from aerial sources through the leaves may have a significant impact on plant contamination and it is also of practical importance in foliar applications of fertilizers, especially of elements such as Fe, Mn, Zn, and Cu. Foliar absorption of radionuclides released into the atmosphere from nuclear weapons testing and nuclear power installations is of especially great concern.

Foliar uptake is believed to consist of two phases—nonmetabolic cuticular penetration, which is generally considered to be the major route of entry, and metabolic mechanisms, which account for element accumulation against a concentration gradient. The second process is responsible for transporting ions across the plasma membrane and into the cell protoplast. Wyttenbach et al.[1553] studied the uptake of As, Br, and I by Norway spruce in order to distinguish between the uptake from soils and from gaseous or soluble compounds in the air. They found a strong positive correlation between the endogenous needle concentrations and the surface loadings, and also insignificant correlations with total soil concentrations of these elements.

Trace elements taken up by leaves can be translocated to other plant tissues, including roots where the excesses of some metals seem to be stored. The rate of trace element movement among tissues varies greatly, depending on the plant organ, its age, and the element involved. Results illustrated in Figure 24 show that Cd, Zn, and Pb absorbed by the tops of brome grass were not likely to move readily to the roots, whereas Cu was very mobile.

A fraction of the trace elements absorbed by leaves may be leached from plant foliage by rainwater. Differences in leaching of trace elements can be related to their function or metabolic association. For example, the easy removal of Pb by washing suggests that the metal was largely a superficial deposit on the leaf surface. In contrast, the small fraction of Cu, Zn, and Cd that can be washed off indicates a greater leaf penetration of these metals than was noted for Pb by Little and Martin[482] and Kabata-Pendias.[374] Moreover, significant absorption of foliar-applied Zn, Fe, Cd, and Hg were reported by Roberts.[657] Foliar leaching by acid rain may involve cation exchange processes, in which the H^+ ion of rainwater replaces microcations held on binding sites in leaf cuticle.[885]

The absorption of trace metals, directly from wet (and dry) deposition by above-ground parts of plants, has been reported often. Morphology of the surface of leaves is an important factor governing foliar uptake of trace elements. Some plants (e.g., lichens, mosses, mushrooms, dandelion, etc.) are especially susceptible to absorb elements and some compounds from aerial sources.

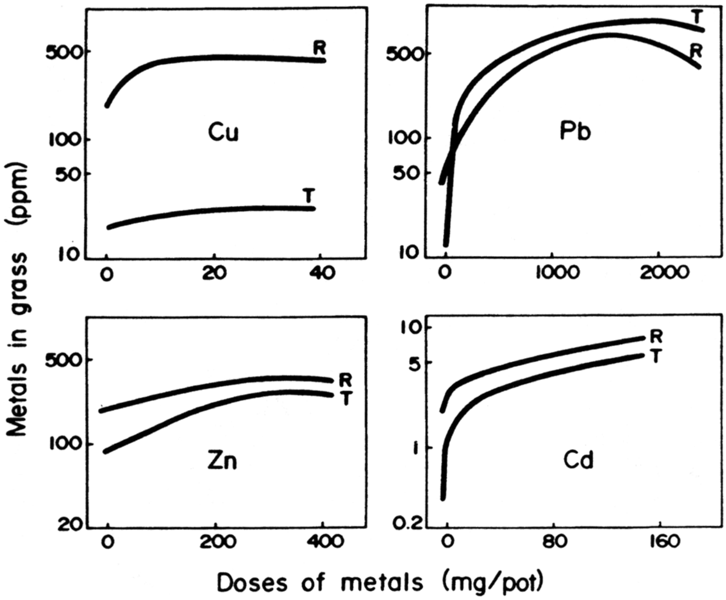

Figure 24 Distribution of heavy metals from aerial sources between the tops (T) and roots (R) of brome grass.[376]

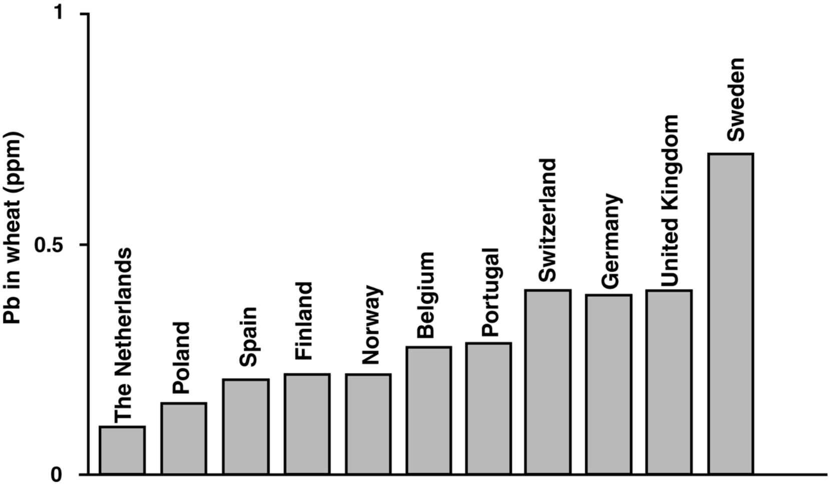

Figure 25 Geometric mean contents of Pb in winter wheat (*Triticale vulgare* L.) collected in 1985 from various countries in Europe. (FAO Cooperative Project Network on Trace Elements—Report, 1991, by M. Verloo *vide* Kabata-Pendias et al.[1358])

Such plants are very suitable for the phytoindication of atmospheric pollution. Also, cereal tops show a relative sensitivity to aerial pollution, revealing the variation in trace metal contents (especially Pb and Ni) mainly due to the absorption from aerial particles (Figures 25 and 26). Dalenberg and van Driel[1270] studied the uptake and translocation of ^{210}Pb from atmospheric deposition. Their results have indicated that 73 to 95% of the total Pb content in plants are taken up by leaves and transported to other plant organs. This was observed not only for leafy plants, such as spinach, but also for cereals.

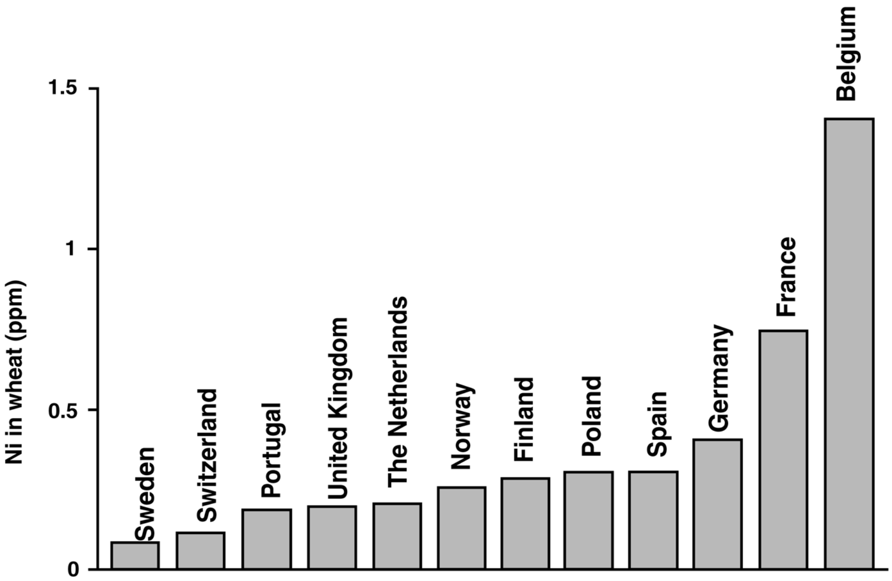

Figure 26 Geometric mean contents of Ni in winter wheat (*Triticale vulgare* L.) collected in 1985 from various countries in Europe. (FAO Cooperative Project Network on Trace Elements—Report, 1991, by M. Verloo *vide* Kabata-Pendias et al.[1358])

III. TRANSLOCATION

The transport of ions within plant tissues and organs involves many processes:

1. Movement in xylem
2. Movement in phloem
3. Storage, accumulation, and immobilization

The chelating ligands are most important in the control of cation translocation in plants. However, numerous other factors such as pH, the oxidation-reduction state, competing cations, hydrolysis, polymerization, and the formation of insoluble salts (e.g., phosphate, oxalate, etc.) govern metal mobility within plant tissues.

Tiffin[788] gave a detailed review of the mechanisms involved in the translocation of micronutrients in plants. It can be summarized that long-distance transport of trace elements in higher plants depends on the vascular tissues (xylem and phloem) and is partly related to the transpiration intensity. Chemical forms of trace metals in phloem exudates differ for each element. Van Goor and Wiersma,[822] for example, reported that Zn was almost all bound to organic compounds, while Mn was only partly complexed.

The distribution and accumulation patterns of trace elements vary considerably for each element, kind of plant, and growth season. As reported by Scheffer et al.,[688a] in the phases of intensive growth of summer barley the amount of Fe and Mn is relatively low, whereas the amount of Cu and Zn is very high. While the first two metals are accumulated mainly in old leaves and leaf sheaths, Cu and Zn seem to be distributed more uniformly through the plant. Differentiation in trace element distribution between various parts of pine trees is also clearly shown by data presented in Table 33. A relatively common phenomenon, however, is the accumulation and immobilization of trace metals in roots, especially when their metal supply is sufficient. The mechanism of exclusion seems also to control the transport of cations from roots to aerial parts.[417]

Table 33 Variation in Trace Element Contents in Pine Trees (ppm DW)[186]

Plant Part	Al	B	Co	Cr	Cu	Fe	Mn	Ni	Pb	Ti	V
Needles											
1 year old	400	18.0	0.9	4.8	4.2	150	430	6.0	0.2	15	0.6
Older	200	24.0	0.8	4.0	2.5	370	740	2.1	0.5	30	1.2
Branches	400	6.0	0.6	1.6	3.0	650	430	1.1	0.6	25	1.8
Knots	120	4.5	0.2	0.8	1.2	78	185	0.3	0.1	6	0.8
Bark	230	4.5	0.4	1.0	2.0	100	123	0.4	0.3	15	2.8
Wood	7	0.9	0.1	0.3	0.6	5	61	0.3	0.1	1	0.2
Roots											
1-mm diameter	1430	6.5	0.1	0.9	3.5	7171	134	1.1	0.3	46	0.6
5-mm diameter	82	3.2	0.7	0.6	1.2	46	50	0.4	0.1	6	0.5

Note: Samples from a pine forest on old alluvial sands in Ukraine.

Brundin et al.[953] have shown that roots of plants growing along stream channels (mainly *Carex* species) as well as aquatic mosses are barrier-free with respect to trace metal uptake. However, physiological barriers are evident with respect to the transport of some metals (e.g., Cu, Zn, and Co) from roots to aerial parts. Most *Carex* species are barrier-free with respect to the translocation of Pb, and partly of Ni, Cr, and Mo.

Horiguchi and Nishihara[1028] studied the association of trace metals with the major constituents of potato tubers and peanut seeds. They found that only a small proportion of metals was distributed in the soluble components of a low molecular weight of peanut seeds, while potato tubers contained higher proportions of the metals in the low-molecular-weight fraction. It is presumed that starch as well as lipid fractions have only a weak affinity for trace metals, and that proteins are the major ligands that form complexes with metals in plants.

The transport of trace elements among plant organs also depends on the electrochemical variables of elements. In general, easily transported from roots to above-earth parts are Ag, B, Li, Mo, and Se; moderately mobile are Mn, Ni, Cd, and Zn; and strongly bound in root cells are Co, Cu, Cr, Pb, Hg, and Fe.

IV. AVAILABILITY

The linear responses of trace element absorption by several plant species in increasing their tissue concentrations from nutrient and soil solutions are illustrated in Figure 27. These responses support the statement that the more reliable methods in diagnosing the available trace element status of soils are those based on element concentrations in the soil solutions rather than methods based on the pool of soluble and/or extractable trace elements. The phytoavailability of trace metals correlates best with the concentration of cationic species in the liquid phase. Table 34 summarizes these relations.

A number of extraction methods have been suggested in recent years for the evaluation of trace element concentrations in soils. In general, they can be classified into separate groups as follows: acids (HCl, NHO_3, aqua regia), chelating agents (EDTA, DTPA [+TEA]), buffered salt solutions (AAAc buffer), and unbuffered salt solutions ($CaCl_2$, $MgCl_2$, $NaNO_3$, NH_4NO_3). Acid extractants, depending on the strength and soil mineralogical composition, can extract nearly total amounts of trace metals. Chelating agents and buffered salt solutions are believed to extract potentially mobile portions of metals. Neutral salt solutions have been introduced as simulating the natural soil solutions and therefore are useful to evaluate the ecological relevance of metals.

Much work has been done on universal extractants for soil tests to assess micronutrient availability. Barber,[930] Cox and Kamprath,[151] and Walsh and Beaton[847] prepared comprehensive reviews

Table 34 Relative Phytoavailability of Different Species of Metals from Soils

Metal Species	Phytoavailability
Simple or complex cations in solution phase	Easy
Exchangeable cations in organic and inorganic complexes	Medium
Chelated cations	Slight
Metal compounds precipitated on soil particles	Available after dissolution
Metals bound or fixed inside organic substances	Available after decomposition
Metals bound or fixed inside mineral particles (primary or secondary soil minerals)	Available after weathering and/or decompositon

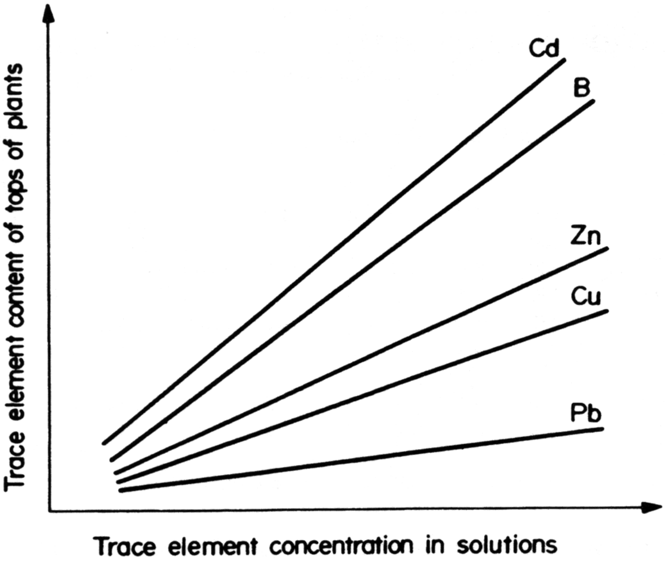

FIGURE 27 Trace element uptake by plants as a function of their concentrations in nutrient solutions.

of chemical tests for the determination of water-soluble, acid-extractable, exchangeable, and complexed or chelated trace elements in soils.

A wide overview of trace element soil tests was recently presented in *Method of Soil Analysis*, edited by Bingham and Bartels.[1225b] In this volume, Amacher discussed extractants used to estimate plant-available Cd, Ni, and Pb in soils which are the same as for other trace metals. Good correlation was obtained for extracted and available metals added at elevated levels to the soils; whereas the correlation was less suitable for the prediction of plant-available quantities of metals under field conditions. Humez et al.[1339] presented different approaches to assessment of mobility of elements in sediments, including a method of kinetics extraction. Neutral salt solutions (e.g., $CaCl_2$, $MgCl_2$, $NaNO_3$) are also proposed as a simulated solution phase of soil for the estimation of bioavailable trace element contents. Barber[930] concluded that 0.01 M $CaCl_2$ at any soil/solution dilution was particularly applicable to trace metal analyses where chelation effects are important. The interpretation of soil testing results is by no means an easy problem and may give reliable information for only a particular soil-plant system. These methods, nevertheless, are widely used, with various results, in agricultural practices. Minnich et al.[1094] stated that extraction procedures are easier and probably provide a better predictive ability for plant Cu uptake than Cu^{2+} activity measurements. The DTPA-extractable Cu and Zn correlated well with metal contents of plant tops.[1047,1094] Minnich et al.[1094] emphasized that continual monitoring of soil solution ion activity or a buffering index is needed to improve predictions of plant ion uptake. The uptake of elements by plant roots is restricted to the liquid phase, therefore the content of metals in the soil solution is of primary importance.[1046] However, more information is needed about multiple ion activity ratios and about antagonistic or synergistic effects of accompanying cations and anions in the soil solution, in relation to uptake and physiological effects of trace metals in plants. Also, there is insufficient information on the availability of organic metal complexes in the solution phase.

Complexing compounds produced on a base of acetic acid (e.g., EDTA, DTPA, EDDHA) and their mixtures with other compounds are more widely used for identifying deficiency problems, mainly with Mn, Cu, Zn, and Fe.[1225b,1401] All soil tests were calibrated to determine deficient levels of micronutrients. Thus, most of these methods should be calibrated to determine phytotoxic levels of soil trace elements. Recently renewed is the earlier concept (Barber[930]) of using extractants that simulate natural soil solution.[151,320] These are solutions of neutral salts, mainly $CaCl_2$, in various concentrations (most frequently 0.01 M). The suitability of this method has been discussed in some publications.[1302,1335] The final conclusion is that $CaCl_2$ extractant can be considered universal because it has more or less the same ionic strength (0.03 M) as the average salt concentration in many soil solutions. It cannot however, serve as a soil test to estimate both deficient and phytotoxic levels of trace metals. To do this, calibration to biological indices is necessary. Possible formation of complex ions with Cl^- in certain soil conditions should be considered. Such complex ions (e.g., $CdCl^+$, $CdCl_3$) can increase the solubility of some trace metals, as observed in the case of Cd.[1330]

The mixed extractant AAAc-EDTA was applied in the large world project on available trace element contents of soils in 30 countries, as carried out by Sillanpää and Jansson.[1441] The relation between Cd, Pb, Co, and Se in crop plants and the pool of soluble forms of elements in soils, despite differences in soil variables and climatic conditions, was acceptably close.

Recently, Coca Cola has been proposed as a relatively simple extractant and is easily applied in soil testing procedures for mobile trace elements.[1482] The active compound in Coca Cola is phosphoric acid, which dissolves 27% of Fe, 38% of Cu, 86% of Zn, and 165% of Mn compared to those extracted by DTPA solution. Due to the relatively stable composition of Coca Cola, such an extractant might be suitable for specific experiments and projects.

The specific properties of plants are very significant in determining the bioavailability of trace elements and are quite variable with changing soil and plant conditions. The availability of different plant species to absorb certain trace elements from the same soil environment is illustrated in Table 35. In fact, different genotypes of the same species uptake different amounts of the trace elements. The wide variation (within the range of a factor of 100) in trace element contents of *Artemisia* species was observed in one meadow ecosystem.[1097] To provide an effective evaluation of the pool of bioavailable trace elements, therefore, techniques based on both soil tests and plant analyses should be used together.

Conditions of plant growth media also have a significant impact on the absorption of trace elements by roots. Findings of Miyasaka and Grunes[1421] indicated that increasing the soil temperature from 8°C to 16°C influenced, by twofold higher, the contents of Cu, Zn, and Mn in leaves of winter wheat. Thus, during a cold season, plants may have low levels of some trace elements that may limit or affect their growth, and also cause a deficiency in grazing animals.

The sampling procedures for each field, each crop, and a specific plant part in the same stage of growth must be standardized for obtaining compatible results that could be classified as deficient, sufficient, or excessive or toxic for plants. Existing soil and plant tests, however, do not satisfactorily predict trace element deficiencies in crop plants that would respond to application of micronutrients.

Ranges of trace element concentrations and their classification for the mature leaf tissue presented in Table 36 are overall approximations and can differ widely for particular soil-plant systems. It is necessary to emphasize that ranges of concentrations of trace elements required by plants are often very close to the content that exerts a harmful influence on plant metabolism. It is not easy, therefore, to make a clear division between sufficient and excessive quantities of trace elements in plants.

Table 35 Variation in Trace Element Content among Various Plants from One Site in the Same Forest Ecosystem[a] (ppm DW)[1045]

Plants	B	Cd	Cu	Fe	Mn	Pb	Zn	Cr	Ni
Grass *Agrostis alba*	3.4	0.6	4.2	80	740	1.2	59	1.0	1.8
Clover *Trifolium pratense*	9.0	0.7	6.0	115	136	2.8	99	1.0	2.2
Plantain *Plantago major*	7.0	1.9	9.8	135	100	2.4	97	1.4	3.0
Mosses									
Polytrichum juniperinum	3.4	0.8	9.2	800	176	22.4	69	2.0	2.0
Entodon schreberi	3.2	0.7	10.3	425	180	13.0	77	2.8	1.6
Lichens									
Parmelia physodes	2.4	0.4	5.0	1100	62	17.0	78	3.2	4.8
Lobaria pulmonaria	2.4	0.5	7.5	1450	66	28.0	74	3.2	2.4
Edible fungi									
Cantharellus cibarius	4.0	1.0	24.5	49	19	1.2	150	0.4	2.2
Leccinum scabra	0.8	2.7	18.0	44	6	<0.1	125	0.4	1.8
Inedible fungi									
Tylopilus felleus	3.5	1.6	35.0	50	14	0.4	180	0.4	1.2
Russula veternosa	6.4	1.0	32.0	28	18	1.0	175	0.4	1.0

[a] Pine and birch forest on light sandy soil near Warsaw, Poland.

Table 36 Approximate Concentrations of Trace Elements in Mature Leaf Tissue Generalized for Various Species (ppm DW)[66,171,279,322,369,381,395,531,916]

Element	Deficient (if less than the stated amounts of essential elements)	Sufficient or Normal	Excessive or Toxic	Tolerable in Agronomic Crops[1081,1357]
Ag	—	0.5	5–10	—
As	—	1–1.7	5–20	0.2[a]
B	5–30	10–100	50–200	100
Ba	—	—	500	—
Be	—	<1–7	10–50	—
Cd	—	0.05–0.2	5–30	0.05–0.5
Co	—	0.02–1	15–50	5
Cr	—	0.1–0.5	5–30	2
Cu	2–5	5–30	20–100	5–20
F	—	5–30	50–500	—
Hg	—	—	1–3	0.2[a]
Li	—	3	5–50	—
Mn	10–30	30–300	400–1000	300
Mo	0.1–0.3	0.2–5	10–50	—
Ni	—	0.1–5	10–100	1–10
Pb	—	5–10	30–300	0.5–10
Se	—	0.01–2	5–30	—
Sn	—	—	60	—
Sb	—	7–50	150	—
Ti	—	—	50–200	—
Tl	—	—	20	—
V	—	0.2–1.5	5–10	—
Zn	10–20	27–150	100–400	50–100
Zr	—	—	15	—

Note: Values are not given for very sensitive or highly tolerant plant species.

[a] FW basis.

Houba and Uittenbogaard[1334] published results of determining 27 trace elements in 140 plant kinds from 66 countries during the period from 1981 to 1993. Each plant kind was represented by a number of samples (a few tens) from various locations, and therefore it is difficult to interpret the variability in trace element contents among plants. Some general trends, however, indicate that Pb is likely to be concentrated in cabbage and tomato leaves, Mo in sugar beet leaves and Chinese cabbage, Se in mushrooms, and Li in potato leaves. Onion bulbs contain elevated amounts of Cr, As, and Ni; lettuce leaves—Cr, Pb, and Cd; and spinach leaves—Li, Ni, and Pb.

V. ESSENTIALITY, DEFICIENCY, AND EXCESS

Knowledge of the importance of certain trace elements for healthy growth and development of plants dates from the last century. At present, 17 trace elements (Al, B, Br, Cl, Co, Cu, F, Fe, I, Mn, Mo, Ni, Rb, Si, Ti, V, and Zn) are known to be essential for all plants, several are proved necessary for a few species only, and others are known to have stimulating effects on plant growth, but their functions are not yet recognized (Table 37). A feature of the physiology of these elements is that although many are essential for growth, they can also have toxic effects on cells at higher concentrations. Hypothetical schemes of the reactions of plants to increasing concentrations of the essential and nonessential trace elements are presented in Figures 28 and 29.

The trace elements essential for plants are those which cannot be substituted by others in their specific biochemical roles and that have a direct influence on the organism so that it can neither grow nor complete some metabolic cycle. The elements needing more evidence to establish their essentiality usually are those thought to be required in very low concentrations (at μg kg^{-1} or ng kg^{-1} ranges) or that seem to be essential for only some groups or a few species of plants.

Bowen[94] classified the functions and forms of the elements in organisms, based on the current state of knowledge, by dividing the trace elements that occur in plants into the following groups:

1. Those incorporated into structural materials—Si, Fe, and rarely Ba and Sr
2. Those bound into miscellaneous small molecules, including antibiotics, and porphyrins—As, B, Br, Cu, Co, F, Fe, Hg, I, Se, Si, and V
3. Those combined with large molecules, mainly proteins, including enzymes with catalytic properties—Co, Cr (?), Cu, Fe, Mn, Mo, Se, Ni (?), and Zn
4. Those fixed by large molecules having storage, transport, or unknown functions—Cd, Co, Cu, Fe, Hg, I, Mn, Ni, Se, and Zn
5. Those related to organelles or their parts (e.g., mitochondria, chloroplasts, some enzyme systems)—Cu, Fe, Mn, Mo, and Zn

In summary, based on extensive literature, trace elements are involved in key metabolic events such as respiration, photosynthesis, and fixation and assimilation of some major nutrients (e.g., N, S). Trace metals of the transition metal group are known to activate enzymes or to be incorporated into metalloenzymes as electron transfer systems (Cu, Fe, Mn, and Zn) and also to catalyze valence changes in the substrate (Cu, Co, Fe, and Mo). Some particular roles of several trace elements (Al, Cu, Co, Mo, Mn, and Zn) which seem to be involved in protection mechanisms of frost-hardy and drought-resistant plant varieties are also reported.[511,718]

The requirements of plants and even of individual species for a given micronutrient have been well-demonstrated by Hewitt[317] and Chapman.[131] If the supply of an essential trace element is inadequate, the growth of the plant is abnormal or stunted and its further development, especially its metabolic cycles, are disordered. Although deficiency symptoms cannot be generalized, they may be quite characteristic for the particular element. Bergmann and Čumakov[66] presented comprehensive illustrations of deficiency (and some toxicity) symptoms in cultivars. The descriptions of deficiency symptoms summed up in Table 38 indicate that chlorosis is the most frequent symptom. Visible symptoms are important in diagnosis of deficiencies; however, disturbance of metabolic processes and consequent losses in production of biomass may occur before the deficiency symptoms are recognized. In order to develop a better diagnostic method, biochemical indicators based on enzymatic assays were proposed by Ruszkowska et al.,[672] Rajaratinam et al.,[639] and Gartrell et al.[258] as a sensitive test for a hidden deficiency of a given micronutrient. The activity of some enzymes

Table 37 Forms and Principal Functions of Trace Elements That Are Essential for Plants[94,142,349,531,614,859]

Element	Constituent of	Involved in
Al[a]	—	Controlling colloidal properties in the cell, possible activation of some dehydrogenases and oxidases
As[a]	Phospholipid (in algae)	Metabolism of carbohydrates in algae and fungi
B	Phosphogluconates	Metabolism and transport of carbohydrates, flavonoid synthesis, nucleic acid synthesis, phosphate utilization, and polyphenol production
Br[a]	Bromophenols (in algae)	—
Co	Cobamide coenzyme	Symbiotic N_2 fixation, possibly also in non-nodulating plants, and valence changes stimulation synthesis of chlorophyll and proteins (?)
Cu	Various oxidases, plastocyanins, and ceniloplasmin	Oxidation, photosynthesis, protein and carbohydrate metabolism, possibly involved in symbiotic N_2 fixation, and valence changes, cell wall metabolism
F[a]	Fluoracetate (in a few species)	Citrate conversions
Fe	Hemo-proteins and nonheme iron proteins, dehydrogenases, and ferrodoxins	Photosynthesis, N_2 fixation, and valence changes
I[a]	Tyrosine and its derivatives (in angiosperms and algae)	—
Li[a]	—	Metabolism in halophytes
Mn	Many enzyme systems	Photoproduction of oxygen in chloroplasts and, indirectly, in No_3^- reduction
Mo	Nitrate reductase, nitrogenase, oxidases, and molybdoferredoxin	N_2 fixation, No_3^- reduction, and valence changes
Ni[a]	Enzyme urease (in *Canavalia* seeds)	Possibly in action of hydrogenase and translocation of N
Rb[a]	—	Function similar to that of K in some plants
Se[a]	Glycene reductase (in *Clostridium* cells) combined with cysteine and methionine	Can replace S in some plants
Si	Structural components	—
Sr[a]	—	Function similar to that of Ca in some plants
Ti[a]	—	Possibly photosynthesis and N_2 fixation
V[a]	Porphyrins, hemoproteins	Lipid metabolism, photosynthesis (in green algae), and, possibly, in N_2 fixation
Zn	Anhydrases, dehydrogenases, proteinases, and peptidases	Carbohydrate, nucleic acid, and lipid metabolism

[a] Elements known to be essential for some groups or species and whose general essentiality needs confirmation.

is correlated mainly with Cu, Fe, and Mo levels in plant tissues. The practical use of the enzymatic assays is, however, greatly limited because of a high rate of variation and of technical difficulties in the determination of the enzymatic activity.

The most widely used diagnostic tests are soil and plant analyses. More specific diagnosis of critical levels of some trace metals in plant tissues should also be related to the ratio of antagonistic elements, as described by Nambiar and Motiramani[560] for Fe:Zn ratios in maize. Concentrations of immobile trace elements in old leaves or in whole plants, unlike those of mobile micronutrients,

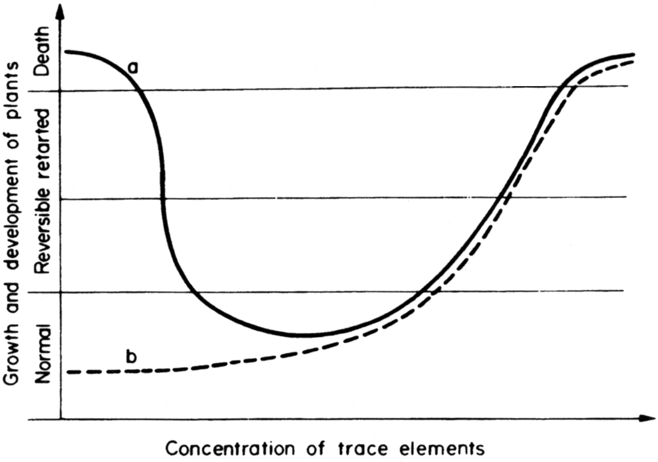

Figure 28 Schematic diagram of plant response to stress from deficiency and toxicity of trace elements: (a) essential trace elements; (b) non-essential trace elements.

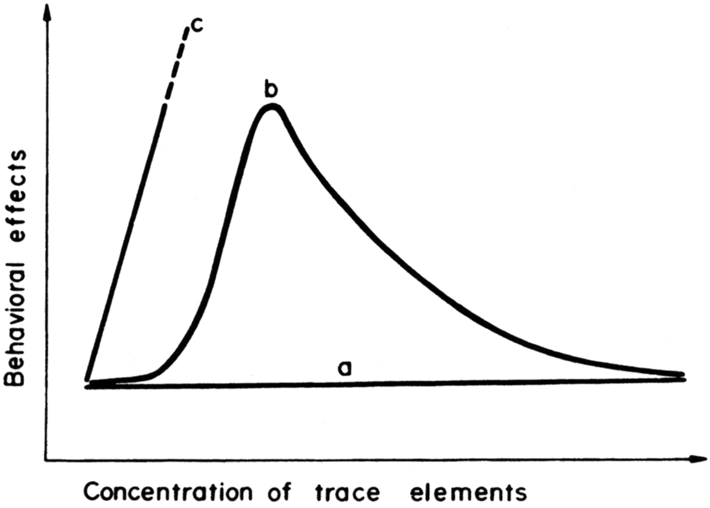

Figure 29 Schematic diagram of behavioral plasticity of plants under chemical stress: (a) no behavioral change of entirely tolerant species; (b) development of behavioral tolerance; (c) reaction of nontolerant species leading to damage of organisms followed by no recovery.

may be misleading in assessing the nutrient status of plants. Nevertheless, plant tissue analysis has been used successfully for assessing deficiencies when based on the normal tissue contents for plant genotypes or species and organs and the stage of plant development. A comprehensive literature has been published in various countries on the diagnosis of trace element deficiencies and their correction through the application of particular micronutrients. Mengel and Kirkby[531] presented the most current information on micronutrients and indicated the need for their application to some cultivars. It should be emphasized, however, that the application of a given micronutrient is effective only if the soil content or the availability of the element is low. High-yield crop plants can suffer from acute or light deficiencies of some micronutrients. Finck[995] gave an example of the extent of the deficiencies (both medium and light) in high-yield grain crops: (1) Mn supply to oats—on brown earths 40% and on calcareous marsh soils about 50% of fields, (2) Cu supply to oats—about 20% of fields on both soil types, and (3) Zn supply to wheat—about 15% of fields on both soil types.

Table 38 Symptoms of Micronutrient Deficiency in Some Common Cultivars[66,114,531,718]

Element	Symptoms	Sensitive crop
B	Chlorosis and browning of young leaves; killed growing points; distorted blossom development; lesions in pith and roots, and multiplication of cell division	Legumes, *Brassica* (cabbage and relatives), beets, celery, grapes, and fruit trees (apples and pears)
Cu	Wilting, melanism, white twisted tips, reduction in panicle formation, and disturbance of lignification and of development and fertility of pollen	Cereals (oats), sunflower, spinach, and lucerne (alfalfa)
Fe	Interveinal chlorosis of young organs	Fruit trees (citrus), grapes, and several calcifuge species
Mn	Chlorotic spots and necrosis of young leaves and reduced turgor	Cereals (oats), legumes, and fruit trees (apples, cherries, and citrus)
Mo	Chlorosis of leaf margins, "whiptail" of leaves and distorted curding of cauliflower, "fired" margin and deformation of leaves due to NO_3 excess, and destruction of embryonic tissues	*Brassica* (cabbage and relatives) and legumes
Zn	Interveinal chlorosis (mainly of monocots), stunted growth, "little leaf" rosette of trees, and violet-red points on leaves	Cereals (corn), legumes, grasses, hops, flax, grapes, and fruit trees (citrus)

Both deficiencies and toxicities of trace elements for plants most commonly result from complex factors that vary with the specific environment. However, many observations and experiments conducted on various soil types in different countries have clearly demonstrated that soil genesis and soil properties are the main factors controlling micronutrient deficiencies. The data summarized in Table 39 present the general relationship between the occurrence of micronutrient deficiencies in plants and soil properties. The most frequently occurring deficiencies are related to extremely acid soils (light sandy) or to alkaline soils (calcareous) with improper water regimes and with excesses of phosphate, N, and Ca, as well as Fe and Mn oxides.

VI. TOXICITY AND TOLERANCE

Metabolic disorders of plants are affected not only by micronutrient deficiencies, but also by their excesses. In general, plants are much more resistant to an increased concentration than to an insufficient content of a given element. Although many observations have been published on the harmful effects of trace element excesses, the nature of these processes is still poorly understood. Basic reactions, as reviewed by Peterson,[609] Foy et al.,[241] Bowen,[94] and Prasad and Strzalka,[1461] related to toxic effects of element excesses are the following:

1. Changes in permeability of the cell membrane—Ag, Au, Br, Cd, Cu, F, Hg, I, Pb, UO_2
2. Reactions of thiol groups with cations—Ag, Hg, Pb
3. Competition for sites with essential metabolites—As, Sb, Se, Te, W, F
4. Affinity for reacting with phosphate groups and active groups of ADP or ATP—A1, Be, Sc, Y, Zr, lanthanides and, possibly, all other heavy metals
5. Replacement of essential ions (mainly major cations)—Cs, Li, Rb, Se, Sr
6. Occupation of sites for essential groups such as phosphate and nitrate—arsenate, fluorate, borate, bromate, selenate, tellurate, and tungstate
7. The damage to photosynthesis apparatus involved in several metabolic alterations is the most significant effect of the excess of trace metals

Table 39 Soil Factors Contributing to Micronutrient Deficiency

			Contributing soil factors			Critical		Some
Element	Soil Units[a]	pH Range	Organic Matter	Water Regime	Other Factors	Deficiency Limit in Soil[b] (ppm)	Plants Responding	Countries of Occurrence
B	Podzols, rendzinas, gleysols, nitosols, and ferralsols	Acid and neutral	Very low or very high	Flooded soils	Light texture, free $CaCO_3$	0.1–0.3 (HW)	Beets, legumes, crucifers, and grapes	Australia, Egypt, France, Poland, Taiwan, U.S., Russia, China, and India
Co	Podzols, histosols, rendzinas, and solonetz	Neutral, alkaline, or strongly acid	High	High moisture	Free $CaCO_3$, high Fe and Mn	0.02—0.3 (AA)[c]	Legumes	Australia, France, Germany, Poland, Sweden, U.S., and Russia
Cu	Histosols, podzols, rendzinas, solonchaks, and solonetz	—	Low or high	HIgh moisture	Light leached soil, high N, P, and Zn, free $CaCO_3$	1–2 (NA, 0.5 *N*) 0.8—3 (NA, 1 *N*) 0.8—1 (Ac-ED) 0.2 (AC)	Cereals, legumes, and citrus	Australia, Egypt, U.S., Russia, and European countries
Fe	Rendzinas, ferralsols, solonetz, arenosols, and chernozems	Alkaline	High with free $CaCO_3$ or low in acid soil	Poor drainage, moisture extremes	Free $CaCo_3$, high P, Mn, and HCO_3^-	0.2—1.5 (DT) 2.5—4.5 (DT) $<$30—35 (Ac-ED)	Citrus, grapes, pineapples, and tomatoes	Throughout the world, and especially in arid and semiarid regions
Mn	Podzols, rendzinas, and histosols	Strongly acid or alkaline	High, e.g., alkaline peats	Moisture extremes	Free $CaCO_3$ and high Fe	1—5 (DT) 20—100 (HR) 1—2 (AC) 14–70 (PA)	Cereals, legumes, beets, and citrus	Australia, France, U.S., and Russia

Mo	Podzols and ferralsols decalcified	Strongly acid to acid	—	Good drainage	High Fe and Al oxides, and high SO_4 -S	0.01—0.6 (AO)[d] $<$0.1 (HW)	Crucifers, cucurbits, and legumes	Australia, India, U.S., and Russia
Se	Podzols, histosols, and ferralsols	Acid	High	Waterlogging	High Fe oxides, and SO_4 -S	$<$0.04 (T)[c]	—	Australia, U.S., and some European countries
Zn	Podzols, rendzinas, and solonetz	Strongly acid or alkaline	Low	—	Free $CaCO_3$, high N and P	1–8 (HA) 1.5–3 (ED) 0.4–1.5 (DT) 0.3–2 (AC)	Cereals, legumes, and citrus	Australia, France, India, U.S., and Russia

Note: Explanation of symbols used for extraction methods determining contents of soluble elements: AA, 2.5% acetic acid; AC, ammonium acetate; AO, ammonium oxalate; DT, DTPA; ED, EDTA; Ac-ED, ammonium acetate-EDTA; HA, 0.1 *N* hydrochloric acid; HR, hydroquinone reducible method; HW, hot water; NA, 0.5 or 1 *N* nitric acid; PA, 0.1 *N* phosphate acid; and T, total.

[a] Generalized soil types assigned to soil units as given in Table 8.

[b] Critical deficiency limits very highly among plant species and soil kinds.

[c] Animal response.

[d] Highly pH dependent.

Recent findings support the idea that metals induce biochemical changes in plants similar to responses elicited by pathogen attack.[1378]

An assessment of toxic concentrations and effects of trace elements on plants is very complex because it depends on so many factors that it cannot be measured on a linear scale. Some of the most important factors are the proportions of related ions that are present in solution and their compounds. For example, the toxicity of arsenate and selenate is markedly reduced in the presence of excess phosphate or sulfate, and metallo-organic compounds may be either much more toxic than cations or much less so. It should also be noted that certain compounds (e.g., oxygenated anions of metals) may be more toxic than their simple cations. Van Assche and Glijsters[1175] reported that enzyme measurements in plants (2-week-old test bean) can be a criterion for the phytotoxic effect of soil pollution with trace metals. The metal toxicity is reflected by the increase in capacity of various enzymes (e.g., peroxidase, dehydrogenase). The specific plant (iso)enzyme reactions on different trace metals were observed.

Several orders of trace element toxicity to plants are presented in the literature and they vary with each experiment and each plant; however, they correlate fairly well with the following factors:

1. Electronegativity of divalent metals
2. Solubility products of sulfides
3. Stability of chelates
4. Bioavailability

Despite the reported diversity in toxicity levels, it can be stated that the most toxic metals for both higher plants and certain microorganisms are Hg, Cu, Ni, Pb, Co, Cd, and possibly also Ag, Be, and Sn.

Although plants adapt rather readily to chemical stress, they also may be very sensitive to an excess of a particular trace element. Toxic concentrations of these elements in plant tissues are very difficult to establish. The values presented in Table 36 give very broad approximations of possibly harmful amounts of trace elements in plants. Visible symptoms of toxicity vary for each species and even for individual plants, but most common and nonspecific symptoms of phytotoxicity are chlorotic or brown points of leaves and leaf margins, and brown, stunted, coralloid roots (Table 40).

A common feature of plants is their ability to prolong survival under conditions of trace element excesses in their environments, mainly in soils. Lower plants especially, such as microorganisms, mosses, liverworts, and lichens, reveal an extremely high level of adaptation to toxic concentrations of certain trace elements. Zajic,[898] Weinberg,[856] and Iverson and Brinckman[344] presented comprehensive reviews on microorganisms involved in the cycling of trace metals and of their resistance to high metal concentrations. Tyler et al.[1171] reported that the depressions by 20 to 40% of most biological activities in forest litter/soil, compared to controls, were measured when concentrations of trace metals (Cu, Zn, and Pb) amounted to 2 to 10 times those of regional baseline samples. McGrath et al.[1089] found that the process of N-fixation is sensitive to increased concentrations of metals in soils. The inhibition by 50% of N-fixation by white clover rhizobium bacteria was at concentrations (ppm DW) of Zn 334, Cu 99, Ni 27, and Cd 10. These authors stated that mechanisms of the inhibition are still unknown and need to be investigated further, because the toxic effects can occur at metal concentrations close to or below the current guidelines for soil protection (see Chapters 2. IV. A and 4. IV. A).

Although the higher plants are believed to be less tolerant of increased concentrations of trace elements, they are also widely known to accumulate these elements and to survive on soils contaminated by large quantities of various trace elements. Antonovics et al.,[33] Peterson,[609] Bradshaw,[101] Woolhouse and Walker,[886] and Tyler et al.[1171] attempted to summarize and define what is implied by the term "tolerance" of plants. This term refers to both the population occurring in an area highly contaminated by trace elements, and to individual plants or species which are able to withstand greater levels of toxicity than are others. Extreme tolerance of many species of bryophytes, lichens, and fungi is widely reported.[1037,1171]

Table 40 General Effects of Trace Element Toxicity on Common Cultivars[66,241,381,395,531,731,916,1009]

Element	Symptoms	Sensitive Crop
Al	Overall stunting, dark green leaves, purpling of stems, death of leaf tips, and coralloid and damaged root system	Cereals
As	Red-brown necrotic spots on old leaves, yellowing or browning of roots, depressed tillering, wilting of new leaves	Legumes, onion, spinach, cucumbers, bromgrass, apricots, peaches
B	Margin or leaf tip chlorosis, browning of leaf points, decaying growing points, and wilting and dying-off of older leaves In severely affected pine trees, necrosis occurs on needles near the ends of shoots and in upper half on the tree	Cereals, potatoes, tomatoes, cucumbers, sunflowers, and mustard, apple, apricots, citrus, walnut
Be	Inhibition of seed germination and reduced growth, degradation of protein enzymes	—
Cd	Brown margin of leaves, chlorosis, reddish veins and petioles, curled leaves, and brown stunted roots Severe reduction in growth of roots, tops, and number of tillers (in rice). Reduced conductivity of stem, caused by deterioration of xylem tissues. Reduction of chlorophyll and carotenoids	Legumes (bean, soybean), spinach, radish, carrots, and oats
Co	Interveinal chlorosis in new leaves followed by induced Fe chlorosis and white leaf margins and tips, and damaged root tips	—
Cr	Chlorosis of new leaves, necrotic spots and purpling tissues, injured root growth	—
Cu	Dark green leaves followed by induced Fe chlorosis, thick, short, or barbed-wire roots, depressed tillering. Changes in lipid content and losses of polypeptides involved in photochemical activities	Cereals and legumes, spinach, citrus seedlings, and gladiolus
F	Margin and leaf tip necrosis, and chlorotic and red-brown points of leaves	Gladiolus, grapes, fruit trees, and pine trees
Fe	Dark green foliage, stunted growth of tops and roots, dark brown to purple leaves of some plants (e.g., “bronzing” disease of rice)	Rice and tobacco
Hg	Severe stunting of seedlings and roots, leaf chlorosis and browning of leaf points	Sugar beets, maize, and roses
Li	Chlorotic and necrotic spots on leaves and injured root growth	Citrus
Mn	Chlorosis and necrotic lesions on old leaves, blackish-brown or red necrotic spots, accumulation of MnO_2 particles in epidermal cells, drying tips of leaves, and stunted roots and plant growth	Cereals, legumes, potatoes, and cabbage
Mo	Yellowing or browning of leaves, depressed root growth, depressed tillering	Cereals
Ni	Interveinal chlorosis (caused by Fe-induced deficiency) in new leaves, gray-green leaves, and brown and stunted roots and plant growth	Cereals
Pb	Dark green leaves, wilting of older leaves, stunted foliage, and brown short roots	—
Rb	Dark green leaves, stunted foliage, and increasing amount of shoots	—
Se	Interveinal chlorosis or black spots at Se content at about 4 ppm, and complete bleaching or yellowing of younger leaves at higher Se content, pinkish spots on roots	—
Ti	Chlorosis and necrosis of leaves, stunted growth	Beans
Tl	Impairment of chlorophyll synthesis, mild chlorosis and slight cupping of leaves, reduced germination of seeds and growth of plants	Tobacco and cereals
Zn	Chlorotic and necrotic leaf tips, interveinal chlorosis in new leaves, retarded growth of entire plant, and injured roots resemble barbed wire	Cereals and spinach

The heavy-metal resistance in plants is of special concern. Practical problems and implications concerning metal-tolerant organisms can be related to:

1. Microbial origin of metal ore deposits
2. Metal cycling in the environment
3. Geobotanical prospecting (i.e., the use of tolerant and sensitive plants to locate natural deposits of metal ores)
4. Microbiological extraction of metals from low-grade ores
5. Establishment of vegetation on toxic waste materials
6. Microbiological treatment of waste waters
7. Development of resistance in microorganisms to metal-containing fungicides and other pesticides

The evolution of metal tolerance is believed to be quite rapid in both microorganisms and sometimes in vascular plants. As stated by Tyler et al.,[1171] tolerant genotypes of some vascular plants may develop within a few years. Developed metal-tolerance of plants may be both phenotypically and genotypically acquired. Evolutionary changes caused by heavy metals have now been recorded in a large number of species occurring on metalliferous soils that differ from populations of the same species growing on ordinary soils. Species of higher plants that show a tolerance to trace elements belong most commonly to the following families: Caryophyllaceae, Cruciferae, Cyperaceae, Gramineae, Leguminosae, and Chenopodiaceae.

The ranges of highest concentrations of trace elements found in various plant species are presented in Table 41. Various fungi are also well-known to be able to accumulate a high proportion of easily soluble and/or easily volatile elements such as Hg, Se, Cd, Cu, and Zn. The "upper critical level" of an element is the lowest tissue concentration at which it has toxic effects. Macnicol and Beckett[1081] made an extensive survey of literature to establish critical levels of 30 elements, most predominant of which are Al, As, Cd, Cu, Li, Mn, Ni, Se, and Zn. The values established by these authors for the "upper critical levels" are quite similar to those presented by others as "excessive or toxic levels" (Tables 36 and 42). They stated that the critical levels for a given element are

Table 41 The Greatest Accumulation of Some Metals (% AW) Reported in Various Plant Species[609,613]

Element	Plant
	>10%
Ni	*Alyssum bertolonii*
Zn	*Thlaspi calaminare, caerulescens*
	1 to 3%
Cr	*Pimelea suteri and Leptospermum scoparium*
Co	*Crotalaria cobaltica*
Ni	*Alyssum bertolonii*
Se	*Astragalus recemosus*
Sr	*Arabis stricta*
U	*Uncinia leptostachya* and *Coprosma arborea*
Zn	*Viola calaminaria*
Mn	*Macadamia neurophylla*
	0.1 to 1%
Cu	*Becium homblei, Aeollantus biformifolius*
Hg	*Betula papyrifera*
W	*Pinus sibiricus*
Zn	*Equisetum arvense*
Ni	*Berkheya coddi*
Pb	*Minuratia verna*

Table 42 Critical Concentrations of Trace Metals in Plant Tissues (ppm DW)

Metal	Levels of Growth Depression In Sensitive Plant Species[1052]	Levels of Growth Depression For 10% Yield Loss[1081]
As	—	1–20
Cd	5–10	10–20
Co	10–20	20–40
Cr	1–2	1–10
Cu	15–20	10–30
Hg	0.5–1	1–8
Ni	20–30	10–30
Zn	150–200	100–500

variable, which reflects both effects of interactions with other elements and developing plant resistance to a high tissue concentration of certain elements.

Microorganisms can very rapidly develop mechanisms of tolerance to excesses of trace metals. Fungi are usually more resistant than bacteria. Lichens reveal a relatively high tolerance to trace metals due to the presence of fungi hyphae. Fungi of mycorrhiza developed at the surface of roots of several plant species, mainly trees, can protect against the transfer of trace metals into root cells from surroundings. These phenomena are observed especially on trees in soil polluted with Cu and Zn.[1525] Turnau et al.[1524] observed in vacuoles of fungi hyphae (*Paxillus involutus*) granules with high contents of P, S, Ca, Al, and Cd. The Cd accumulation inside fungal vacuoles suggests the possibility of immobilization of metals by the symbiotic fungus. Hamon et al.[1321a] reported that Cd and Zn in the rhizosphere of radish existed mainly as immobile forms complexed by organic compounds, while dissolved Cd and Zn were largely uncomplexed in unplanted soil. The authors concluded that plants mainly absorb the free metal ions from soil solution.

Toxicity of trace metals to microorganisms and microbial processes in agricultural soils has been extensively reviewed by Giller et al.[1310] The authors emphasized that the results of numerous laboratory ecotoxicological studies are the most difficult to meaningfully extrapolate to evaluate data on toxic effects that are likely to occur in the field.

A concept of "metal (Mn) equivalent" (related to "Zn equivalent" of trace metals to crop plants) in the toxicity to soil respiration has been proposed by Saviozzi et al.[1480] and is calculated as the sum of the amounts of the available metals, and related to the least toxic one: Mn equivalent = Mn +1.95 Pb + 2.1 Ni + 2.5 Zn + 6.7 Cd + 6.7 Cu. Pb, Ni, and Zn show about twice and Cd and Cu about seven times the toxic effects of Mn.

Mechanisms of trace element resistance in plants have been the subject of several detailed studies which indicated that both highly specific and multiple metal tolerance may appear, as reported by Antonovics et al.,[33] Bradshaw,[101] Simon,[728] Foy et al.,[241] and Cox and Hutchinson.[149] These authors summed up possible mechanisms involved in metal tolerance. They distinguished external factors, such as low solubility and mobility of cations surrounding plant roots, as well as effects of metal ion antagonisms. The real tolerance, however, is related to internal factors. This is not a mechanism of tolerance in a simple sense, but consists of several metabolic processes:

1. Selective uptake of ions
2. Decreased permeability of cell walls or other differences in the structure and function of membranes
3. Immobilization of ions in various organs (synthesis of immobilizing compounds including the formation of minerals, and/or fixation by charged ligands)
4. Alteration in metabolic patterns—increased enzyme system that is inhibited, or increased antagonistic metabolite, or reduced metabolic pathway by passing an inhibited site, or decreased requirement for products of inhibited synthesis
5. Adaptation to toxic metal replacement of a physiological metal in an enzyme

6. Release of ions from plants by leaching from foliage, guttation, leaf shedding, and excretion from roots
7. Release of volatile organic metal compounds (e.g., Hg, Pb, and Sn), mainly as methylated metals that are very toxic species to most organisms
8. Excretion from leaf tips in the form of salts

In addition to the mechanisms mentioned, phenomena of avoidance of polluted substrates are reported. This is observed especially in the behavior of microorganisms which are capable of developing on better (less contaminated) substrate. Some vascular plants, while growing on topsoil heavily contaminated by trace metals, can develop roots in deeper soil layers.[1171]

Selective uptake of ions is related to a capability of plants for active selective sorption and discrimination of available ions or compounds in the soil. Selective transport of ions to the tops taken up by roots is also observed. This selectivity depends most probably on immobilization mechanisms. Mechanisms of selective sorption and transport of trace ions can be broken down under a critical concentration of trace elements, and a passive flux of ions within a plant organism takes place (see Chapter 5, Sections II and III).

Decreased permeability of cell walls is closely associated with the immobilization. These mechanisms of the plant tolerance to metals (Al, Cd, Zn, Mn, and Pb) are broadly reviewed by Foy[998] and Tyler et al.[1171] Binding to the cell wall, including wall impermeability, is observed in various vascular plants, bryophytes, lichens, fungi, and microoganisms. Several compounds such as thioneins, sulfides, pectic substances, and organic acids (e.g., uronic, mannuronic, norstictic—in lichens only) are involved in metal complexation. Thus, synthesis of immobilizing compounds and/or fixation by charged ligands are responsible for the removal of trace ions from plant metabolism by deposition (storage) in fixed and insoluble forms in various organs and organelles. Roots are the most common storage for the excess of trace metals, but also foliage and seeds are known to accumulate deposited forms of different trace elements. Tyler et al.[1171] stated that the immobilization in cell wall ligands is most probably a key reaction in reducing the toxicity of trace metal excess.

Kvalevsky[1373,1374] reported that in old above-earth parts of plants, several mineral forms of trace elements can be distinguished; for example, FeAsS (arsenopyrite), ZnS (sphalerite), PbS (galena), MoS (molybdenite), HgS (cinnabar), and also some other trace element minerals, in the forms of carbonates, sulfates, fluorides, wolframites, etc. Other metals like Ag and Au were observed in the form of thin microscopic flakes ($< 2\ \mu$m). He reported that more than 30 elements can be temporarily excluded from physiological processes and stored in plant tissues as inactive minerals.

The biochemical resistance is not yet well-recognized, and may involve several other mechanisms of the immobilization. The alteration in metabolic patterns is related to an increase of the enzyme system that is inhibited, or to an increase of antagonistic metabolite. This also may be associated with a decreased requirement for products of the inhibited syntheses or with a reduction of metabolic pathways by passing an inhibited site of a part of the metabolic system. The nature of an adaptation to toxic metal contents induced into an enzymatic system needs a better understanding. The great flexibility of enzymatic systems and variability among plant species are involved in the evolution of metal tolerance of which several points are still not clear. Considerable evidence was given by Antonovics et al.[33] and Cox and Hutchinson[149] that tolerant plants may also be stimulated in their growth by higher amounts of metal, which reveals a physiological need for an excess of a particular metal by a single plant genotype or species.

Tyler et al.[1171] discussed whether plants that become tolerant to trace metals may be equally productive as nontolerant species or populations. These authors concluded that: "The action of the tolerance mechanism often imparts a demand for metabolic energy, which would make tolerant forms less competitive under normal conditions than their nontolerant counterparts." Therefore, the growth of plants under the stress of elevated concentrations of trace metals is highly limited. In most cases, the morphology of those plants is altered, and salt excretion can be observed at the tips of leaves in some plants. In oats grown in soil heavily polluted with trace metals (mainly Zn and Pb), the composition of salt extraction was (in % of oven-dried weight): Zn 0.76, Pb 0.15, Mn 0.068, and Cu 0.039.[1399]

The tolerance of some plants to elevated concentrations of trace metals in growth media and in tissues creates a health risk to humans and animals. This is a special problem in cases of trace elements that are easily tolerated by plants and highly toxic to humans, as for example Cd. Therefore, health-related limits for certain elements in food plants are carefully controlled by national and international legislation. The contemporary limits can be changed in the future as more pertinent data are collected. Tolerant plants, due to their ability to grow in contaminated substrates, and due to the accumulation of extremely high amounts of trace metals, may create a great health risk by forming a polluted link in the food chain.

The excess of trace elements—both essential and nonessential to plants —has a deteriorating impact on metabolic processes. In some cases, toxic effects are specific for a given element (see Table 40). Plants develop different mechanisms to protect against their excess. These mechanisms are, in general, related to the root (mainly root tips, meristems) exudates containing polygalacturonic acid that fix metals outside or within root cells, and to the production of phytochelates (various derivatives of glutathione) fixing metals and displacing either in vacuoles or on cell membranes.[1459,1542,1551]

VII. INTERACTION

A chemical balance in living organisms is a basic condition for their proper growth and development. Interactions of chemical elements are also of similar importance to deficiency and toxicity in the physiology of plants. Interactions between chemical elements may be both antagonistic and synergistic, and their imbalanced reactions may cause a real chemical stress in plants.

Antagonism occurs when the combined physiological effect of two or more elements is less than the sum of their independent effects, and synergism occurs when the combined effects of these elements is greater. These interactions may also refer to the ability of one element to inhibit or stimulate the absorption of other elements in plants (Figure 30). All these reactions are quite variable and may occur inside the cells, within the membrane surfaces, and also surrounding plant roots. Interaction processes are controlled by several factors and these mechanisms are still poorly understood, although some data are available.[241,581,840]

Interactions between major and trace elements summarized in Table 43 clearly show that Ca, P, and Mg are the main antagonistic elements against the absorption and metabolism of several trace elements. Some synergistic effects, however, have also been observed for antagonistic pairs of elements, depending on the specific reaction of the plant genotype or species.

Antagonistic effects occur most often in two ways—the macronutrient may inhibit trace element absorption and, in turn, the trace element may inhibit absorption of a macronutrient. These reactions have been observed especially for phosphate, but have also been reported for other macronutrients whose uptake and metabolic activity may be inhibited by several trace elements.[395,463]

Most important for practical application are the antagonistic effects of Ca and P on heavy metals such as Be, Cd, Pb, and Ni that often constitute a health hazard. Both major nutrients, Ca and P, are known to play a significant role in the integrity of cell membranes, and therefore any imbalance in these nutrients may affect interaction processes either in the nutrient solution external to or at the surface of root-cell membranes. It is noteworthy that although the antagonistic effects of P and Ca on many trace cations and anions are frequently reviewed in the literature, the antagonistic impact of Mg on trace metals is only occasionally reported. The addition of Mn and Mg to a solution reduced the mortality of nematodes (*Steinernema carpocapsae*) due to the excess of several trace metals.[1346]

Deficiency of one trace element essential to a plant can facilitate uptake of other micronutrients. The compensatory absorption of micronutrients under deficiency stress is reported for several

Table 43 Interactions Between Major Elements and Trace Elements in Plants[251,381,531,554,663]

Major Element	Antagonistic Elements	Synergistic Elements
Ca	Al, B, Ba, Be, Cd, Co, Cr, Cs, Cu, F, Fe, Li, Mn, Ni, Pb, Sr, and Zn	Cu, Mn, and Zn
Mg	Al, Be, Ba, Cr, Mn, F. Zn, Ni[a], Co[a], Cu[a] and Fe[a]	Al and Zn
P	Al, As, B, Be, Cd, Cr, Cu, F, Fe, Hg, Mo, Mn, Ni, Pb, Rb, Se, Si, Sr, and Zn	Al, B, Cu, F, Fe, Mo, Mn, and Zn
K	Al, B, Hg, Cd, Cr, F, Mo, Mn, and Rb	—
S	As, Ba, Fe, Mo, Pb, Se, and Zn	F[b] and Fe
N	B, F, Cu, and Mn	B, Cu, Fe, and Mo
Cl	Br and I	—
Na	Mn	—
Si	B, Mn	—

[a] Reported for microorganisms.

[b] Mutual pollution causes significant injury.

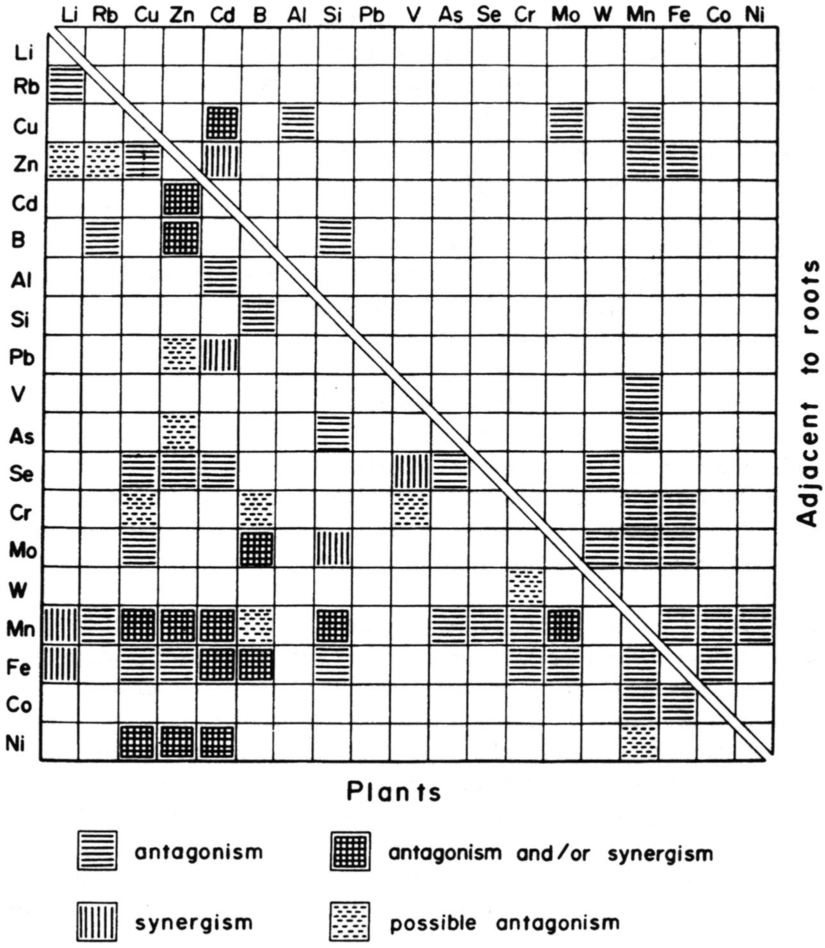

Figure 30 Interactions of trace elements within plant organisms and adjacent to plant roots.

elements and most commonly for Mn and Cu, and for Fe and Cu, Zn, and Mn.[1466] Antagonistic, additive or synergistic, reponse of plants to binary mixtures of elements seems to be a concentration-dependent effect. It initially was observed by Chaney and Hornick[129] for the Cd/Zn relationship. Recent findings presented by Sharma et al.[1485] indicated that when only one element of binary mixtures, Cu/Cd, Cu/Zn, and Cd/Zn, exceeds some critical level of toxicity, the joint effect is either synergistic or additive. This clearly indicates that interaction effects are less metal-specific at high concentrations than at low metal concentrations.

Interrelationships between elements in different soils and/or plant species are of multivariant character. These relationships may be attributed to the ionic competition at the sorption sites of soil particles and also to properties of the surface root cell membrane and root exudates.

Interactions observed within plants between trace elements have also indicated that these processes are quite complex, being at times both antagonistic and synergistic in nature, and occasionally are involved in the metabolism of more than two elements (Figure 30). The greatest number of antagonistic reactions have been observed for Fe, Mn, Cu, and Zn, which are, obviously, the key elements in plant physiology (Table 37). These trace metals are linked to processes of absorption by plants and to the enzymatic pathway. The other trace elements often involved in antagonistic processes with these four trace metals are Cr, Mo, and Se.

Synergistic interactions between trace elements are not commonly observed. Those reported for Cd and other trace metals such as Pb, Fe, and Ni may be artifacts resulting from the destruction of physiological barriers under the stress of excessive concentrations of heavy metals. Moreover, several reactions that occur in the external root media and affect root uptake should not be directly related to metabolic interactions, but the two reactions are not easily separated. Some interactions among trace metals are still unpredictable; for example, the addition of Ni- (organic and inorganic forms) enhanced Cu, Zn, and Mn uptake by winter wheat, whereas the addition of Pb increased Cu and Zn.[1442]

VIII. BIOINDICATION

Indicator species are organisms that serve as a measure of the environmental conditions that exist in a given locale. These may be various animal and plant organisms and their organs, or products (e.g., honey). Earlier indicator plants were used in geobotanical prospecting to give evidence of a certain geological phenomenon. At present, it is a widely used method in environmental studies. Also monitoring, which is systematically checking the chemical state of the environment, is often based on bioindicators/biomonitors. Several characteristics of an ideal bioindicator have been given by various authors, and are summarized by Wittig.[1546] In general, an acceptable bioindicator requires the following:

- Suitable accumulation rate of some or selected elements
- Toxitolerance with no sensitivity to the accumulating element/substance
- Present in large amounts in the ecosystem under investigation
- Wide distribution in various environments, and wide geographic range
- Easy to identify and sample
- No seasonal differences in availability and applicability
- Existence of a correlation between accumulation and input to the ecosystem

There are several other conditions required for suitable bioindication and biomonitoring methods. These conditions are related to standardized sampling and analytical methods, comparing results with other monitoring methods, and possible retrospective and long-time investigation periods.

Dandelion is reported quite frequently as a useful environmental indicator, since this plant fulfills most of the listed demands.[1278,1356,1470] An evaluation of metal pollution in selected regions of Poland using dandelion is presented on Table 44. Dandelion leaves grown in the industrial region (Region SW) contain more trace metals than dandelion leaves from other areas. The RDB value identifies a very high relative deviation from background values of all metals in plants from industrial regions. The order of relative accumulation of metals is the following: Ni > Cd > Zn >

Table 44 Metals in Leaves of Dandelion Grown in Different Regions of Poland (ppm)[1356]

Metal[a]	Country N = 780	All Regions N = 240	Region SW N = 60	Region SE N = 70	Region NW N = 60	Region NE N = 50
Cd	0.5	0.6	1.2	0.6	0.5	0.4
	−20	0	50	0	−20	−50
Cu	9.4	9.4	13.4	10	8.4	7
	−27	−22	10	−20	−42	−71
Cr	0.8	0.8	0.7	1.3	0.7	0.4
	25	25	14	53	14	−50
Mn	60	65	74	103	69	42
	0	7	18	41	13	−18
Ni	3.4	1.3	4.2	6.4	3.1	1.9
	50	−53	52	68	35	−5
Pb	1.1	1.2	3	1	1	0.5
	−81	−66	33	−100	−100	−300
Zn	45	50	72	67	35	40
	0	10	37	32	−28	−12

[a] Upper values for metals are Geometric Means, and lover are RDB (Relative Deviation to Background) values, RDB = {[AM − RF]/RF} × 100. RF, reference contents (mg/kg DW): Cd 0.6, Cr 0.6, Cu 12, Mn 60, Ni 2, Pb 2, Zn 45.

Pb > Mn > Cu. Also, needles of pine trees (e.g., Scots pine, Norway spruce) and chicory roots and shoots are often used for evaluation and monitoring of environmental pollution.[1279,1496,1553] A good indication of industrial pollution in eastern Siberia was obtained by Arzhanova and Elpatevsky[1206] analyzing oak leaves which contain, after washing, up to (in ppm): Cd 7.7; Cu 21; Zn 264; and Pb 1155. Roots of aquatic plants as well as aquatic mosses have also been reported as very suitable phytoindicators in certain environments.[1483]

Soil microorganisms are considered good candidates for bioindication of soil metal pollution. However, Parkhurst et al.[1449] have described some problems with using a population of microorganisms or microbial activity as soil biomonitors. These include a large natural variation in population size and activity of microorganisms in soils and their sensitivity to all chemical and physical soil factors. Some examples, however, indicate that the bioassay could be used to assess the bioavailability and harmful effects of trace metals.[1462] Screening for the presence of rhizobia can be a rapid method for the soil bioassay of toxic effects of trace metals and allows the determination of the bioavailable pool of metals in soils.[1310,1332]

The inhibitory effect on soil bioactivity expressed as the soil respiration, differs considerably among trace metals but is always a function of metal contents. The general order of toxicity of metals to microorganisms can be presented as follows: Ag > Cu > Cd > Ni > Zn > Pb > Mn. Two metals, Cu and Zn applied as sulfates to the soil at concentrations up to 2000 ppm, affect soil microbiota: fungi (glucophilic, cellulose-decomposing, thermophilic, and thermotolerant), bacteria, and actinomycetes, generally causing reduction in their populations and soil enzyme activities.[1325] Soil enzyme activity has been used as a sensitive indicator of the effect of trace metals on soils. Most soil enzymes are inhibited by metals (e.g., the contents of Cu, Cr, and As at the levels (in ppm) 900, 842, and 1124, respectively) decrease enzyme activity in the following order (relative to control values): phosphatase 70%; urease, 31%; sulphatase, 25%; and dehydrogenase, 17%.[1461] Alkaline and acid phosphatase is reported to be most sensitive to an excess of Cd, Co, and Zn.[1443]

CHAPTER 6

Elements of Group I

I. INTRODUCTION

The alkali trace elements of the subgroup Ia (new group I) are Li, Rb, and Cs. The common characteristic of the alkali elements is the single electron in the outermost energy level, resulting in highly reactive chemical behavior. The relative bonding force holding these monovalent cations is presented most often in the order $Cs^+ > Rb^+ > Li^+$. These cations do not usually form complex ionic species, but can be bound in some chelates and organometallic compounds.

The subgroup Ib (new group II) contains Cu and the noble metals Ag and Au. Cu occurs most often as the divalent cation, but can also form single monovalent cations and complex anions. This metal shows many unusual features, including an affinity to combine with S, Se, and Te, and is of great importance in biochemistry. Chemical characteristics of Ag are somewhat similar to those of Cu; however, its role in biochemistry is largely unknown. Au has relatively slight chemical reactivity. Its simple monovalent and trivalent cations exist usually in negligible amounts, thus biogeochemical properties of Au are mostly related to its complex ions.[453] A geochemical relationship is observed between Cu, Ag, and Au.

II. LITHIUM

A. Soils

Li is widely distributed throughout the Earth's crust and is likely to be concentrated in acidic igneous rocks and sedimentary aluminosilicates. Li is also likely to be associated with the minerals of the late pegmatitic stage, for example, micas (mainly biotite), pyroxenes, etc. The mean Li content of magmatic rocks is lower than that of sedimentary rocks (Table 45). Li abundance in the Earth's crust ranges from 25 to 40 ppm. Li is very mobile in geochemical processes and preferably enters silicate minerals rather than sulfide minerals. It is also readily absorbed by clay minerals. During weathering, Li is released from the primary minerals relatively easily in oxidizing and acid media and then is incorporated in clay minerals, is also slightly fixed by organic matter, and is fixed by Mn-oxides and accumulated in phosphate rocks. Thus, the Li content of soils is controlled more by conditions of soil formation than by its initial content in parent rocks. The Li distribution in soil profiles follows the general trends of soil solution circulation; however, it may be highly irregular.[864]

The abundance of Li in surface soils, as presented in Tables 9 and 46, seems to be correlated with soil units. Grand means for Li vary from 1.3 ppm in light organic soils to 56 ppm in calcareous soils. Lower contents of Li are reported for light sandy soils, especially those derived from glacial drift in a humid climate. In the arid climatic zones, Li follows the upward movement of the soil

Table 45 Lithium, Rubidium, Cesium, Copper, Silver, and Gold in Major Rock Types

Rock Type	Li (ppm)	Rb (ppm)	Cs (ppm)	Cu (ppm)	Ag (ppb)	Au (ppb)
Magmatic Rocks						
Ultramafic rocks Dunites, peridotites, pyroxenites	0.5–X.0	0.1–2	0.X	10–40	50–60	5
Mafic rocks Basalts, gabbros	6–20	20–45	0.5–1.5	60–120	100	0.5–3
Intermediate rocks Diorites, syenites	20–28	100	0.6	15–80	50–70	3.2
Acid rocks Granites, gneisses	25–40	150	2–5	10–30	40	1.2–1.8
Acid rocks (volcanic) Rhyolites, trachytes, dacites	15–45	100–200	3	5–20	50	1.5
Sedimentary Rocks						
Argillaceous sediments	60	120–200	5–10	40–60	70	3–4
Shales	50–75	140–160	6–8	40	70–100	2.5–4
Sandstones	10–40	45	0.5–2	5–30	50–250	3–7
Limestones, dolomites	5–20	5–30	0.5–2	2–10	100–150	2–6

Note: Values commonly found, based on various sources.

solution and may precipitate at top horizons along with easily soluble salts of chlorites, sulfates, and borates. These reactions explain a relatively higher Li content of soils such as solonchaks, kastanozems, and prairien soils. Also, intrazonal young soils derived from alluvium reveal elevated Li concentrations. The Li content in mineral surface soils of Poland is highly and positively correlated with clay fraction. Its median values (of about 100 samples for each textural soil group) increase in the following order (in ppm): sandy light soils 3.8, light loamy soils 5.8, medium loamy soils 8.8, and heavy loamy soils 12.9.[1351] Average Li content in reference soils of the U.S. is 33 ppm and in soils of China, it is 35 ppm.[1313] Geometric mean Li content in surface Venezuelan soils varies from 2.0 to 13.9 ppm upon different transection near the Caribbean shore.[1273]

In the initial processes of soil formation, Li seems to be highly mobile, while later it may become more stable due to its firm bonding with clay minerals.[864] However, as Shakuri[713] reported, water-soluble forms of Li in the soil profile reach up to about 5% of the total soil content and therefore Li is likely to occur in ground waters of areas having elevated Li contents in rocks and soils. Exchangeable soil Li is reported to be strongly associated with Ca and Mg.[164]

B. Plants

The soluble Li in soils is readily available to plants; therefore, the plant content of this element is believed to be a good guide to the Li status of the soil.[279] There are considerable differences in the tolerance of various plant species to Li concentrations, as well as in the plants' ability to take up this element. Borovik-Romanova and Bielova[92] calculated the index of the biological concentrations, based on the ratio of Li in plant ash to Li in topsoil. For plants of the Rosaceae family with the highest mean Li content (Table 47), this index is 0.6; while for plants of the Polygonaceae, it is 0.04. The highest value of this index, 0.8, however, was calculated for plants of the Solanaceae, members of which are known to have the highest tolerance to Li. Some plants of this family when grown in an aridic climatic zone accumulate more than 1000 ppm Li.[725] The highest uptake of Li was reported for plant species growing on solonetz and solonchak soils or other soils having increased contents of alkali metals.

Table 46 Lithium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	U.S.	<5–50	16.5	706
	Russia	17–60	34	92
	New Zealand	5–72	31	864
	Poland	0.01–12	6	1351
Loess and silty soils	New Zealand	—	95	864
	U.S.	9–30	20.5	706
Loamy and clay soils	New Zealand	1.4–130	45.5	864
	U.S.	10–64	23.5	706
	Poland	0.1–38	15	1351
Soils on glacial till	Denmark	—	6.2	801
Fluvisols	New Zealand	65–160	98	864
Gleysols	New Zealand	50–100	68	864
Rendzinas and other calcareous soils	Russia	—	42	7
	New Zealand	60–105	80	864
	U.S.	6–88	26.5	706
Kastanozems and brown soils	Russia	31–48	37	7, 92
	New Zealand	9–175	57.5	864
Ferralsols	Russia	10–25	17	92
Solonchaks and solonetz	Russia	23–53	42	7, 92
	New Zealand	36–68	55	864
Chernozems	Russia	20–65	45	7, 92, 713
	U.S.	8–40	22.5	706
Prairien and meadow soils	Russia	—	73	713
Histosols and other organic soils	Denmark	0.5–3.2	1.6	1, 801
	New Zealand	0.01–2.8	1.2	864
	U.S.	10–57	24	706
Forest soils	Russia	25–65	50	7, 92, 713
Various soils	Denmark	—	8.6	801
	New Zealand	10–100	64	864
	Great Britain	—	25	818
	New Guinea	6–28	15	164
	U.S.	0.7–16	5.5	976

Table 47 Lithium Content of Plant Families (ppm DW)

Family	Russia. (Mean) (92)	U.S. (Range) (29, 725, 94)	New Zealand (Range) (864)
Rosaceae	2.9	—	—
Ranunculaceae	2.0	—	—
Solanaceae	1.9	0.01–31 (1120)	—
Violaceae	1.3	—	—
Leguminosae	0.67	0.01–3.1	<0.03–143
Compositae	0.55	—	—
Cruciferae	0.54	—	—
Chenopodiaceae	0.32	—	—
Urticaceae	0.24	—	—
Gramineae	0.24	0.07–1.5	<0.02–13
Polygonaceae	0.10	—	—
Lichenes	—	0.02–0.3[a]	—

Note: References are given in parentheses.

[a] Worldwide data.

Li appears to share the K^+ transport carrier and therefore is easily transported in plants, being located mainly in leaf tissues. The Li content of edible plant parts presented in Table 48 shows that some leaves accumulated a higher proportion of Li than did storage roots or bulbs. However, a higher Li content is very often reported for roots. The ratio of root to top for Li in ryegrass was 4.4, while

Table 48 Lithium Content of Plant Foodstuffs[131,197,705]

Plant	Tissue Sample	Mean Content (ppm)	
		DW Basis	AW Basis
Celery(a)	Leaves	6.6(a)	—
Chard(a)	Leaves	6.2(a)	—
Corn(a)	Ears and stover	0.8(a)	—
Corn(b)	Grains	0.05(b)	—
Cabbage	Leaves	0.5	4.9
Carrot	Roots	0.2	2.3
Lettuce	Leaves	0.3	2.0
Onion	Bulbs	0.06	1.6
Potato	Tubers	—	<4
Tomato	Fruits	—	<4
Apple	Fruits	—	<4
Orange	Fruits	0.2	5.3

for white clover it was 20.[864] This may suggest that a difference in plant tolerance to Li concentration is related mainly to mechanisms of biological barriers in root tissues. Li is concentrated, rather, in above-earth parts of plants. This is especially noticeable in plants growing in industrial regions; for example, the leaves:roots ratio for Li in dandelion from a rural region is 0.8, and from an industrial region it is 5.0.[1351]

Wallace et al.[844a] reported that, in most experimental treatments, bush beans accumulated more Li in shoots than in roots while growing in a solution culture with high concentrations of Li. They reported also that higher levels of Li decreased the Zn content in leaves and increased Ca, Fe, and Mn content in all plant tissues.

Although Li is not known to be an essential plant nutrient, there is some evidence that Li can affect plant growth and development.[29] However, stimulating effects of several Li salts reported by various authors have never been confirmed. This observed stimulation may also be related to the influence of other factors, including secondary effects of anions associated with Li. Szentmihalyi et al.[1160] recently reported somewhat higher Li concentrations in plant foodstuffs than those cited in Table 48. Despite their detailed investigation, the role of Li in higher plants has not yet been clarified.

Increased Li concentration in soil is toxic to some plant species. Citrus trees are known to be the most susceptible to injury by an excess of Li, which is reported to be toxic at a concentration in leaves of 140 to 220 ppm. Threshold concentrations of Li in plants are highly variable, and moderate to severe toxic effects of 4 to 40 ppm Li concentration in citrus leaves have been observed.[279] In high-Li soils, damage to root tips of corn as well as necrotic spots in the interveinal leaf tissues and other nonspecific injury symptoms, mainly chlorotic and necrotic spots on leaves and injured root growth, have been observed.[29] Resistant to a high concentration of Li are plants of the *Solanaceae* family which may accumulate, when grown in salic soils, even above 1000 ppm Li. Citruses are sensitive to elevated levels of Li in soils and their growth in salt-enriched soil can be significantly reduced due to high Li contents.

Ca inhibits Li uptake by plants; therefore, the addition of lime to high-Li soil may reduce toxic effects of this element. Li is also toxic to many microorganisms, although the fungi *Penicillium* and *Aspergillus* adapt easily to higher Li concentrations in their growth media.

III. RUBIDIUM

A. Soils

Rb abundance in the major rock types reveals its geochemical association with Li, and therefore it has higher concentrations in acidic igneous rocks and sedimentary aluminosilicates (Table 45). In weathering, Rb is closely linked to K; however, its bonding forces to silicates appear to be

Table 49 Rubidium Content of Surface Soils of the U.S. (ppm DW)[706]

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<20–120	50
Light loamy soils	30–100	60
Loess and soils on silt deposits	45–100	75
Clay and clay-loamy soils	45–120	80
Alluvial soils	55–140	100
Soils over granites and gneisses	<20–210	120
Soils over volcanic rocks	20–115	65
Soils over limestones and calcareous rocks	50–100	75
Soils on glacial till and drift	30–80	65
Light desert soils	70–120	95
Silty prairie soils	50–100	65
Chernozems and dark prairie soils	55–115	80
Organic light soils	<20–70	30
Forest soils	<20–120	55

stronger than those of K; therefore, the K:Rb ratio continually decreases in soil-forming processes. The behavior of Rb in sedimentary and pedogenic processes is controlled mainly by adsorption on clay minerals. Franz and Carlson[999] observed that Rb markedly decreased the rate and activation energy of K release from micaceous minerals. The Rb content of soils is largely inherited from the parent rocks, as is indicated by the highest mean Rb contents, 100 to 120 ppm, in soils over granites and gneisses, and in alluvial soils (Table 49). The lowest mean Rb concentrations (30 and 50 ppm) were reported by Shacklette and Boerngen[706] for sandy and organic soils, and by Markert and Lieth[1086] for peat bogs (1 to 10 ppm). The mean Rb content in light loamy soils of Poland was established as 66 ppm by Dobrowolski,[181] and in deep loess deposits in Russia it was given as 96 ppm by Waganov and Nizharadze[1181] while means for soils of various countries range from 33 to 270 ppm as given by Wedepohl.[855] Naidenov and Travesi[558] reported Rb in Bulgarian soils to be within the range of 63 to 420 ppm (mean, 179). Govindaraju[1313] reported recent results for Rb in reference soils ranging from 15 to 140 ppm (mean 106 ppm) in soils from China and from 69 to 1141 ppm (mean 86) in soils from the U.S. Organic matter and micaceous clay minerals increase the sorption capacity of soils for Rb. A positive correlation between the Rb content and clay fraction in loess deposit was established.[1181]

B. Plants

Rb apparently is easily taken up by plants, as are other monovalent cations. It may partly substitute for K sites in plants, as their properties are similar, but cannot substitute for K metabolic roles; therefore, in high concentrations, it is rather toxic to plants. If some plants (e.g., sugar beets) are deficient in K, Rb together with Na can stimulate the growth.[211] The radionuclide ^{86}Rb is used in K studies of the soil-plant-water system.

Despite the chemical similarity of Rb to K, Rb uptake and transportation within plants were reported to be different from those of K.[749,839] Tyler[1170] described increased availability of Rb to a wide range of vascular plants and fungi, with soil acidity. Such a soil condition does not stimulate plant absorption of K. Thus, effects of interactions between Rb and K on their availability to plants need more basic information. The Rb content of green plants differs for each species and for parts of plants, as is shown in Table 50. Rühling et al.[1135] found Rb to range from 14 to 37 ppm (DW) in mosses from the Nordic countries. Zajic[898] reported concentrations of Rb in fungi to vary from 3 to 150 ppm. Some bacteria are known to accumulate Rb and other monovalent cations in subcellular vesicles.[856] Horowitz et al.[325] found the highest Rb content to be more than 100 ppm in some fungi. However, most of the higher plant species analyzed by these authors contained Rb in the range of 20 to 70 ppm (DW).

Table 50 Rubidium Content of Plant Foodstuffs and Fodders (ppm DW)[381,588,710]

Plant	Tissue Samples	Mean Content
Cereal	Grains	4
Corn	Grains	3
Onion	Bulbs	1
Lettuce	Leaves	14
Cabbage	Leaves	12
Bean	Pods	51
Soybean	Seeds	220
Apple	Fruits	50
Avocado	Fruits	20
Clover	Tops	44
Lucerne (alfalfa)	Tops	98
Grass	Tops	130

IV. CESIUM

A. Soils

Geochemical characteristics of Cs are similar to those of Rb, but Cs appears to have a greater affinity to be bound to aluminosilicates. Cs is concentrated mainly in acidic igneous rocks and argillaceous sediments (Table 45), as are other monovalent trace cations.

Cs released by weathering in soils is strongly adsorbed, but there is very little information on the Cs status of soils. Using old data cited by Wedepohl,[855] the range of Cs in soils can be calculated as 0.3 to 26 ppm. Koons and Helmke[409] gave the range to be from 0.3 to 5.1 ppm Cs in four Canadian reference soils, and Naidenov and Travesi[558] found Cs levels in Bulgarian soils to range from 2.2 to 16.7 ppm, being the highest in surface forest soil and chernozems. Waganov and Nizharadze[1181] reported the Cs mean content of deep loess deposit in the European part of Russia to be 3.2 ppm (DW). Markert and Lieth[1086] found Cs in peat bogs in Germany and in Sweden to be within the range 0.1 to 1 ppm (DW). These values correspond closely to Cs occurrence in rocks, with the highest values indicating also a possible Cs accumulation in organic horizons of soils. Govindaraju[1313] reported that the Cs contents in reference soils from China range from 2.7 to 21.4 ppm (mean 9.31 ppm), and in soils from the U.S., from 0.41 to 5.07 (mean 3.03 ppm).

B. Plants

Cs apparently is not an essential component of plant tissues, and there are few data on its occurrence in plants. As Wedepohl[855] reported from old analytical results, Cs in species of flowering plants was found to range from 3 to 89 ppm (average, 22). Aidiniyan[7] found 0.5 to 1 ppm Cs in tea leaves (AW), and Inarida et al.[1032] found Cs in different kinds of tea leaves to be widely variable, from 0.01 to 0.31 ppm (DW), with the highest averages in jasmine tea of China (0.25 ppm) and in black tea of India (0.21 ppm). Wallace[840] reported Cs in desert plants to range from 0.03 to 0.4 ppm (DW), with a mean value of 0.1 ppm. Ozoliniya and Kiunke[588] analyzed Cs in different parts of three crops—lettuce, barley, and flax. Each plant accumulated Cs in roots (highest value, 0.32 ppm DW) and in old leaves (highest value, 0.16 ppm DW), while in young leaves Cs reached the highest concentration, 0.07 ppm, in flax. Montford et al.[547] reported Cs to range from 0.2 to 3.3 ppb (FW) in vegetables and from <0.1 to 2.9 ppb (FW) in fruits. Rühling et al.[1135] found Cs to range from 0.13 to 0.48 ppm (DW) in moss samples from the Nordic countries.

Souty et al.[749] and Yudintseva et al.[896] reported that Cs is relatively easily taken up by plants, although its absorption by roots appeared not to parallel K absorption. An addition of lime and peat to soil greatly inhibited the bioavailability of this metal.

C. ^{137}Cesium

One of many Cs isotopes, ^{137}Cs is of special environmental concern because it is a by-product of atomic energy production and nuclear weapons testing. Large amounts of these long-lived radioisotopes are released through accidents at nuclear plants. The geochemical characteristics of this radionuclide are fairly similar to those of nonradioactive Cs; therefore, ^{137}Cs released into the atmosphere becomes strongly adsorbed by clay minerals and also by organic matter in soils, and appears to migrate in soils quite slowly.[1090a] However, Comans et al.[968] reported easy post-depositional mobilization of particle-bound ^{137}Cs, probably caused by ion exchange with NH_4 in anoxic solid-liquid systems.

The fate of ^{137}Cs in various soils, 5 years after the fallout following the Chernobyl accident, was investigated by Mondini et al.[1424] The distribution of this radionuclide was related to organic matter content (highly concentrated in the top organic soil layer) and to the CEC. Its content was higher in calcareous soils than in soils derived from siliceous parent material. The highest concentrations of the radionuclide, which ranged from 841 to 1622 Bq/kg, were in the litter layers.

Median values for the inventory of ^{137}Cs in topsoils of Belarus, about a decade after the Chernobyl accident, ranged from 103 to 1500 kBq/m^2, and the highest concentration was as much as 600 times higher than the pre-accident value.[1360] The authors estimated that about 90% of the inventory of ^{137}Cs is contained in the top 3 to 7 cm soil layer. Results of recent studies on the mobility of ^{137}Cs issued from the Chernobyl accident (1986) indicate the presence of increased contents of clay minerals in soils. Fe and Mn sesquioxides and organic matter decrease the mobility, and thus the migration rate of this nuclide.[1317] Concentrations of ^{137}Cs in surface paddy field soils of Japan range from 1.7 to 28.2 Bq/kg.[1512a] Surface soils in the Tatra Mountain area, in Poland, contain this radionuclide within the range of 160 to 650 Bq/kg.[1314]

Recently, the role of microbiota in the behavior of radionuclides has been extensively studied.[1370] Horizontal distribution of radionuclide deposits and temporal pattern of radiocontamination are directly correlated with the seasonal microbiota activity. Also, climatic factors are of great importance in governing the behavior of radionuclides in the environment; however, more studies in this field are needed.[1249] The distribution of ^{137}Cs in soils and plants is a subject of several detailed environmental studies (Table 51).

Grogan et al.[1016] studied soil-plant transfer factors for several radionuclides and found that ^{137}Cs is relatively easily taken up by winter wheat. Some grasses can accumulate up to 36% of the total amount of ^{137}Cs from the growth media after the first five harvests, and the concentrations of this radionuclide in grass correlates curvilinearly with its content of the growth media.[1292] Schimmack et al.[1140] reported that the rates of vertical migration of ^{134}Cs and ^{137}Cs deposited on grassland soil by fallout from the reactor accident in Chernobyl were considerably faster (0.2 and 0.3 cm hr^{-1}) than those for the long-term migration of ^{137}Cs from the global fallout of weapon-testing. Meriwether et al.[1090a] found ^{137}Cs only in the top 15 to 20 cm of the soils of Louisiana, within the range from 1 to 92 Bq kg^{-1}.

Table 51 Concentrations of ^{137}Cs (nCi g^{-1}) in Various Plants Grown on Soils with the Addition of 0.03 nCi kg^{-1} [290,292]

	Sandy Soil		Loamy Soil		Chernozem	
Plant and Part	**FW**	**DW**	**FW**	**DW**	**FW**	**DW**
Cabbage, leaves	4.0	34.9	0.4	6.3	0.6	8.3
Carrot, roots	0.9	6.5	—	—	0.2	1.5
Beet, roots	1.0	5.1	0.4	2.2	0.3	1.6
Potato, tubers	1.3	5.9	1.0	2.3	0.6	2.3
Cucumber, fruits	0.3	8.1	0.1	2.5	0.1	2.4
Tomato, fruits	0.11	2.5	0.02	0.6	0.03	1.2
Oat, straw	—	10–19	—	—	—	—
Oat, grain	—	3–15	—	—	—	—

Plant uptake of ^{137}Cs has been studied because of concern about radioactive emissions from nuclear tests and stations, especially after the Chernobyl accident in 1986. A willow grown on a ^{134}Cs artificially contaminated site took up only a small fraction of this nuclide since most of ^{134}Cs was returned in autumn by litter fall or leached by rainwater.[1311] On the other hand, *Amaranthus* and *Helianthus* species are reported to accumulate a significant amount of ^{137}Cs and are suggested as an alternative for the phytoremediation of polluted sites.[1283] As reported by Tsukada et al.,[1522] ^{137}Cs is more easily taken up by rice than the stable Cs, apparently due to a higher biological activity of this radionuclide compared to Cs. Radioactive Cs in lichens sampled from 1986 to 1988 from the Tatra Mountains National Park in Poland was at similar levels, ranging from 1510 to 8120 Bq/kg, and was about tenfold higher than that measured in 1985 (range 480–790 Bq/kg).[1314]

Recent studies in a Lithuanian forest indicated that during the period from 1986 to 1992, the radioactivity in lichens due to ^{137}Cs and ^{134}Cs decreased by a factor of two to three orders (10–100 times).[1281] In Scotland, on the other hand, up to 50% of ^{137}Cs emitted during the Chernobyl catastrophy remains in the surface soil layer.[1331] However, mycorrhiza of the root of heathers acts as a barrier and limits the transfer of this radionuclide from root to tops. The highest accumulation of radiocesium is in mushroom pericarp, and therefore the health-related limit for ^{137}Cs in edible mushrooms is established in Europe at 600 Bq/kg.[1357] The median content of radiocesium in 110 samples of mushrooms (65 species) collected in 1990 in Japan was ^{137}Cs 60 Bq/kg, and ^{134}Cs $<$7 Bq/kg. Soil-mushroom transfer factors were in the range 5.5 to 13.[1563]

V. COPPER

A. Soils

Cu in the Earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks (Table 45). Cu forms several minerals of which the common primary minerals are simple and complex sulfides. These minerals are quite easily soluble in weathering processes and release Cu ions, especially in acid environments. Therefore, Cu is considered among the more mobile of the heavy metals in hypergenic processes. However, Cu is a very versatile trace cation and in soils or depositional material exhibits a great ability to chemically interact with mineral and organic components of soil. The Cu ions can also readily precipitate with various anions such as sulfide, carbonate, and hydroxide. Thus, Cu is a rather immobile element in soils and shows relatively little variation in total content in soil profiles (Figure 31).

Although soluble, therefore mobile and available, forms of Cu in soils are of great importance in agronomic practice, total Cu content of soils gives basic information for geochemical studies. Total Cu distribution in surface soils of various countries is presented in Table 52. In compiling

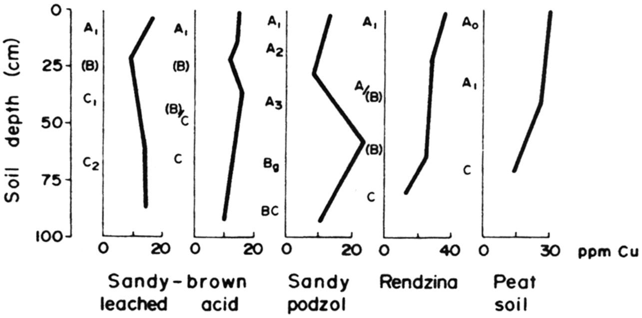

Figure 31 Distribution of Cu in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

Table 52 Copper Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Sandy soils and podzols	Australia	22–52	—	792
	Israel	—	16[a]	644
	Poland	1–26	8	91, 378, 382
	Romania	3–34	18	1127
	Nigeria	7–12	9	817
	U.S.	1–70	14	706
	Russia	1.5–29	11	900
Loess and silty soils	Israel	—	25[a]	644
	China	18–46	26	1068
	East Germany	—	21	428
	West Germany	14–31	—	689
	Poland	8–54	19	91, 378, 382
	Nigeria	21–41	31	817
	U.S.	7–100	25	706
Loamy and clay soils	Germany	—	14	428
	Germany	16–70	—	689
	Great Britain	—	37	876
	Poland	4–36	15.5	91, 378, 382
	Romania	9–44	27	1127
	U.S.	7–70	29	706
	Russia	4–21	12	346, 900
Soils on glacial till	Denmark	—	13.2	801
	Poland	3–14	6	974
Fluvisols	Egypt	50–146	80	561
	India	114–160	—	640
	Israel	—	34[a]	644
	Poland	16–28.5	22	378
	Russia	11.5–36	25	900
Gleysols	Australia	38–61	—	792
	Great Britain	—	31	876
	Madagascar	35–40	—	557a
	Poland	3–53	12.5	378, 683
Rendzinas	Australia	6.8–43	—	522
	Egypt	11–13	12	561
	Germany	35–46	—	428
	Israel	—	35[a]	644
	Poland	7–54	16	378, 382, 685
	U.S.	7–70	21	706
	Russia	7–23	15	900
Kastanozems and brown soils	Australia	83–140	—	792
	China	17–33	23	1068
	Romania	8–32	17	1127
	Russia	14–44.5	25.5	343,900
Ferralsols	Australia	2–96	—	522
	China	15–150	41	1068
	India	44–205	—	640
	Israel	—	60[a]	644
	Ivory Coast	1–100	—	650
	Madagascar	15–40	—	557a
Solonchaks and solonetz	India	55–112	—	640
	Madagascar	15–60	—	557a
	Russia	9–37	19	12, 351, 900
Chernozems	Bulgaria	26–38	29	774
	Poland	6.5–53	19	378, 683
	U.S.	10–70	27	706
	Russia	16–70	27.5	346, 351, 900
Prairien and meadow soils	Surinam	1–22.5	—	178

(*Continued*)

Table 52 Copper Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
	China	18–35	26	1068
	Former Soviet Union	13–70	35	12, 900
Histosols and other organic soils	Denmark	4–24	15	1, 801
	Israel	27–41[a]	—	644
	Ivory Coast	1–3	—	650
	Poland	1–113	6	682, 683
	U.S.	1–100	15	706
	Russia	5–23	12.5	900
Forest soils	China	—	22	225
	U.S.	7–150	17	218, 219
	Russia	12.5–32	22	346, 900
Various soils	Canada	5–50	22[a]	521
	Czech Republic	23–100[a]	—	64
	Denmark	—	12.5	801
	Great Britain	11–323	23	100, 876
	Italy	7–200	24	946
	Japan	4.4–176	34	395
	Poland	1–31	7.6	1045
	U.S.	3–300	26	706
	Russia	1–60	28	432, 900

[a] Data for whole soil profiles.

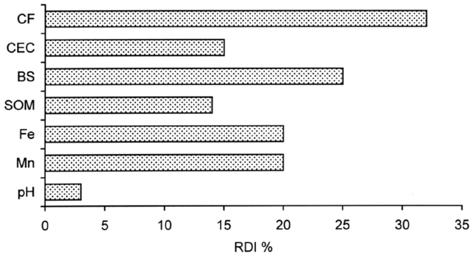

Figure 32 Relative explanation index (RDI) of statistically significant relationship between Cu and soil parameters in mineral soils at the 99% confidence level (N = 780). Soil parameters: CF—clay fraction <0.02 mm; CEC—cation exchange capacity; BS—base saturation; SOM—soil organic matter; Fe—total content; Mn—total content; pH—in water (soil:water ratio 1:2.5).

this table, an attempt was made to exclude contaminated soils; therefore, the mean values for Cu in the given soil groups can be considered as background Cu contents. The mean levels for Cu vary from 13 to 24 ppm, being highest for kastanozems and chernozems and lowest for podzols and histosols (Table 9). Quite similar Cu background contents were calculated for the surface soils of the U.S. from data given by Shacklette and Boerngen.[706] Ferrasols and fluvisols from several countries are reported to contain very high Cu levels (Table 52). The Cu geometric mean of over 32,000 agricultural soil samples of Poland is only 6.5 ppm, which is due to the predomination of light sandy acid soils. However, the variations in the spatial distribution is remarkable, indicating both relation to parent materials and to the impact of industrial and/or agricultural pollution.[1514] The concentration of Cu in 3045 samples of surface soil from major agricultural production areas of the U.S. varies from <0.6 to 495 ppm (geometric mean, 18 ppm).[1329] The regularity in large-scale Cu occurrence in soils indicates that two main factors, parent material and soil formation processes, govern the initial Cu status in soils. Also, the clay fraction contributes significantly to the Cu content of soils. As the RDI value indicates, this is a main soil parameter influencing Cu soil status (Figure 32). Other soil properties, such as Fe and Mn oxides, and base saturation, explain about 15 to 25% of all impact factors.

The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons. This phenomenon is an effect of various factors, but above all, Cu concentration in surface soils reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element.

Table 53 Copper Contamination in Surface Soils (ppm DW)

Site and Pollution Source	Country	Mean or Range of Content	Ref.
Old mining area	Great Britain	13–2000	166, 915, 959
Nonferric metal mining	Great Britain	415–733	166
	Japan	456–2020	395
Metal-processing industry	Australia	847	57
	Belgium	16–1089	1142
	Bulgaria	24–2015	774
	Canada	1400–3700[a]	245
	Japan	26–206[b]	926
	Poland	72–620	380, 1014
	Romania	1387	1126
	Russia[f]	121–4622	1217
Urban gardens, orchards, and parks	Australia	210	795
	Canada	11–130	332
	Japan	31–300	395
	Philippines	352	1178
	Poland	12–240	159
	U.S.	3–140	628
	Russia	50–83[c]	394
Sludged, irrigated, or fertilized farmland	Holland	265	314
	Great Britain	40–800	959, 1134
	Poland	80–1600	682
	U.S.	58–130[d]	1186
	Germany	187–280	176
Application of fungicides	Germany	273–522	652
	Great Britain	60–380	959
	Kenya	883[e]	1059

[a] For 3 to 6.3 km distance from a smelter.

[b] Paddy soils.

[c] Vineyard.

[d] Plot experiment, 9 years after sludge addition 33 to 180 t ha^{-1}, respectively.

[e] Coffee plantation.

[f] Up to 10 km distance from a smelter.

The Cu balance in surface soils of different ecosystems presented in Table 17 shows clearly that the atmospheric input of this metal may partly replace the removal of Cu by biomass production and in some cases may even exceed the total output of the metal from soils. Contemporarily observed soil contamination with Cu can lead to an extremely high Cu accumulation in top soils (Table 53).

1. Reactions with Soil Components

Although the most common mobile Cu in the surface environment is believed to be the cation with the valence of +2, several ionic species may occur in soils (Figure 33). However, Cu ions are held very tightly on both inorganic and organic exchange sites. The processes controlling fixation by soil constituents are related to the following phenomena:

1. Adsorption
2. Occlusion and coprecipitation
3. Organic chelation and complexing
4. Microbial fixation

Adsorption mechanisms of Cu have been extensively studied by many scientists and comprehensive publications concerning the physical and chemical behavior of the metal in soils are

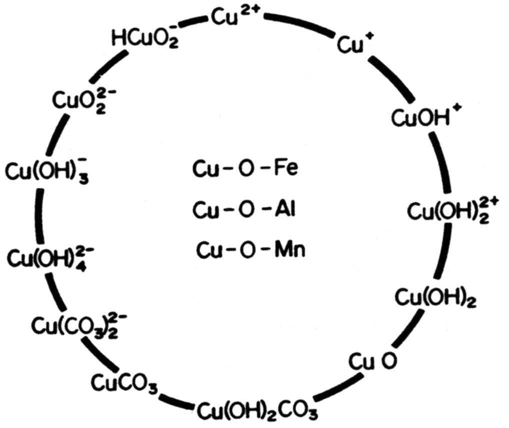

Figure 33 Ionic species, compounds, and bonds of Cu occurring in soils.

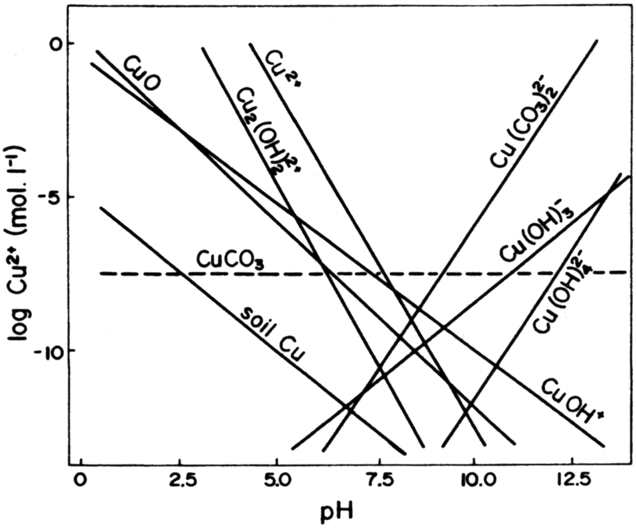

Figure 34 Schematic diagram of solubility of Cu ionic species and Cu compounds in soil.[475,518]

available in papers by McLaren and Crawford,[527] McBride,[518] James and Barrow,[352] and Kitagishi and Yamane.[395] Nonspecifically adsorbed Cu due to ionic bond formation is an easily exchangeable cation. The specific sorption of Cu is related to the reaction with electron-pair donors, and forms rather strong bonds of a relatively high covalency.

Very high correlation was found between *aqua regia* (pseudo total) Cu and DTPA-soluble Cu, while very low correlation was found between $CaCl_2$ and *aqua regia* or DTPA-soluble Cu.[1276]

All soil minerals are capable of absorbing Cu ions from solution and these properties depend on the surface charge carried by the adsorbents. The surface charge is strongly controlled by pH; therefore, the adsorption of Cu ion species can be presented as a function of pH (Figure 34). This type of Cu adsorption is likely to be most important in soils with a large content of variable-charge minerals.[352] Bodek et al.[948] stated that of two mobile Cu species, $CuOH^+$ is the preferably sorbed cation rather than Cu^{2+}.

Many authors have reported that Cu can be adsorbed by minerals within the range from 0.001 to 1 μM dm^{-3} or from 30 to 1000 μM g^{-1}. The greatest amounts of adsorbed Cu have always been found for Fe and Mn oxides (hematite, goethite, birnessite), amorphous Fe and Al hydroxides, and clays (montmorillonite, vermiculite, imogolite). Harter[307] reported that the most significant correlation was obtained between Cu adsorption and the sum of bases for the surface soils, while in the subsurface horizons the adsorption of Cu was highly related to vermiculite content.

Occlusion, coprecipitation, and substitution are involved in nonspecific adsorption of Cu. Nondiffusible fractions of soil Cu are most probably incorporated in various mineral structures. Some soil minerals, such as Al and Fe hydroxides, carbonates, and phosphates, and to some extent also silicate clays, have a great affinity to bind a part of the soil Cu in a nondiffusible form, which is the most stable portion of the metal in soil. In this chemisorption, the formation of oxygen bridge bonds may also be involved (Figure 33).

Chelation and complexing are the key reactions governing Cu behavior in most soils. The ability of the organic soil constituents to bind Cu is well-recognized, and there are a tremendous number of comprehensive publications on this subject. Stevenson and Fitch[758] stated that the maximum amount of Cu^{2+} that can be bound to humic and fulvic acids is approximately equal to the content of acidic functional groups. In general, this corresponds to the sorption of from 48 to 160 mg of Cu per gram of humic acid. Sapek[682] reported the maximum sorption capacity of peat-muck soil to be from 130 to 190 meq per 100 g of peat, while Ovcharenko et al.[587] calculated Cu sorption as 3.3 g kg^{-1} of humic acid. These values, however, will differ greatly depending on the physical and chemical properties of organic substances.

Organic binding of Cu in soils differs to some extent from that described for other divalent ions. According to Bloom and McBride[80] and Bloomfield,[81] peat and humic acids strongly immobilize the Cu^{2+} ion in direct coordination with functional oxygens of the organic substances. Ponizovsky et al.[1458] found that the retention of Cu^{2+} by organic-rich soils differs from mechanisms of exchange of alkali and alkali earth metal cations and should be regarded as triple Cu^{2+}, Ca^{2+}, and H^+ cation exchange. Binding of Cu by soils is related to the formation of organic complexes and is highly dependent on soil pH.[1511]

To sum up the key role played by organic matter in the behavior of soil Cu, it can be emphasized that humic and fulvic acids are likely to form stable complexes when Cu is present in small amounts and that organic matter can modify several Cu reactions with inorganic soil components.

Microbial fixation plays a prominent role in the binding of Cu in certain surface soils. The amount of Cu fixed by the microbiomass is widely variable and is affected by various factors, such as metal concentration, soil properties, and growing season (Table 26). Microbial fixation of Cu is an important step in the ecological cycling of this metal.

Although Cu is one of the least mobile heavy metals in soil, this metal is abundant, as free and complexed ions, in soil solutions of all types of soils. Concentrations of Cu in soil solutions obtained by various techniques from different soils vary from 3 to 135 $\mu g\ L^{-1}$, which corresponds to Cu concentrations of 0.047 to 2.125 μM (Table 16). Overall solubility of both cationic and anionic forms of Cu decreases at about pH 7 to 8. It has been estimated that hydrolysis products of Cu ($CuOH^+$ and $Cu_2(OH_2)_2^{2+}$) are the most significant species below pH 7, while above pH 8 anionic hydroxy complexes of Cu become important (Figure 34). As Sanders and Bloomfield[677] stated, the solubility of $CuCO_3$ is not pH dependent and this compound seems to be a major inorganic soluble form of Cu in neutral and alkaline soil solutions, while nitrate, chloride, and sulfate do not complex a significant portion of Cu in the soil solution. However, the most common forms of Cu in soil solutions are soluble organic chelates of this metal. Although very little is known of the kinds of soluble organic Cu forms, about 80% of the soluble Cu forms have been estimated to be organic chelates.[320] McBride and Blasiak[519] reported that due to a great affinity of Cu for organic complexing, soluble Cu-organic forms appear to comprise most of the Cu solution over a wide range of pH. Organic complexing of Cu has a prominent practical implication in governing the bioavailability and the migration of Cu in soil. The bioavailability of soluble forms of Cu depend most probably on both the molecular weight of Cu complexes and on the amounts present. Compounds of low molecular weight liberated during decay of plant and animal residues as well as those applied with sewage sludges may greatly increase the availability of Cu to plants. In summary, it should be emphasized that the concentrations of Cu in soil solutions are principally controlled by both the reactions of Cu with active groups at the surface of the solid phase and by reactions of Cu with specific substances.

Cu deficiencies most often result from management practices used during crop production (e.g., overliming, P fertilization, organic matter amendment).

2. Contamination of Soils

Contamination of soil by Cu compounds results from utilization of Cu-containing material such as fertilizers, sprays, and agricultural or municipal wastes as well as from industrial emissions (Table 53). Some local or incidental Cu input to soils may arise from corrosion of Cu alloy construction materials (e.g., electric wires, pipes).

Major sources of pollution (mainly nonferric metal smelters) present halos in which Cu concentrations in surface soils decrease with distance, which is especially pronounced in a downwind direction (Figure 35). While main point sources of industrial pollution have a local environmental impact, they also contribute to the global long-distance pollution of the atmosphere. Airborne fallout of Cu pollutants differs greatly in a specific area and for parts of the continents, being the greatest in central Europe. Heindrichs and Mayer[310] reported the atmospheric input of Cu to be 224 g ha^{-1} year^{-1} for Germany, which is, comparatively, the highest value (Table 17).

The addition of Cu to cultivated soils with applied fertilizers, chemicals, and wastes has recently been extensively investigated. Tiller and Merry[795] reviewed all basic problems of Cu behavior in contaminated soils and the assessment of the environmental impacts. Mingelgrin and Biggar[1093] studied the behavior of Cu species in sewage sludges under various conditions and observed that the increase of easily soluble Cu in sludges on drying in soils can be a source of Cu contaminations of plants, and in some cases also of groundwater. In the surface soil layer of vineyards, after 50 to 100 years of applied fungicides, the content Cu forms dissolved by various extractants were as follows (in ppm): aqua regia 220, DTPA 82.5, and $CaCl_2$ 0.23.[1276] As a result of using a copper sulfate fungicide (Bordeaux mixture) for more than 100 years, Cu concentrations in top vineyard soils in France vary from 100 to 1500 ppm.[1225] The disposal of metal-contaminated sludge can also be a significant source of Cu in a soil. In sewage sludge-treated soil, Cu accumulations up to 1170 ppm have been reported.[1264]

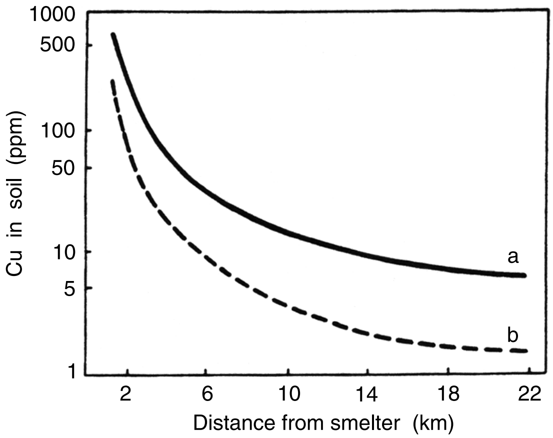

Figure 35 Smoothed patterns for Cu concentrations in soils as a function of downwind distance from a Cu smelter (mean values of 3 years); (a), total content; (b), soluble content.[380]

The most important statement on Cu contamination of soils is the great affinity of surface soils to accumulate this metal. As a consequence, Cu content of soils has already been built up to the extremely high concentration of about 3500 ppm Cu from industrial sources of pollution and of about 1500 ppm Cu from agricultural origins of the metal (Table 53). The threshold value of 100 ppm Cu (Table 6) has been exceeded in several contaminated surface soils. The highest soil contamination with Cu up to above 4500 ppm is reported for the area surrounding the Cu-Ni smelter in the Kola Peninsula.[1217]

The amelioration techniques based mainly on the addition of lime, peat (organic matter), and phosphate to soils bring variable effects related to the soil and plant factors. It should, however, be kept in mind that Cu stored in surface soils influences their biological activity and may become availabile to plants under various conditions. According to results of the experiment carried out by Boon et al.[1236] planting a Cu-tolerant grass (*Agrostis capillaris* L.) on Cu-contaminated acid soil (750 kg Cu ha^{-1}) can significantly increase the biological activity of a soil.

B. Plants

1. Absorption and Transport

Numerous studies have greatly increased the present knowledge of Cu absorption mechanisms. The mechanisms of Cu absorption are still far from clear, but it may be stated that, although there is increasing evidence of the active absorption of Cu, passive absorption is likely to occur, especially in the toxic range of this metal in solutions.

In root tissue, Cu is almost entirely in complexed forms; however, it is most likely that the metal enters root cells in dissociated forms. Graham[280] compared the results of different studies carried out on the rates of Cu absorption by higher plant roots and stated that these rates are among the lowest of the essential elements, varying from pico- to micromole hr^{-1} g^{-1} (DW) of roots in the physiological concentration range (0.01 to 20 μM Cu).

Despite the great complexity of the absorption mechanisms, a relationship between the concentration of the metal measured in either a nutrient solution or a soil solution and in the soil that supports plants can be observed, especially in the toxic range (Figures 36 and 37). The rate of Cu uptake by plants, however, widely differs with species of the metal. Grupe and Kuntze[1019] found that anthropogenic metal (added in the form of Cu oxide) is more available to barley than that of pedogenic origin (Figure 2).

The movement of Cu among various parts of plants plays a predominant role in the plant's utilization of Cu. The strong capability of root tissues to hold Cu against the transport to shoots under conditions of both Cu deficiency and Cu excess has been observed. These processes are not yet fully understood; however, Loneragan[490] and Tiffin[788] concluded that excretion of Cu from root cells into the xylem and phloem saps where Cu occurs in mobile forms is a key process in the Cu nutrition of plants.

The concentrations of Cu in xylem and phloem saps range from traces to 140 μM and seem to correlate with the concentrations of amino acids. The Cu mobility within plant tissues strongly depends on the level of Cu supply, being the highest with a "luxury" supply.[490] However, Cu has low mobility relative to other elements in plants and most of this metal appears to remain in root and leaf tissues until they senesce; only small amounts may move to young organs. Therefore, the young organs are usually the first to develop symptoms of Cu deficiency.

The distribution of Cu within plants is highly variable. Within roots, Cu is associated mainly with cell walls and is largely immobile. The highest concentrations of Cu in shoots are always in phases of intensive growth and at the luxury Cu supply level. Scheffer et al.[688a] showed that distribution of Cu in barley leaves is relatively uniform for a given stage of plant growth.

A considerable proportion of the Cu present in green tissues appears to be bound in plastocyanin and in some protein fractions. There is also a tendency to accumulate Cu in reproductive organs

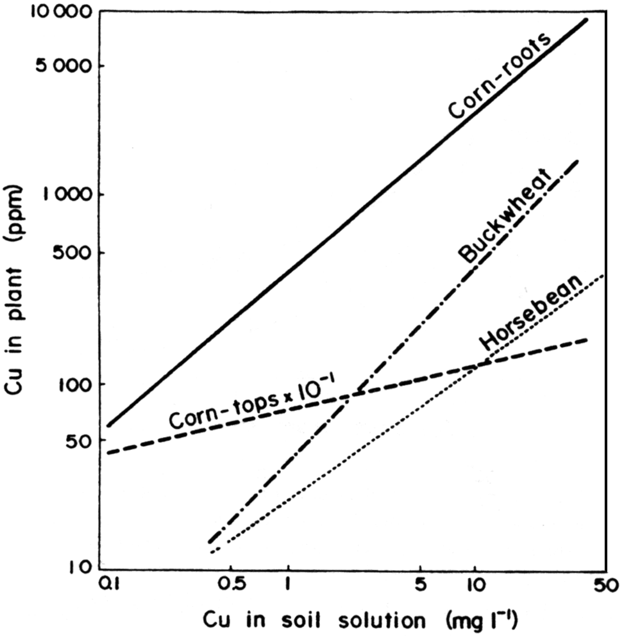

Figure 36 Relationship between Cu content of plants and its concentration in soil solution obtained from Cu-contaminated soils.[379]

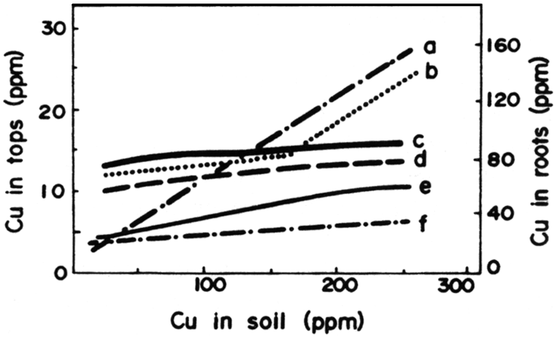

Figure 37 Cu uptake by plants and organs from Cu-contaminated soils. (a) Valencia orange roots; (b) potato stalks; (c) pasture herbage; (d) lettuce leaves; (e) barley grains; (f) wheat grains.[176,231,783]

of plants; this, however, differs widely among plant species. The highest concentrations of Cu have been found in the embryo of cereal grains and in the seed coat. Loneragan[490] cited Cu concentration in the embryo to be from 2 to 18 ppm and from 8 to 23 ppm in the seed coat, while in whole seeds the highest value was 4 ppm (DW). These proportions do not correspond closely to those reported by Liu et al.,[484] who found a more uniform distribution of Cu throughout the barley grain.

2. Biochemical Functions

Very extensive studies have been made on the forms and behavior of Cu in plants. All findings described in a number of outstanding textbooks can be summarized as follows:

1. Cu is mainly complexed with organic compounds of low molecular weight and with proteins.
2. Cu occurs in the compounds with no known functions as well as in enzymes having vital functions in plant metabolism.

3. Cu plays a significant role in several physiological processes—photosynthesis, respiration, carbohydrate distribution, N reduction and fixation, protein metabolism, and cell wall metabolism.
4. Cu influences water permeability of xylem vessels and thus controls water relationships.
5. Cu controls the production of DNA and RNA, and its deficiency greatly inhibits the reproduction of plants (reduced seed production, pollen sterility).
6. Cu is involved in the mechanisms of disease resistance. This resistance of plants to fungal diseases is likely to be related to an adequate Cu supply. There is also evidence that plants with enriched Cu concentrations are susceptible to some diseases. These phenomena may indicate that the role of Cu in disease resistance is an indirect one.

The most important practical implications are related to deficiency and toxicity of Cu. Cu deficiency affects physiological processes and therefore plant production. However, as Bussler[115] stated, in most of the processes affected by the Cu deficiency the shortage of Cu operates indirectly. This explains the difficulties in the assessment of Cu needs and Cu availability to plants. The Cu-deficient concentration in the nutrient solution for cereal growth is given as 5 μg L^{-1}.[317] Jewell et al.[1039] grew Cu-deficient barley at the level of about 1 μg L^{-1} (12.5 ng cm^{-3}). These authors observed a high irregularity in both pollen development and fertility and described some reorganization of nuclear structure.

Although Cu deficiency is widespread (Table 39) and has long been known, diagnosis and correction of the deficiency still need more study. Different methods have been applied to diagnosis using plant symptoms, soil testing, or biochemical assays. However, when these approaches are used singly, results are so crop and soil specific that the development of a universal test seems unlikely. Recently Robson and Reuter,[660] Gartrell et al.,[258] and Mengel and Kirkby[531] suggested that the tissue test should be considered together with other relevant information (field observations, soil analysis, etc.) for the most accurate assessment of the need for Cu applications.

The deficiency levels of Cu in plants show large genetic differences; however, some generalizations are presented in Table 36 which indicate that Cu levels less than 2 ppm are likely to be inadequate for most plants. The threshold contents of Cu in soils that were established using different procedures differ widely (Table 39) and their use is not encouraged for the determination of Cu deficiency for various crops.

Removal of Cu by crops is negligible when compared to its content in soil. An average cereal crop removes Cu in amounts of about 20 to 30 g ha^{-1}, whereas forest biomass removes about 40 g ha^{-1} $year^{-1}$. Gartrell[257] pointed out that comparing the excesses of Cu applied and the amounts removed in farm produce and leached with percolating waters shows that "depletion of soil reserves" is an unlikely explanation for the appearance of Cu deficiency over a short period. Cu application to soils has a long-term effect, and 10 years after Cu fertilization the contents of Cu were still increased in pasture herbage. Repeated Cu applications to soils can lead to toxic concentrations of this metal for some crops. Minnich et al.[1094] observed that the Cu concentration in shoot tissues of snapbeans increased linearly with the Cu content of the sludge applied, while the Cu content of roots was dramatically increased with both the Cu content and the proportion of sludge in the growth media.

Despite the general Cu tolerance of plant species and genotypes, this metal is considered to be highly toxic. General symptoms of the Cu toxicity listed in Table 40 show that Cu-induced chlorosis and root malformation are the most common characteristic symptoms of this toxicity. Recently, the effects of excess Cu on photosynthetic electron transport have been studied intensively. All recent findings can be summarized to show that the decrease of photosynthetic efficiency resulting from Cu-induced destabilization of the photosystem is connected with an inhibition of its donor side and the primary photochemical processes.[1394] The growth depression of sensitive plants was observed at 15 to 20 ppm (DW) Cu in tissues,[1052] and 10% yield decrease is most likely at 10 to 30 ppm (DW) Cu.[1081]

Based on the statements made by Woolhouse and Walker[886] and Sandmann and Boger,[678] the processes induced by an excess of Cu^{2+} and Cu^{+} ions may be summarized as follows:

1. Tissue damage and elongation of root cells
2. Alteration of membrane permeability, causing root leakage of ions (e.g., K^{+}, PO_4^{3-}) and solutes

3. Peroxidation of chloroplast membrane lipids and inhibition of photosynthetic electron transport
4. Immobilization of Cu in cell walls, in cell vacuoles, and in nondiffusible Cu-protein complexes
5. Damage to DNA, and in consequence, inhibition of photosynthetic processes.

Excess Cu in tropical plantations is of special concern. In plantations of citrus, coffee, cacao, tea, olives, and vineyards, Cu-fungicides have been applied for quite a long time. Now, microorganisms have developed a resistance to Cu, but the accumulation of this metal in surface soils is harmful to many new plant species. In old plantations, a significant increase in Cu content is noticed in consumed parts of plants. For example, tea leaves contain Cu from 20 ppm (Kenya) to about 80 ppm (Japan), of which up to 30% is easily extracted by hot water. The Cu concentrations in tea drinks are from 9 to 19 ng L^{-1}.[1550]

Prediction of the Cu content of soil that results in toxic effects on plants is extremely complex. Before toxic symptoms and yield reductions are evident, the nutritive value of the crops having increased Cu levels seems to create the most significant health risk. A number of observations that Tiller and Merry[795] reported on the depressed plant growth, especially retarded seed germination and seedling and root development, resulted from excess Cu concentrations in surface soils.

McGrath[1407] described that some 24 Cu hyperaccumulating species have been recorded in various families, but as yet no data are available on their use in phytoextraction of this metal.

3. Interactions with Other Elements

For optimal development, the plant must have not only an appropriate amount of active Cu in the cells, but also a balance of chemical elements. Due to the significant functions of Cu in enzymes and its variable valence, ions which have similar affinity as Cu to proteins and other compounds may have antagonistic interrelationships. Many complex interactions of Cu with other elements are observed within plant tissues and also in the external root media, particularly in the uptake-transport processes.

Cu-Zn interactions are commonly observed.[280,654] These metals apparently are absorbed by the same mechanism and therefore each may competitively inhibit root absorption of the other.

Cu-Fe antagonism is indicated as Cu-induced chlorosis. High levels of Cu in the plant decrease the Fe content in chloroplasts.[647] Fe, on the other hand, reduces Cu absorption from soil solutions, especially on peat soils. The optimal Cu:Fe ratio varies for different plant species. The toxic effects of Cu can be decreased by the addition of Fe. However, a synergistic effect of Cu on Fe absorption by rice seedlings was reported by Kitagishi and Yamane.[395]

Cu-Mo interactions are closely related to N metabolism. Cu interferes with the role of Mo in the enzymatic reduction of NO_3. The mutual antagonism existing between these elements is highly dependent on plant species and kind of N nutrition. Cu aggravates Mo deficiency in plants, especially those using N from NO_3, because Cu interferes with the role of Mo in the enzymatic reduction of NO_3. Some vegetables are quite susceptible to Mo deficiency if growing in soil with a high level of Cu; and in other plants, the deficiency of Cu is increased with the application of Mo to the soil.[581]

Cu-Cd interactions are reported by some authors as both antagonistic and synergistic in the element uptake by roots. Synergism may be a secondary effect of the damage to membranes due to the imbalanced proportions of the metals. Cu-Se interactions are observed mainly as inhibited Cu uptake with increased Se level. Cu-Mn interactions are reported to be both synergistic and antagonistic in the uptake processes under defined conditions and at high concentrations. Cu-Ni synergism is observed in similar conditions as Cu-Mn relationships. Cu-Al antagonism leads to the reduction of Cu uptake by roots under Al toxic levels, especially in acid soils.

Cu-Cr interrelationships may occur within plant tissues, as well as in the external root media. Antagonistic reactions apparently are related to the variable valency of Cr. Significant information on synergistic interconnections between Cu-F and Cu-Ag in microbial metabolisms were reported by Gadd and Griffiths.[251]

Interrelationships between Cu and major elements are presented in Table 43. Cu and N interact most strongly in the nutrition of plants. The concentrations of the two elements are highly correlated in shoots of a wide range of species and are related to the formation by protein of strong complexes with Cu. On the other hand, plants with high N levels readily show symptoms of Cu deficiency that results from increased growth.

Cu-P antagonisms occur in root media where phosphates have a strong tendency to adsorb Cu. High phosphate levels in soils also reduce mycorrhizal absorption of Cu. An excess of Cu, in contrast, inhibits activity of phosphatase thereby diminishing the availability of P.[813]

Cu-Ca interactions are highly complex and apparently are cross-linked with the range of pH in the growth media. The affinity of carbonates to precipitate Cu is the most common reaction leading to Cu deficiency in soils within the alkaline range of pH or having free $CaCO_3$. Liming is the most frequent practice in the amelioration of Cu-contaminated soils. The relatively common occurrences of reduced Cu contents in plants that have an increased supply of some nutrients are often related to secondary effects of Cu dilution resulting from enhanced growth rates of the plant.

4. Concentrations in Plants

The appropriate content of Cu in plants is essential both for health of the plant and for the nutrient supply to man and animals. Some plant species have a great tolerance to increased concentrations of Cu and can accumulate extremely high amounts of this metal in their tissues (Table 41).

The concentration of Cu in plant tissues seems to be a function of its level in the nutrient solution or in soils (Figures 36 and 37). The pattern of this relationship, however, differs among plant species and plant parts.

Opinions appear to vary considerably as to which factor, soil or plant, affects concentrations of Cu in plant tissues to a higher degree. Anke et al.[32] reported a significant variation in Cu uptake by red clover from different soils, while Kähäri and Nissinen[388] found fairly uniform Cu levels in timothy from different soils. These authors, however, did not support their results with information on the Cu status of soils (Table 54).

Cu contents of various plants from unpolluted regions of different countries range from 1 to XO ppm (DW) (Tables 55, 56, and 57). Cu in ash of a variety of plant species is reported to range from 5 to 1500 ppm.[710] in several species growing under widely ranging natural conditions, Cu contents of whole plant shoots do not often exceed 20 ppm (DW), and thus this value is most often considered to indicate the threshold of excessive contents (Table 36). However, under both natural and man-induced conditions, the majority of plant species can accumulate much more Cu, especially in root, storage tissues (Table 58). Coffee (*Coffea arabica*) shoots and their brown bark are also reported to contain extremely high levels of Cu, up to 4186 ppm (DW). [1058] The significance of

Table 54 Variation in Copper Content of Red Clover (Bud Stage) and Timothy (Immature Stage) as Influenced by Soil Factors (ppm DW)

	Red Clover[32]		
Soil Parent Material	**Meadow**	**Cultivated Field**	**Timothy[388]**
Phyllite	11.1	11.3	—
Porphyry	11.5	10.2	—
Basalt	9.6	10.0	—
Loess or silt	9.7	9.8	4.1
Granite	9.2	9.7	—
Alluvial loamy deposit	9.0	9.8	4.8
Diluvial sand	8.4	8.1	3.9
Glacial till	8.5	7.5	4.0
Moor and peat	6.4	6.3	4.0

Table 55 Mean Levels and Ranges of Copper in Grass and Clover at the Immature Growth Stage from Different Countries (ppm DW)

Country	Grasses Range	Grasses Mean	Clovers Range	Clovers Mean	Ref.
East Germany	7.4–15.0	10.1	7.6–15.0	10.5	31, 32, 65
Finland	3.8–4.8	4.3	—	—	388
Hungary	3.6–8.4	5.0	4.2–16.2	10.5	803
Japan	1.3–33.1	6.9[a]	2.0–12.5	6.5[b]	395
New Zealand	7.3–13.4	10.5[c]	8.1–17.5	11.7[d]	536
Poland	2.2–21.0	6.0	4.2–20.9	11.3	381
U.S.	1.5–18.5	9.6	10.2–29.0	16.2	172
Russia ecosystems					
Meadow-bog	1.1–3.8	1.8	8.8–20.0	12.5	806
Forest-steppe	1.1–3.9	2.6	5.1–24	14.8	806
Forest	2.2–3.8	3.0	—	6.4	806

[a] *Dactylis glomerata.*

[b] *Trifolium repens.*

[c] *Lolium perenne.*

[d] *Trifolium pratense.*

Table 56 Mean Copper Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis (547, 574)	FW Basis (395, 1187)	DW Basis (705)	DW Basis (354, 381)	DW Basis (354)	AW Basis (705)	AW Basis (354)
Sweet corn	Grains	0.60	1.5	1.4	2.1	—	54	88
Bean	Pods	1.7	10.0[a]	5.1	—	8	73	126
Cabbage	Leaves	0.33	0.3	2.9	3.3	4	31	40
Lettuce	Leaves	0.11	1.7[b]	8.1	—	6	58	42
Beet	Roots	—	—	—	8.1	5	—	87
Carrot	Roots	0.22	0.58	4.6	8.4	4	65	70
Onion	Bulbs	0.69	0.37	4.6	6.0	4	110	68
Potato	Tubers	0.38	1.3	3.7	6.6	3	88	105
Tomato	Fruits	0.65	0.65	8.8	—	6	73	84
Apple	Fruits	0.03	—	1.1	—	—	63	—
Orange	Fruits	0.11	0.4[c]	1.9	—	—	52	—

Note: References are given in parentheses.

[a] Pulses.

[b] Spinach.

[c] *Citrus unshiu* (Satsuma orange).

elevated contents of Cu in feed and food plants that reflect man-made pollution needs evaluation from the environmental health point of view.

A number of projects have been carried out recently on Cu levels in edible plants, since about 30% of daily Cu intake by adults in Europe is from cereals and potatoes.[1247] Based on monitoring studies in Poland (5000 to 7000 sample sites), the geometric mean concentrations of Cu were calculated (in ppm) for: cereal grain 3.7, for potatoes 4.5, and for grasses 5.5.[1514] These are a bit lower values than presented for other countries (Tables 55 to 57). Wolnik et al.[1549] gave, for the U.S., a mean content of Cu in potatoes as 0.96 ppm and in sweet corn 0.45 ppm. The recent reference for food compositions in the U.S. gives the following values for Cu in some categories of plant food (ppm FW): (a) vegetables: range 0.1–3.2, the lowest value for celery root, and the highest for garlic cloves; (b) fruits: range 0.3–4.0, the lowest value for grapes, and the highest for avocados, without skin; (c) cereals: range 0.3–13.0, the lowest value for oats, whole grain, and the highest for rye, whole grain; and (d) nuts: range 0.2–23.8, the lowest value for fresh coconut meat, and the highest for shelled Brazil nuts.[1291]

Table 57 Copper Content of Cereal Grains from Different Countries (ppm DW)

Country	Cereal	Range	Mean	Ref.
Afghanistan	Barley	—	6.3	446
	Wheat	—	4.1	446
Australia	Wheat	1.3–5.0	3.5	391, 867
Canada	Oats	—	5.5	514
Egypt	Wheat[a]	4.5–10.3	6.7	213
Finland	Wheat[a]	4.7–6.9	5.7	508
	Wheat[b]	3.7–6.8	5.3	508
Germany	Barley	1.8–6.2	—	65
	Oats	2–4	—	65
	Wheat	6–10	—	65
Great Britain	Barley	2.5–6.0	4.3	783
Japan	Rice	—	2.8[c]	395
	Wheat (flour)	—	1.1[c]	395
Norway	Barley	2.1–9.2	5.5	446
	Wheat[a]	2.1–6.1	4.0	446
Poland	Rye	1.4–7.0	3.6	1045
	Oats	1.0–5.2	2.2	1045
	Triticale	—	3.2	667
	Wheat[b]	2.6–6.5	3.8	267, 355
U.S.	Barley	4–15	—	484
	Rye	4–8	—	490, 492
	Rice	0.5–5.1	1.9[c]	1187
	Triticale	—	7.8	490, 492
	Wheat	0.6–5.4	4.5	906
Russia	Barley	—	5.2	586
	Oats	2.3–4.2	3.2	586
	Wheat[b]	3.8–6.5	5.1	586

[a] Spring wheat.

[b] Winter wheat.

[c] FW basis.

Various microorganisms are known for their resistance to a high concentration of Cu (see Chapter 4, Section IV.A). Zabawski and Boratyński[1195] reported that *Penicillium* species may accumulate up to about 20,000 ppm (DW) Cu from the solution containing 100 ppm Cu. Micromycetes seem to develop resistance to Cu in soils contaminated with this metal. *Penicillium* species isolated from the Cu-polluted soil absorbed less Cu and grew better under increased doses of the metal than *Penicillium chrysogenum* isolated from the unpolluted soil (Figure 38).

VI. SILVER

A. Soils

The geochemical characteristics of Ag are similar to those of Cu, but its concentration in rocks is about 1000 times lower than Cu (Table 45). Ag is easily released by weathering and then precipitated in alkaline reduction-potential media and in media enriched in S compounds.

Ag can form several ionic species, such as simple cations (Ag^+, Ag^{2+}, AgO^+) and complexed anions, mainly with Cl and S: $AgCl_2^-$, $AgCl_3^{2-}$, $AgCl_4^{3-}$, $Ag(HS)_2^-$, $Ag_2S_3H_2^{2-}$, $Ag(S_2O_3)_2^{3-}$, and $Ag(SO_4)_2^{3-}$. Despite several mobile complexes, Ag apparently is immobile in soils if the pH is above 4. There is some evidence that MnO_2 has a strong affinity for Ag and appears to be the most significant sorbent of Ag in soils.[948] Humic substances are known to absorb and complex Ag. Sikora and Stevenson[1148] studied the impact of organic substances on the availability of Ag. Maximum

Table 58 Copper Content of Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean or Range of Content	Country	Ref.
Metal processing industry	Lettuce, leaves	64	Australia	57
	Blueberry, leaves	75	Canada	866
	Grass, tops	21	Great Britain	1005
	Grass, tops	20–70[a]	Canada	245
	Horsetail, tops	70–250[a]	Canada	245
	Sugar beet, leaves	79–590	Poland	1161
	Dandelion, tops	73–274[b]	Poland	380
	Dandelion, roots	22–199[b]	Poland	380
	Wheat, grains	21	Poland	1006
Urban garden	Radish, roots	2–14	Great Britain	167
	Leafy vegetables	4–19	U.S.	628
Sludged or irrigated farmland	Grass, tops	14–38	Holland	297
	Rice, grains	4	Japan	395
	Rice, roots	560	Japan	395
	Potato, tubers	5	Germany	176
Fungicide treatment	Coffee[c]		Kenya	1058
	Medium roots	21.6		
	Fine roots	154.0		
	Trunk wood	6.7		
	Trunk bark	1122.5		
	Whole stems	9.4		
	Foliage	409.4		
	Beans	17.6		

[a] For 1.6- to 5.8-km distance from a smelter.

[b] For 0.5- to 2.5-km distance from a smelter.

[c] 68-year-old coffee bushes, 236 ppm Cu in surface soil.

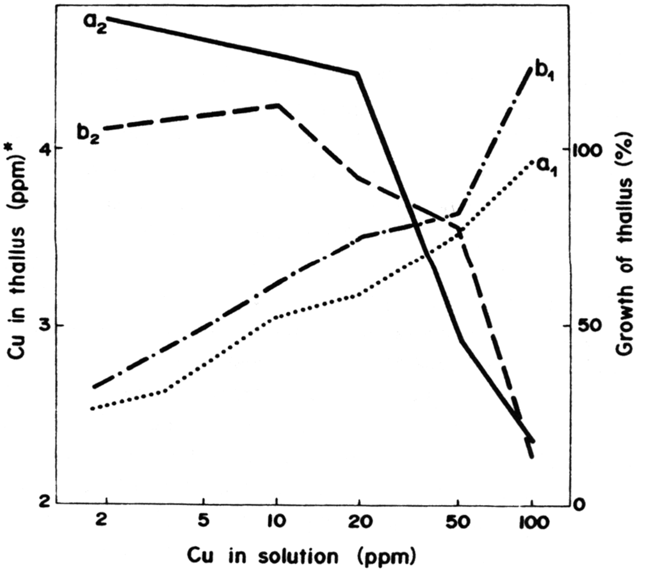

Figure 38 Copper accumulation and relative growth of thallus of soil micromycetes as a function of the metal concentration in nutrient solution. (a_1) *Penicillium* sp. from soil polluted with Cu—accumulation of metal, (a_2) growth of *Penicillium* sp., relative to control, (b_1) *Penicillium chrysogenum* from unpolluted mineral soil—accumulation of metal, (b_2) growth of *Penicillium chrysogenum,* relative to control.[1195] *Values given in powers of ten.

binding capacity of HA and FA ranges from 0.81 to 1.85 mM Ag g^{-1} at pH 6.5, and it is more closely related to the magnitude in N contents of the humic substances than to acidic functional group contents.

The literature published on Ag distribution in the environment has been reviewed by Smith and Carson[739] and Mukherjee[1430] and shows the common range of Ag in soil to be 0.03 to 0.4 ppm. Ag in Canadian soils ranges from 0.2 to 3.2 ppm and for British standard soil samples Ag was reported to average 0.4 ppm.[96,629,818] Recently calculated by Jones et al.,[1042] background Ag levels were <0.1 ppm, while soils contaminated by past mining activities in Wales contained up to 9 ppm Ag. The sorption of Ag by soil components was very strong, and nearly half of the total Ag was "residual" in very immobile species. Thus, Ag showed a marked surface enrichment in all contaminated soils.

Data given by Shacklette and Boerngen[706] show Ag in the plow zone of mineral soil to be 0.7 ppm, and in soils rich in organic matter, to be from 2 to 5 ppm. An average Ag content given for soils by Wedepohl[855] ranges from 0.01 to 5 ppm, and values established by Bowen[94] range from 0.01 to 8 ppm. The Ag concentrations in soils of Poland do not exceed 1 ppm, with the exception of soils from the Cu smelter vicinity where the highest Ag content was 16 ppm.[1390] All higher values for Ag in soils are found in mineralized areas. Davies and Ginnever[168] found up to 44 ppm Ag in soils from the vicinity of old base metal mines, and Guseva[1321] found up to 30 ppm in soils from Moscow surroundings. The EDTA-soluble Ag in Japanese soils ranges from 0.024 to 0.167 ppm, and in polluted soils is greater than 1.5 ppm.[1208] Kiriluk[394] reported the range of Ag from 0.44 to 0.93 ppm in chernozems of vineyards. Jones and Peterson[1043] described that adsorption and retention of Ag by HA and FA in soils may limit its phytoavailability. Thus, the excess of Ag in soils of a low organic matter content is more phytotoxic than in soils of a high organic content.

B. Plants

Ag concentrations in plants are reported by Smith and Carson[739] to range from 0.03 to 0.5 ppm (DW). Chapman[131] established the intermediate range of Ag in plant foodstuffs as 0.07 to 2.0 ppm (DW). According to Gough et al.[279] and Shacklette,[705] the mean Ag content of plant ash is usually less than 5 ppm.

Ag concentrations differ greatly between plant species and between times of sample collection. Horowitz et al.[325] reported that Ag in plants sampled in September was much lower than in plants sampled in May. They found Ag in plants to range from 0.01 to 16 ppm (DW), with the highest values being for fungi and green algae.

The amount of Ag absorbed by several plants (e.g., horsetail, lichens, mosses, fungi, and some deciduous trees) seems to be related to the amount of the metal in soils. Thus, Ag can be concentrated to toxic levels in plants growing in Ag-mineralized areas.[120,417] Soil Ag is apparently deposited in root tissues in the form of Ag_2S and/or metallic, and therefore is excluded from metabolic processes. However, $AgNO_3$ can be easily taken up by plants, and is toxic in relatively low concentrations ($<8.5\ \mu M\ L^{-1}$). $AgNO_3$ is reported to be the most toxic compound to terrestrial plants, of which the most sensitive are lettuce (NOEC at concentration 0.75 mg L^{-1}), radish and corn (NOEC at concentration 7.5 mg L^{-1}).[1465] Ag is very toxic to heterotrophic bacteria and is widely used as an aseptic substance. However, some bacteria (e.g., *Thiobacillus forroxidans*) are capable of accumulating great amounts of Ag.[1430]

Wallace et al.[841] wrote that about 5 ppm Ag in the tops and above 1500 ppm in the roots of bush beans (DW) greatly reduced yields, but the plants grew without symptoms of toxicity. Ozoliniya[1109] on the other hand reported that 10 ppb Ag in the nutrient solution stimulated the growth of grass roots without producing a higher root mass. This author speculated that some cations (e.g., Ag, Co, and Cu) can indirectly change cell metabolism, resulting in a higher growth rate of cells. As described by Hendrix and Higinbotham,[315] Ag can substitute for K^+ sites in membranes and thus inhibit the absorption of other cations by roots. Ag compounds are known to precipitate bacterial proteins as well as to form insoluble complexes with ribonucleic acids.[856] Ag ions have a great affinity for binding sulfhydryl groups of some organic compounds.

VII. GOLD

A. Soils

Au is a rare element in the Earth's crust and its average concentration in rocks does not exceed the order of magnitude 0.00X ppm (Table 45). Au is relatively stable in hypergenic zones; however, under certain weathering conditions, it is known to form several complex ions, $AuCl_2^{2-}$, $AuBr_4^-$, AuI_2^-, $Au(CN)_2^-$, $Au(CNS)_4^-$, $Au(S_2O_3)_2^{3-}$ that are readily mobile. However, Au seems to be transported most often in the form of organometallic compounds or chelates.[97] Thus, the chemistry of Au in soils is essentially a chemistry of complex compounds since no simple Au cations exist in soil solutions.[453]

Lakin et al.[453] studied Au distribution in soil profiles and showed that, depending on the origin of soil material and its weathering stage, Au can be present in fine soil particulates or in cobbles and pebbles, Au is most often enriched in the humus layer because it can act as a reductant and precipitation medium for mobile forms of Au. However, distribution of Au within soil profiles may follow different trends, depending on its content in parent rocks.

There is a relative paucity of information on the Au content of soils. The Au status in normal soils may be established to be within the range from 0.6–20 ppb.[1313] Roslakov[664] gave the range of background contents of Au in soils as ranging from 0.8 to 8.0 ppb, with the greatest amounts in chernozems and kastanozems. Lakin et al.[453] reported that in mineralized areas, Au in forest mull ranged from 0.05 to 5.0 ppm, while mineral-size fractions contained from 0.04 to 0.44 ppm Au. Soils from the Au mine region in New Zealand contain 30 to 48 ppb of this metal.[1544]

B. Plants

Plants can absorb Au in soluble forms, and when Au enters the root vascular systems of plants, it can be easily transported to the tops. In reducing media, however, Au precipitates on the cell surface and thus inhibits membrane permeability.

Root exudates of cyanogenic plants are known to dissolve Au. The ability of microorganisms to solubilize elemental Au is still being discussed, but findings were not clear-cut.[1042a] Cyanogenic plants and some deciduous trees are able to accumulate even greater than 10 ppm Au (DW).[453,711] Horsetail is also known as a good indicator for Au; however, Cannon et al.[120] reported Au to be in the range of 0.1 to 0.5 ppm (AW) in horsetail species from Alaska, and only slightly higher Au concentrations were found in plant samples from mineralized areas. Various plant species collected from mineralized areas of British Columbia contained from 0.7 to 6.5 ppm Au (DW), and the herbaceous plant *Phacelia sericea* (family Hydrophyllaceae) appeared to be the best Au accumulator.[263] Data reviewed by Shacklette et al.[710] indicate that the Au content of plants ranges from 0.0005 to 125 ppm (AW). All anomalous high Au contents of plants are reported for plants of mineralized areas. Williams et al.[1544] reported a broad range of Au, from 224 to 7450 ppm, in lichens from the vicinity of an Au mine in New Zealand.

Oakes et al.[574] found Au in fruits and vegetables in the range of 0.01 to 0.4 ppb (FW), while Bowen[94] reported 1 to 40 ppb (DW) for other vascular plants. According to Ozoliniya and Kiunke,[588] Au in barley and flax is detectable only in the roots, in the range of 14 to 22 ppb (DW). After Girling et al.,[263] background Au concentrations are typically <1 ppb (DW) in vegetation. Several plant species are relatively resistant to higher Au concentrations in tissues. Au toxicity leads to necrosis and wilting by loss of turgidity in leaves.

CHAPTER 7

Elements of Group II

I. INTRODUCTION

Trace elements of Group Ia (new group 2) belong to the alkaline earths (Be, Sr, and Ba) and behave similarly to Ca and Mg. The microcations favor coordination with oxygen donors and do not usually form complex ions species. The Sr and Ba cations are more similar to Ca than to Mg, and Sr^{2+} in particulars very close in size to Ca^{2+}. A characteristic of these cations is the small ionic radius and high charge:radius ratio. These cations can replace each other, while the small size Be prevents their replacement by other ions. The common characteristic of the alkaline earths is their association with the carbon cycle; therefore, the processes of solution of hydrogen carbonates and the precipitation of carbonates strongly control the behavior of these metals in the terrestrial environment. Be in the terrestrial environment is more susceptible to hydrolysis and complexation processes than other elements of this group.

Group IIb (new group 12) is composed of three metals of the transition series—Zn, Cd, and Hg. They have comparatively high electronegativity values and easily form bonds with nonmetals of significant covalent character. They occur most often as divalent cations and show a great affinity to combine with S anions and with several organic compounds; thus, they are all of great importance in biochemistry. They are also known to form inorganic complex ions. Unlike the sulfides of the elements of Group IIa, the sulfides of Zn, Cd, and Hg are insoluble in water. However, the compounds of Zn and Cd immediately hydrolyze, but the corresponding compounds of Hg are rather resistant to hydrolysis. The three metals are all relatively mobile in the Earth's surface and their cycling may be highly modified by their accumulation by plants and organic debris.

II. BERYLLIUM

A. Soils

Be, the lightest of the alkaline earths, although widely distributed, exists in relatively small quantities, comprising less than 10 ppm of the major rock types. This metal is likely to concentrate in the acid magmatic rocks, and is associated with micas and some dark minerals. Its concentration in argillaceous sediments and shales is also enhanced and ranges from 2 to 6 ppm (Table 59). During rock weathering, Be usually remains in the residuum and resembles Al in its geochemical nature; however, its behavior is much different in various environments because of its small size, relatively high ionization, and electronegativity.

Be occurs most often as the divalent cation, but its complex ions are also known—$(BeO_2)^{2-}$, $(Be_2O_3)^{2-}$, $(BeO)^{6-}$, and $(Be_2O)^{2+}$. Thus, Be is present in soils primarily in oxidic-bonded forms. In the alkaline environment, Be forms complex anions such as $Be(OH)CO_3^-$ and $Be(CO_3)_2^{2-}$.

Table 59 Beryllium, Strontium, Barium, Zinc, Cadmium, and Mercury in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock Type	Be	Sr	Ba	Zn	Cd	Hg
Magmatic Rocks						
Ultramafic rocks						
Dunites, peridotites, pyroxenites	0.X	2–20	0.5–25.0	40–60	0.03–0.05	0.0X
Mafic rocks						
Basalts, gabbros	0.3–1.0	140–460	250–400	80–120	0.13–0.22	0.0X
Intermediate rocks						
Diorites, syenites	1.0–1.8	300–600	600–1000	40–100	0.13	0.0X
Acid rocks						
Granites, gneisses	2–5	60–300	400–850	40–60	0.09–0.20	0.08
Acid rocks (volcanic)						
Rhyolites, trachytes, dacites	5.0–6.5	90–400	600–1200	40–100	0.05–0.20	0.0X
Sedimentary Rocks						
Argillaceous sediments	2–6	300–450	500–800	80–120	0.30	0.20–0.40
Shales	2–5	300	500–800	80–120	0.22–0.30	0.18–0.40
Sandstones	0.2–1.0	20–140	100–320	15–30	0.05	0.04–0.10
Limestones, dolomites	0.2–2.0	450–600	50–200	10–25	0.035	0.04–0.05

Table 60 Beryllium Content of Surface Soils of Different Countries (ppm DW)

Country	Range	Mean	Ref.
Brazil	0.44–1.69	0.92	927
Canada	0.10–0.89	0.35	244
Czech Republic	4.01–4.55	4.28	1136
Great Britain	—	2.7	818
Indonesia	0.31–1.22	0.7	927
India	0.33–0.77	0.48	1225a
Japan	0.27–1.95	1.17	928
New Zealand	0.82–1.33	0.99	927
Thailand	0.20–5.50	1.46	927
U.S.	0.04–2.54	0.54	976
U.S. (Alaska)	<1–7	1.5	1012
Russia	1.1–1.6	1.3	1123
Russia	1.01–2.73	—	927
Yugoslavia	2.49–4.97	3.52	927

The abundance of Be in surface soils has not been investigated on a large scale. The most intensive studies made by Shacklette and Boerngen[706] for soils of the conterminous U.S. gave the mean content of 1.6 ppm for various soil units (Table 60). In soils of Poland, Be ranges from <1 to 5 ppm,[1357] and geometric means range within 0.3 to 0.7 ppm and show a positive correlation with the content of clay fraction (Table 20). Govindaraju[1313] reported the Be content in reference soils from different countries to range from 1.4 to 4.4. ppm. Asami[925] found in 27 unpolluted surface soils of Japan a Be range from 0.27 to 1.95 ppm, average 1.17 ppm. Asami and Fukazawa[928] reported background levels of Be for andosols from 0.59 to 1.57 ppm, and for calcareous soils from 0.67 to 2.47 ppm. The mean content of Be in topsoils of the other countries varies from 0.35 to 3.52 ppm (Table 60).

Organic substances are known to bind Be easily; therefore, Be is enriched in some coals and accumulates in organic soil horizons. Be may substitute for Al and for some divalent cations, and therefore is strongly bound by montmorillonitic clays. Hädrich et al.[298] reported the range in Be concentrations in soil solutions as 0.4 to 1.0 $\mu g\ L^{-1}$. Although Be appears to be rather immobile in soils, its readily soluble salts, such as $BeCl_2$ and $BeSo_4$, can be available and therefore toxic to plants. The distribution of Be in the soil profiles also reflects the leaching processes of the element and shows its accumulation in the subsoil layers. The concentration of Be in soil solutions varies from 0.21 $\mu g\ L^{-1}$ in surface soil layer to 1.1 $\mu g\ L^{-1}$ in mother material (leucogranite). Be is highly soluble under the condition of acid (pH 3.4) forest soil.[1376] This may have serious environmental consequences in temperate climate regions.

Due to some new technologies that employ Be (rocket fuels and light, hard, and high corrosion-resistant alloys), as well as to coal combustion, there is concern that Be may be increasing in agricultural soils. There is not much information on Be in contaminated soils, which were reported to range from 15 to 50 ppm Be in the vicinity of smelters and coal power stations in Poland, while the control soils contained less than 1 ppm Be.[592] The report of studies conducted by Asami[925] in the neighborhood of Be factories in Japan showed that topsoils less than 500 m from the pollution source contain on average up to 8.56 ppm Be (range 6.5–55.0 ppm). These concentrations, measured in 1976, showed a significant increase of Be pollution when compared with earlier data.

Among the seven isotopes of Be, only ^{9}Be is stable. The others, mainly ^{7}Be and ^{10}Be, are produced by nuclear reactions induced either by cosmic rays or by accelerator mass spectrometry. As Bourles[1240] described, both radionuclides reveal a great affinity for either inorganic or organic particles of soil. ^{10}Be is especially likely to be concentrated in organic-rich soil.

B. Plants

Be apparently is easily taken up by plants when it occurs in soluble forms in soils. Its concentration in plants under natural conditions is reported to range from 0.001 to 0.4 ppm (DW) and to range from <2 to 100 ppm in plant ash.

Be concentrations as high as 250 ppm (AW) are reported for an accumulator plant (*Vaccinium myrtillus*).[855] Some plant species in the Leguminosae and Cruciferae families have a pronounced ability to accumulate Be, particularly in their root tissue.[283]

Although Be is known to be concentrated mainly in roots, Krampitz[425] reported a relatively high Be content in lettuce leaves (0.033 ppm DW) and tomato fruits (0.24 ppm DW), and Bowen[94] stated that Be in lichens and bryophytes ranged from 0.04 to 0.9 ppm (DW). Padzik and Wlodek[592] gave the content of Be in grass from an industrial area as 0.19 ppm (DW). Bohn and Seekamp[84] found that plant Be increased up to 20 ppm (DW) at 100 ppm Be addition to the soil.

Vaessen and Szteke[1527] broadly reviewed Be concentrations in plant food of several countries. The range of mean values for Be in vegetables is 0.0002 to 0.077 ppm (FW), the lowest for tomatoes and the highest for parsley roots. Reported contents of Be in various berries have not exceeded 0.002 ppm (FW).

Be absorption mechanisms of plants seem to be similar to those involved in the uptake of Mg^{2+} and Ca^{2+}. However, these elements have antagonistic interactions, and Be is able to replace Mg^{2+} in some plants. Gough et al.[279] and Krampitz[425] reported stimulating effects of the dilute solution of $Be(NO_3)_2$ on growth of several plant species, microorganisms in particular (*Aspergillus niger*). Biochemical mechanisms of this phenomenon, however, are not clear.

On the other hand, the toxicity of Be to plants has been frequently reported. Toxic Be concentrations in mature leaves range most often from 10 to 50 ppm (DW). This range is highly variable for each plant species and growth condition. Be contents in willow leaves grown in the Sudeten Mountains and of Turkish hazel grown in Wroclaw (Poland) varies from 4 to 39 ppm, and from 7 to 32 ppm, respectively. The increased concentrations of Be indicate polluted sites and periods of high industrial emissions.[1336,1477]

Relatively low Be concentrations in solution, ranging from 2 to 16 ppm or from 10^{-3} to 10^{-4} M Be^{2+}, is highly toxic to plants. Gettier and Adriano[1009] observed that collard and wheat root length were decreased 50% by Be at concentrations of 5 to 10 ppm in the nutrient solution. Most Be taken up by plants remains in the roots and only a very small proportion of absorbed Be is translocated to above-ground plant parts. Visual symptoms of the Be toxicity, aside from reduced growth, are not evident, but

Be concentrations greater than 8 mg Be L^{-1} totally inhibited seed germination. Be is known to inhibit the germination of seeds and the uptake of Ca and Mg by roots, to have diverse effects on P absorption, and to degrade some proteins and enzymes. These processes, however, are not fully understood. Although specific symptoms of Be toxicity to plants are not known, the common symptoms are brown, retarded roots and stunted foliage. Although at present there is no evidence that Be in food plants can be a health risk to man, more data are needed to evaluate the risk.[285]

III. STRONTIUM

A. Soils

Sr is a relatively common trace element in the Earth's crust and is likely to concentrate in intermediate magmatic rocks and in carbonate sediments (Table 59). Geochemical and biochemical characteristics of Sr are similar to those of Ca; thus, Sr is very often associated with Ca and, to a lesser extent with Mg, in the terrestrial environment. The Sr to Ca ratio seems to be relatively stable in the biosphere and therefore is commonly used for the identification of built-up concentrations of Sr in a particular environment. A Ca:Sr ratio less than 8 indicates a possible toxicity of Sr. During the formation of calcareous and sulfuric sediments, Sr is mobilized as easily soluble strontianite ($SrCO_3$), and later deposited as celestite ($SrSo_4$). The concentration of this mineral in terrestrial material is an environmental risk.[1445]

Sr is easily mobilized during weathering, especially in oxidizing acid environments, and then it is incorporated in clay minerals and strongly fixed by organic matter, but most Sr is precipitated as biogenic carbonates, largely in the form of invertebrate shell material. This element is known to occur mainly as Sr^{2+} ions; however, its chelated forms play an important role in cycling, which is closely associated with Ca cycling.

Sr content of soils is highly controlled by parent rocks and climate, and therefore its concentrations range in surface horizons from 715 to 1000 ppm (Table 61), being highest in Russian chernozems and in forest soils. Soils derived from glacial till under the humid climate of Denmark are reported to be very poor in Sr, whereas these kinds of soils from the U.S. are relatively rich in this element (Table 61). Mean contents of Sr as calculated for American topsoils range from 110 to 445 ppm, being the highest in desert soils and soils derived from magmatic rocks. Sr mean content for the worldwide soil units is the highest for cambisols (210 pm) and the lowest for podzols (87 ppm) (Table 9). Govindaraju[1313] reported that the Sr contents in reference soils from China range from 26 to 150 ppm, and in soils from the vicinity of a polymetallic ore field from 180 to 380 ppm. Aqua regia-soluble Sr in Venezuelan surface soils varies from 13 to 39 ppm (geometric mean values).[1227] The mean content of Sr in surface mineral soils of Poland varies from 10 to 24 ppm,[1357] whereas HCl (1:4) soluble Sr averages less than 10 ppm, and above 100 ppm in some calcareous soils and soils in industrial regions of Poland.[1390]

The Sr distribution in soil profiles follows the general trends of soil solution circulation. However, it may also be irregular, depending on soil properties. In acid soils, Sr is highly leached down the profile. In organic surface layers of soils in Norway, an enrichment in Sr content as compared to C horizons is explained as evidence of the atmospheric input of sea-salt.[1505] In calcareous soils, Sr may be replaced by various cations and, in particular, hydrogen ions. Displacement of Sr by Ca solutions has practical implications in the reclamation of contaminated soils.[450]

Sr exists in the geologic formations in several isotopic forms, of which ^{88}Sr is the most abundant. The ^{87}Sr:^{86}Sr ratio is used in age determinations since ^{87}Rb decays to ^{87}Sr. ^{90}Sr is produced in many nuclear processes and is considered to be one of the most biologically hazardous radioactive elements for man. Since Ca and Sr are known to be the carrier elements for ^{90}Sr, the cycling of ^{90}Sr is related to that of Ca and Sr.

Numerous studies have been carried out on ^{90}Sr in biological environments. Several authors stated that ^{90}Sr as a pollutant is easily mobile in light soils and therefore is readily taken up by

Table 61 Strontium Content of Surface Soil of Different (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	—	118	196
	New Zealand	350–570[a]	—	861
	U.S.	5–1000	125	706
Loess and silty soils	New Zealand	220–380[a]	—	861
	U.S.	20–1000	305	706
Loamy and clay soils	New Zealand	18–86[a]	—	861
	U.S.	15–300	120	706
	Former S.U.	280–310	295	714
Soils on glacial till	Denmark	—	14.7	801
Solonetz	Former S.U.	—	181	1031
Kastanozems	Former S.U.	70–280	175	714, 1031
Chernozems	Former S.U.	73–147	93	1031, 1123
	U.S.	70–500	170	706
Prairien and meadow soils	Former S.U.	150–500	300	714
Rendzinas	U.S.	15–1000	195	706
Histosols and other organic soils	Denmark	—	92	801
	U.S.	5–300	110	706
Forest soils	Former S.U.	—	675	714
	U.S.	20–500	150	706
Various soils	Canada	30–500[b]	210	521
	Denmark	—	17.2	801
	Great Britain	—	261	818
	U.S.	7–1000	200	706

[a] Soil derived from basalts and andesites.

[b] Data for whole soil profiles.

plants.[603,676,791] Pavlotskaya et al.[604] reported the easy coprecipitation of ^{90}Sr by hydrous Fe oxides, which leads to its accumulation in Fe-rich soil horizons.

The distribution of ^{90}Sr, about a decade (1986–1995) after the Chernobyl accident, varies in the territory of Belarus, from 1.64 to 109 kBq m^{-2}. As Kagan and Kadatsky[1360] reported, ^{90}Sr inventories in soils vary from so called "global impact effect" up to 70 times the pre-accident value. The migration of this radionuclide in soil profiles is relatively high, especially in the floodplain where up to 30% of its content in the top soil layer is below 5 cm depth. In topsoil horizons along the Prypec River in Belarus, ^{90}Sr is concentrated up to 340 Bq kg^{-1}, and is reported to be also highly mobile.[1384]

B. Plants

The Sr concentration in plants is highly variable and is reported to range from <1 to 10,000 (DW) and to 15,000 ppm (AW). Its common amounts, however, calculated as the mean for different food and feed plants, range from about 10 to 1500 ppm (DW) (Table 62). The lowest mean contents of Sr were found in fruits, grains, and potato tubers, whereas legume herbage contained from 219 to 662 ppm (DW). Bowen gave the broad range in Sr concentrations in lichens as 0.8 to 250 ppm (DW). In the European forest ecosystems of Russia and Germany, the following concentrations of Sr in blueberries are reported: 4.5 to 5.5 ppm for Russia (near Moscow), and 2.9 to 3.9 ppm for Germany.[1400]

Sr uptake by roots is apparently related to both the mechanisms of mass-flow and exchange diffusion.[209] The Ca to Sr ratio of uptake was proposed by some authors to determine the source of these cations and the rate of their uptake. Wallace and Romney[842] reported that Sr is not very readily transported from roots to shoots; however, the highest concentrations of Sr are often reported for tops of plants.[710]

Interactions between Sr and Ca are complex, for they may compete with each other, but Sr usually cannot replace Ca in biochemical functions. Weinberg[856] reported that the enzyme amylase with Sr^{2+} substituted for Ca^{2+} had full activity, but varied in some physical properties. Liming of soil may have both inhibiting and stimulating effects, depending on soil and plant factors.[450] However, in bush beans

Table 62 Mean Levels and Ranges of Strontium in Food and Feed Plants (ppm DW)[131,381,514,574,705,853]

Plant	Tissue Sample	Range	Mean
Wheat	Grains	0.48–2.3	1.5
Oats	Grains	1.8–3.2	2.5
	Green tops	9–31	20
Corn	Grains	0.06–0.4	—
Lettuce	Leaves	—	74
Spinach	Leaves	45–70	—
Cabbage	Leaves	1.2–150	45
Bean	Pods	1.5–67	18
Soybean	Leaves	58–89	—
Carrot	Roots	1.5–131	25
Onion	Bulbs	10–88	50
Potato	Tubers	—	2.6
Tomato	Fruits	0.4–91	9
Apple	Fruits	0.5–1.7	0.9[a]
Orange	Fruits	—	0.5[a]
Clover	Tops	95–850	219
Lucerne (alfalfa)	Tops	50–1500	662
Grass	Tops	6–37	24

[a] FW basis.

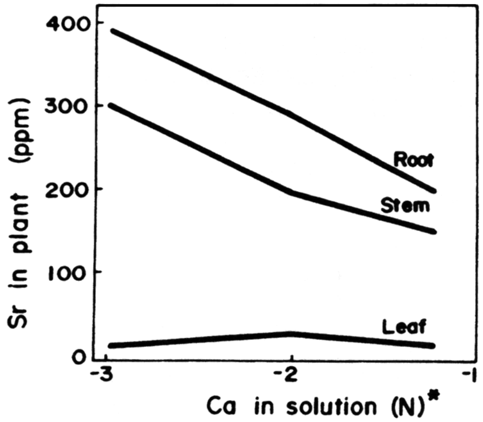

Figure 39 Effects of Ca on Sr distribution in bush beans exposed 48 hr to 10^{-3} *N* Sr in solution culture.* Ca normality is given in powers of ten.[842]

grown in solution culture, Ca decreased Sr content, particularly in root and stem (Figure 39). Reported interactions between Sr and P apparently are related to processes in soil; however, opinions vary as to the effects of P on Sr adsorption by plants.[175,439]

There are not many reports of Sr toxicity in plants, and plants vary in their tolerance to this element. Shacklette et al.[710] gave the toxic Sr level for plants as 30 ppm (AW). There is no evidence that stable Sr at levels present in the biosphere has any deleterious effects on man and animals; however, the accumulation of the radionuclide ^{90}Sr in food and feedstuffs is of the greatest environmental concern.

^{90}Sr is relatively easily taken up by plants, but its availability may be inhibited by the application of Ca, Mg, K, and Na to soils. Beans grown on soil treated with ^{90}Sr accumulated up to 565 nCi g^{-1} (DW) in leaves, while in grains, only 24 nCi g^{-1} (DW).[290] ^{90}Sr in oats in a similar experiment ranged in straw from 17 to 137 nCi g^{-1} (DW) and in grains ranged from 1 to 11 nCi g^{-1} (DW).[291,292] Alamo switchgrass can accumulate up to 44% of the total amount of ^{90}Sr from the growth media after the first five harvests, and the uptake of this radionuclide is correlated curvilinearly with subratum.[1292] Also, *Amaranthus* species are reported to be effective in phytoextraction of this nuclide from soils in the Chernobyl exclusion zone.[1283]

IV. BARIUM

A. Soils

In the Earth's crust, Ba is likely to concentrate in intermediate and acid magmatic rocks and commonly ranges in concentration from 400 to 1200 ppm (Table 59). In geochemical processes, Ba is usually associated with K^+ due to their very similar ionic radii (Table 12), and therefore its occurrence is linked with alkali feldspar and biotite.

Ba released by weathering is not very mobile because it is easily precipitated as sulfates and carbonates, is strongly adsorbed by clays, is concentrated in Mn and P concretions, and is specifically sorbed onto oxides and hydroxides (Tables 22 and 23). Ba easily displaces other sorbed alkaline earth metals from some oxides (MnO_2, TiO_2), but on the other hand is displaced from Al_2O_3 by alkaline earth metals (Be, Sr.)[948] Varnishes formed at the surface of aridic soils always have an enrichment in Ba. In some tropical soils, Ba occurs in the mobile form of hollandite, $Ba_2Mn_8O_{16}$, and is easily available to plants. In soils of temperate humid climate zones, Ba is likely to be fixed by Fe-oxides and become immobile.

Ba in topsoils and rocks has similar ranges in concentration (Table 63). The reported range for soil Ba, on a world scale, is from 19 to 2368 ppm. Ba distribution among the soil units shows much lower contents in histosols (mean 175 ppm) than in the other soils (range of means from 330 to 520 ppm) (Table 9). Govindaraju[1313] reported the Ba content in reference soils from China to range from 180 to 1210 ppm, and for soils of the U.S. from 290 to 2240 ppm. The high concentration of Ba in Chinese soils is related to the Au ore field.

Table 63 Barium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	—	207	196
	New Zealand	270–780[a]	—	861
	U.S.	20–1500	400	706
	Belarus	180–260	220	493
Loess and silty soils	New Zealand	240–590[a]	—	861
	U.S.	200–1500	675	706
	Belarus	—	960	493
Loamy and clay soils	New Zealand	19–200[a]	—	861
	U.S.	150–1500	535	706
	Belarus	—	240	493
	Bulgaria	—	402	558
Fluvisols	Belarus	—	240	493
	Bulgaria	—	691	558
Rendzinas	U.S.	150–1500	520	706
Chernozems	Russia	475–620	525	4, 1123
	Bulgaria	—	458	558
	U.S.	100–1000	595	706
Histosols and other organic soils	Belarus	—	84	493
	U.S.	10–700	265	706
Forest soils	Russia	—	560	4
	U.S.	150–2000	505	706
	Bulgaria	397–850	631	558
Various soils	Bulgaria	492–2368	838	558
	Canada	262–867	669	409
	Great Britain	—	672	818

[a] Soils derived from basalts and andesites.

Table 64 Mean Levels and Ranges of Barium in Food and Feed Plants (ppm)[267,381,574,705]

Plant	Tissue Sample	DW Basis Range	DW Basis Mean	FW Basis Mean
Cereal	Grains	4.2–6.6	5.5	—
	Green tops	132–181	160	—
Sweet Corn	Grains	—	0.034	—
Snap bean	Pods	—	7	0.4
	Seeds	1–15	8	—
Cabbage	Leaves	—	4.8	1.3
Lettuce	Leaves	—	9.4	0.5
Carrot	Roots	2–50	13	0.14
Onion	Bulbs	3–75	12	—
Potato	Tubers	1.3–35	5	0.7–1.4
Tomato	Fruits	—	2	—
Apple	Fruits	—	1.4	0.03
Orange	Fruits	—	3.1	0.17
Clover	Tops	142–198	170	—
Lucerne (alfalfa)	Tops	—	100	—

Ba in soils may be easily mobilized under different conditions; therefore, its concentrations in soil solutions show considerable variation, from 43 μg L^{-1} (loamy soil) to 307 μg L^{-1} (sandy soil).[1169] Turski et al.[1169] found that the input of Ba from aerial sources and P-fertilizers increases its output (leaching and plant uptake). Thus, the Ba budget in rural soils shows a steady increase.

B. Plants

Although Ba is reported to be commonly present in plants, it apparently is not an essential component of plant tissues. The Ba content ranges from 1 to 198 ppm (DW), being the highest in leaves of cereal and legumes and the lowest in grains and fruits (Table 64). The highest concentrations of Ba, up to $>$10,000 ppm (DW), are reported to be in different trees and shrubs and in Brazil nuts.[710] In the European forest ecosystems of Russia and Germany, the following concentrations of Ba in blueberries are reported: 8 to 60 ppm for Russia (near Moscow), and 5 to 31 ppm for Germany.[1400]

Plants may take up Ba quite easily from acid soils; Weinberg[856] reported a high affinity of Ba^{2+} to be bound to the surface of yeast. There are, however, only a few reports on toxic Ba concentrations in plants. Chaudry et al.[134] gave 1 to 2% (DW) Ba in plants as highly toxic, while Brooks (see Shacklette et al.)[710] stated that 220 ppm (AW) is moderately toxic.

Possible toxicity of Ba to plants may be greatly reduced by the addition of Ca, Mg, and S salts to the growth medium. Antagonistic interactions between these elements and Ba (Table 43) may occur in both plant tissues and soils.

V. RADIUM

Ra occurs in the environment as radioactive nuclides of which ^{224}Ra, ^{226}Ra, and ^{228}Ra are the common products of the uranium and thorium decay chains.[226] Ra is the most stable and relatively frequent radionuclide in the biosphere. The geochemistry of ^{226}Ra is entirely governed by ^{230}Th.

Bowen[94] reported ^{226}Ra to range in rocks from 0.6 to 1.1 ng kg^{-1} and in soil to be 0.8 ng kg^{1}. This radionuclide in vegetation ranged from 0.03 to 1.6 ng kg^{-1} (DW).

Megumi and Mamuro[529] studied the concentrations of U-series nuclides in soils derived from granites and found that they increase with decreases in particle size (Figure 40). They reported that divalent Ra cations seem to be strongly absorbed by hydrous oxides of Mn and Fe.

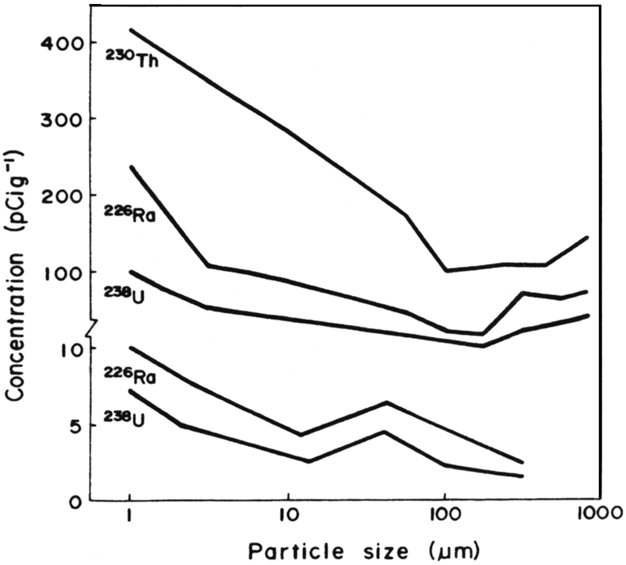

Figure 40 Concentration of some radionuclides in soil particle size from the B horizon of soils derived from two different granites in Japan.[529]

Taskayev et al.[773] reported stable complexing of ^{226}Ra in soils where this radionuclide ranged from 36 to 351 pg g^{-1}. ^{226}Ra was most mobile under very acid conditions and its solubility ranged from about 1 to 10% of its content in the surface soils.

The ^{226}Ra content of the surface soils is higher than that of deeper soil horizons and this is because the radionuclide has recently been added to soils from anthropogenic sources. As Martell[509] stated, P and K fertilizers increased the ^{226}Ra in the plowed layer of soils, and according to data presented by Moore and Poet,[550] the manufacturing of P fertilizers and cement, as well as coal combustion, are the main sources of the radionuclides of Ra.

VI. ZINC

A. Soils

Zn seems to be distributed rather uniformly in the magmatic rocks, and only its slight increase in mafic rocks (80 to 120 ppm) and its slight decrease in acid rocks (40 to 60 ppm) is observed (Table 59). The Zn concentration in argillaceous sediments and shales is enhanced, ranging from 80 to 120 ppm; while in sandstones and carboniferous rocks, concentrations of this metal range from 10 to 30 ppm. The Zn occurs chiefly as single sulfides (ZnS), but is also known to substitute for Mg^{2+} in silicates.

The solubilization of Zn minerals during weathering produces mobile Zn^{2+}, especially in acid, oxidizing environments. Zn is, however, also easily adsorbed by mineral and organic components and thus, in most soil types, its accumulation in the surface horizons is observed (Figure 41).

Mean total Zn contents in surface soils of different countries and of the U.S. range from 17 to 125 ppm (Table 65). Thus, these values may be considered as background Zn contents. The highest means were reported for some alluvial soils, solonchaks, and rendzimas, while the lowest values were for light mineral and light organic soils (Table 9). Grand mean Zn for worldwide soils may be calculated as 64 ppm. Geometric means for Zn in all mineral soils of Poland differ significantly for various textural groups; for example, for sands—33 ppm; for light loams—52 ppm; and for heavy loams—80 ppm (Table 49). In agricultural soils of the U.S., the geometric mean for Zn is 42.9 ppm, within the range of <3 to 264 ppm as given by Holmgren et al.,[1329] and the median Zn content, as presented by

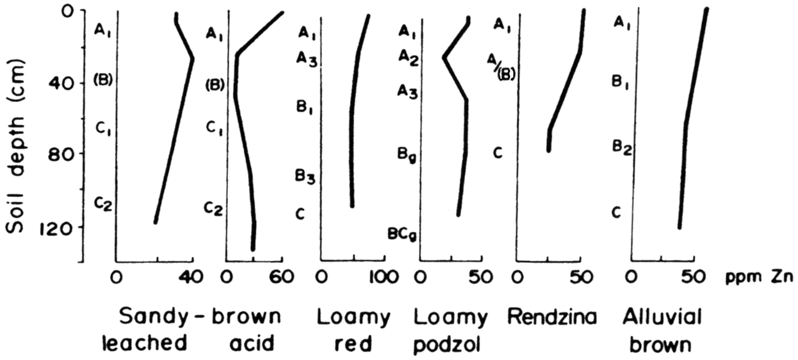

Figure 41 Distribution of Zn in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

White et al.,[1541] varies slightly depending on the source of data and is 50 ppm (USGS) or 54 ppm (USDA).

The Zn balance in surface soils of different ecosystems shows that the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass (Table 17). Only in nonpolluted forest regions of Sweden is the discharge of Zn by water flux reported to be higher than its atmospheric input.[816]

1. Reactions with Soil Components

The most common and mobile Zn in soil is believed to be in forms of free and complexed ions in soil solutions, but several other ionic species that occur as nonspecifically and specifically adsorbed cations can also be easily mobilized in soils (Figure 42). The important factors controlling the mobility of Zn in soils are very similar to those listed for Cu, but Zn appears to occur in more readily soluble forms. Many studies of Zn adsorption and retention in soils were reviewed by Lindsay,[476] and it has been shown that clays and soil organic matter are capable of holding Zn quite strongly; thus the solubility of Zn in soils is less than that of $Zn(OH)_2$, $ZnCO_3$, and $Zn(PO_4)$ in pure experimental systems.

Processes involved in Zn adsorption are not yet completely understood; however, some generalizations can be made from studies reported by Lindsay,[475] Farrah and Pickering,[228] Peneva,[605a] Kuo and Mikkelsen,[440] and Wada and Abd-Elfattah.[834] There are two different mechanisms of Zn adsorption: one in acid media related to cation exchange sites, and the other in alkaline media that is considered to be chemisorption and is highly influenced by organic ligands.

McBride and Blasiak[519] stated that nucleation of Zn hydroxide on clay surfaces may produce the strongly pH-dependent retention of Zn in soils (Figure 43). The adsorption of Zn^{2+} can be reduced at lower pH (<7) by competing cations and this results in easy mobilization and leaching of Zn from light acid soils (Table 15). At higher pH values, while an increase of organic compounds in soil solution becomes more evident, Zn-organic complexes may also account for the solubility of this metal (Figure 43). In sandy, acid soils, on the other hand, organic matter seems to be the most important soil component for binding Zn, while oxides (hydro) of Al, Fe, and Mn appear to be of minor importance.

As Zyrin et al.[911] reported, Zn in soils is associated mainly with hydrous Fe and Al oxides (14 to 38% of total Zn) and with clay minerals (24 to 63%), while its readily mobile fractions and its organic complexes make, respectively, 1 to 20 and 1.5 to 2.3%. Recent findings[1355] have supported these calculations, indicating that the clay fraction controls up to about 60% of Zn distribution in soils (Figure 44).

Table 65 Zinc Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	39–86	—	792
	New Zealand	14–146	42	870
	Poland	5–220	24	378, 382
	Romania	25–188	61	1127
	U.S.	5–164	40	706
	Russia	3.5–57	31	271, 900
	Germany	40–76	—	689
Loess and silty soils	New Zealand	—	61	870
	Poland	17–127	47	378, 382
	Romania	—	73	42
	U.S.	20–109	58.5	706
	Russia	40–55	48	271
	Germany	58–100	—	689
Loamy and clay soils	Canada	15–20	17	692
	Great Britain	—	70	876
	New Zealand	31–177	79	870
	Poland	13–362	67.5	378, 382
	Romania	37–101	75	1127
	U.S.	20–220	67	706
	Russia	9–77	35	271, 900
	Germany	40–50	—	689
Soils on glacial till	Denmark	—	28	801
	Poland	19–52	40	974
Fluvisols	Bulgaria	—	62	752
	Great Britain	67–180	125	166, 786
	New Zealand	53–67	60	870
	Poland	55–124	84.5	378
	Russia	34–49	42	900
Gleysols	Australia	31–62	—	792
	Chad	25–300	—	39
	Great Britain	—	54	876
	New Zealand	60–84	73	870
	Poland	13–98	50.5	378
	Russia	26.5–79	52.5	900
Rendzinas	Poland	58–150	77	378, 382
	China	54–570	236	1124
	U.S.	10–106	50	706
	Russia	23–71	47	271, 900
	Germany	—	100	689
Kastanozems and brown soils	Australia	29–79	—	792
	Chad	25–100	—	39
	China	44–770	98	1068
	New Zealand	30–67	53.5	870
	Romania	27–113	57	1127
	Russia	32.5–54	43	343, 900
Ferralsols	Chad	25–145	—	39
	China	20–600	180	1068
	Israel	200–214	—	644
Solonchaks and solonetz	Bulgaria	39–63	—	752
	Chad	25–100	—	39
	New Zealand	54–68	62	870
	Russia	44–155	100	12, 900
Chernozems	Bulgaria	63–97	—	752
	Poland	33–82	61.5	378
	U.S	20–246	83.5	706
	Russia	39–82	57	712, 900

(*Continued*)

Table 65 Zinc Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Prairien and meadow soils	Bulgaria	88–98	—	752
	China	51–130	87	1068
	Former S.U.	31–192	105	12, 89, 271, 900
Histosols and other organic soils	Bulgaria	—	80	752
	Denmark	48–130	72.5	1, 801
	New Zealand	21–34	27	870
	Poland	13–250	60	382
	U.S.	5–108	34	706
	Russia	7.5–74	34	271, 900
Forest soils	Bulgaria	35–106	—	752
	China	—	85	225
	U.S.	25–155	45.7	218, 219
	Russia	42.5–118	71.5	900
Various soils	Bulgaria	39–99	65	541
	Canada	20–110	57	629
	Canada	10–200	74[a]	521
	Chad	25–90	—	39
	Denmark	—	31	801
	Great Britain	20–284	80	100, 786, 818, 876
	Japan	10–622	86	395
	Italy	16–157	68	946
	New Zealand	45–88	59	870
	Poland	3–762	46.6	1045
	Romania	35–115	61	43
	U.S.	13–300	73.5	706
	Russia	47–139	78	900

[a] Data for whole soil profiles.

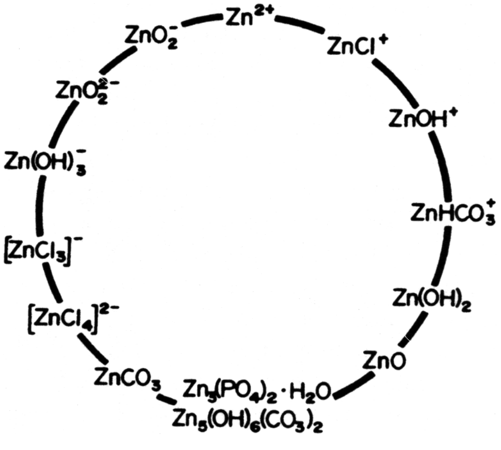

Figure 42 Ionic species and compounds of Zn occurring in soils.

Abd-Elfattah and Wada[2] found the highest selective adsorption of Zn by Fe oxides, halloysite, allophane, and imogolite and the lowest by montmorillonite. Thus, clay minerals, hydrous oxides, and pH are likely to be the most important factors controlling Zn solubility in soils, while organic complexing and precipitation of Zn as hydroxide, carbonate, and sulfide compounds appear to be of much lesser importance. Zn can also enter some layer lattice silicate structures (e.g., montmorillonite) and become very immobile.

Soil organic matter is known to be capable of bonding Zn in stable forms; therefore, the Zn accumulation in organic soil horizons and in some peats is observed. However, stability constants of Zn-organic matter in soils are relatively low, but a high proportion of Zn is bound to organic

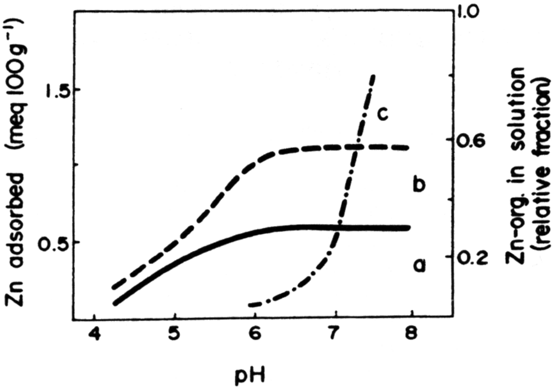

Figure 43 Influence of soil pH on adsorption of Zn at (a) 20 ppm and (b) 40 ppm Zn levels in initial solutions and on formation of soluble Zn-organic complexes in the solution of loamy silt soil (c).[519]

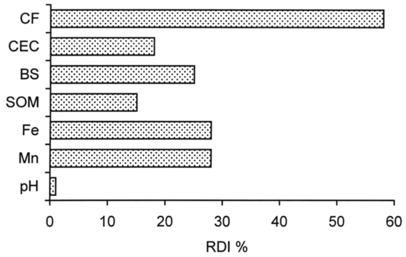

Figure 44 Relative explanation index (RDI) of statistically significant relationship between Zn and soil parameters in mineral soils at the 99% confidence level (N = 780). Soil parameters: CF—clay fraction <0.02 mm; CEC—cation exchange capacity; BS—base saturation; SOM—soil organic matter; Fe—total content; Mn—total content; pH—in water (soil:water ratio, 1:2.5).

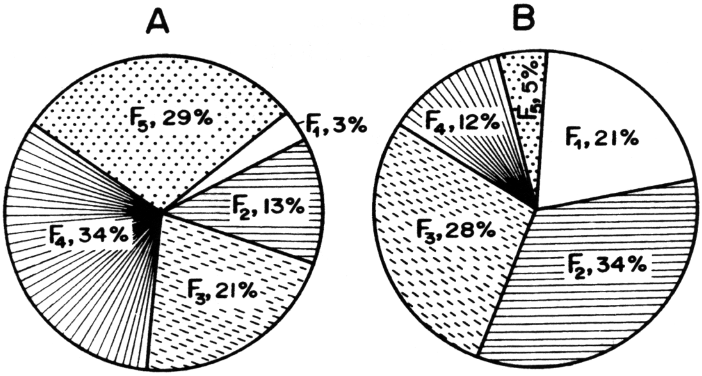

Figure 45 Variation in Zn species in soils under sludge application: (A) unsludged soil, (B) sludged soil. Zn species: (F_1) easily soluble; (F_2) exchangeable; (F_3) associated with hydrous oxides; (F_4) bound to organic matter; and (F_5) residual.[985]

matter in mineral soils. The addition of sewage sludges to these soils modifies the distribution pattern of Zn, increasing significantly two Zn species—easily soluble and exchangeable (Figure 45). Wada and Abd-Elfattah[834] gave the range in maximum Zn adsorption by different soils as 16 to 70 μeq g^{-1} for Ca-saturated samples. This finding supports several statements about Ca-exchange sites with high selectivities for Zn. Shukla et al.[721] reported, on the other hand, that the order of Zn adsorption in different cation-saturated soil was the following: $H < Ca \leq MG < K < Na$.

Zn is considered to be readily soluble relative to the other heavy metals in soils. The Zn concentrations in soil solutions range from 4 to 270 μg L^{-1}, depending on the soil and the techniques used for obtaining the solution (Table 16). Itoh et al.[341] reported a maximum of 17,000 μg Zn in

1 L of solution and this value is, apparently, for highly contaminated soils. However, in natural but very acid soils ($pH < 4$), Zn concentration in solutions was reported to average 7137 $\mu g\ L^{-1}$. The concentration of Zn in soil solutions of podzols of Taiga (Russia) varies from 20 to 350 $\mu g\ L^{-1}$ and is higher in the upper layer.[1426] Although Zn is highly soluble in solution of peaty soils, it occurs mainly in colloidal forms (up to 60% of total content). Zn anionic organic and inorganic complexes account for up to 40%, whereas cationic forms are present only below 10%.[1427]

Zn is most readily mobile and available in acid light mineral soils. As Norrish[570] stated, the Zn fraction associated with the Fe and Mn oxides is likely to be the most available to plants. Acid leaching is very active in Zn mobilization; thus, losses of this metal are observed in certain horizons, particularly of podsols and brown acid soils derived from sands (Figure 41).

Solubility and availability of Zn is negatively correlated with Ca-saturation and P compounds present in soils. This relationship may reflect both adsorption and precipitation processes, as well as interactions between these elements. However, soluble Zn-organic complexes and complex anionic forms of Zn (Figures 42 and 43) may account for the relative solubility and availability of Zn in soils with a high pH range. This is supported by Bloomfield,[81] who found that Zn was mobilized from the basic carbonates and from the oxides produced by aerobically decomposing plant material. Zn oxides added to a soil are easily transformed to other species, mainly carbonates.[1357] However, Zn in metallic and sulfide forms seems to be relatively stable in a specific condition of composted municipal solid waste.[1259] In soils heavily polluted with Zn, the formation of Zn-pyromorphite, $Zn_5(PO_4)_3OH$, was observed, mainly at the surface of grass roots, which suggests the impact of the rhizosphere on this process.[1263]

The immobilization of Zn in soils rich in Ca and P, in well-aerated soils with S compounds, and in soils containing enhanced amounts of certain Ca-saturated minerals such as allophane, imogolite, and montmorillonite, as well as hydrous oxides, has an important practical impact on the Zn deficiency of plants. Zn deficiencies most frequently result from management practices used during crop production (e.g., overliming, P fertilization, organic matter amendment).

2. Contamination of Soils

The anthropogenic sources of Zn are related, first of all, to the nonferric metal industry and then to agricultural practice. Contemporarily observed soil contamination with Zn has already brought Zn to an extremely high accumulation in topsoils in certain areas (Table 66). Additional problems related to Zn pollution are changes in the metal speciation. For example, in soil (loamy sand, pH 6.1, OM 1.25%) amended with Zn-enriched sewage sludge, an increase was observed of easily available Zn species from 3% to 21%, and weakly bound or exchangeable Zn species, from 21% to 34% of the total Zn content (Figure 45).

Calculating the first half-life of Zn in contaminated soils in lysimeters showed that Zn decrease was relatively rapid and that soil containing 2210 ppm Zn will reduce Zn content by half during 70 to 81 years.[395] These results, however, were reported for paddy soils with a long drainage period. Based on results of other experiments, the half-life of Zn as a pollutant in soil may be much longer. Amelioration of Zn-contaminated soils is commonly based on controlling its availability by the addition of lime or organic matter or both. Soluble Zn-organic complexes that occur particularly in municipal sewage sludge are very mobile in soils and therefore are easily available to plants.[451] Zn contamination of soils may create an important environmental problem.

B. Plants

1. Absorption and Transport

Soluble forms of Zn are readily available to plants and the uptake of Zn has been reported to be linear with concentration in the nutrient solution and in soils (Figure 46). The rate of Zn

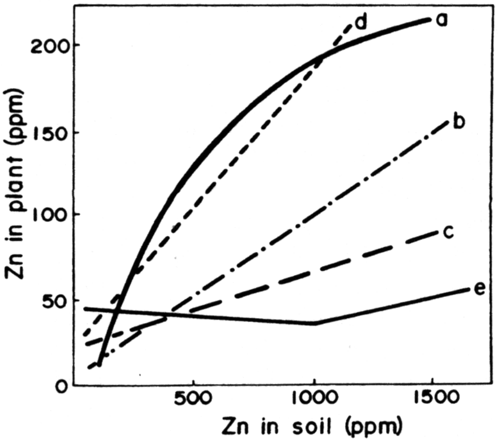

Figure 46 Zn uptake by plants from soil contaminated by this metal. (a) Pasture herbage, (b) wheat straw, (c) wheat grains, (d) potato stalks, (e) potato tubers.[176,783]

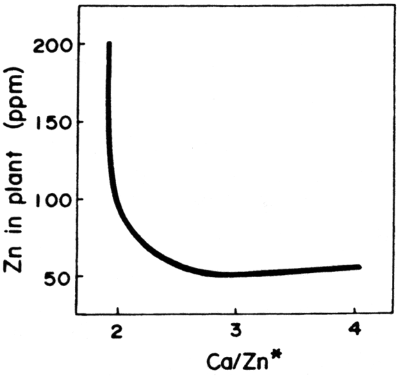

Figure 47 Zn content of cereal tops at the boot stage as a function of Ca/Zn ratio in the soil solution. *Ca/Zn ratio is given in powers of ten.[915]

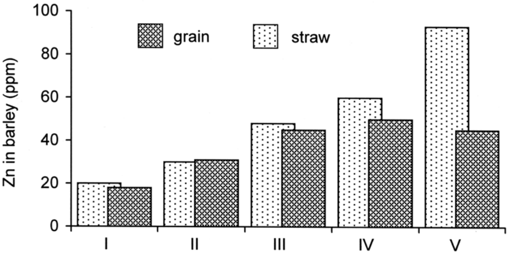

Figure 48 Impact of Zn added, as Zn and Pb smelter flue-dust, to the soil on concentration of Zn in spring barley grain and straw. Zn levels in soils (ppm): I, 60 (blank); II, 560; III, 960; IV, 4060; V, 15,060.[1357]

absorption differs greatly among both plant species and growth media. The composition of the nutrient solution, particularly the presence of Ca, is of great importance (Figure 47). At a high pH value (7.2–7.8), Zn uptake by barley is also closely correlated with its content in soils (Figure 48). Only the Zn transport to grain has not been increased at the soil-Zn level above 50 ppm; this suggests an effect of a biological barrier.

Disagreement exists in the literature whether Zn uptake is an active or a passive process. Moore,[548] Loneragan,[489] and Hewitt[317] have reviewed this topic, and it may be summed up that several controversial results strongly suggest that Zn uptake is mostly metabolically controlled; however, it can also be a nonmetabolic process. Fusuo Zhang et al.[1004a] reported that root exudates of Zn-deficient cereal plants were active in mobilizing both Zn and Fe from various precipitations in soils.

The form in which Zn is absorbed by roots has not been precisely defined. There is, however, general agreement on the predominating uptake of both hydrated Zn and Zn^{2+}. Several other complex ions and Zn-organic chelates may also be absorbed.[489,788,856] Halvorsen and Lindsay[302] concluded that only Zn^{2+} was absorbed by corn roots and that very low concentrations of that ion species are adequate for plant growth.

Several findings support the general statement that Zn is generally bound to soluble low-molecular-weight proteins; however, the formation of Zn-phytate and other insoluble Zn complexes was also reported by Weinberg[856] and Tinker.[798]

Fractions of Zn bound to light organic compounds in xylem fluids and in other plant tissue extracts may suggest its high mobility in the plant.[789,822] Tinker[798] reported that the portion of Zn bound in complexes with a negative charge constitutes more than half of the total metal present in the plant.

Some authors regard Zn as highly mobile, while others consider Zn to have intermediate mobility. Indeed, when given luxury supplies of Zn, several plant species have mobilized appreciable quantities of this metal from old leaves to generative organs; but when under Zn-deficiency conditions, the same species have mobilized little, if any, Zn from old leaves. Hence, in summary of several findings, it may be stated that Zn is likely to be concentrated in mature leaves. However, Scheffer et al.[688a] reported the highest Zn content of barley leaves, sheaths, and internodes to always be during the phase of intensive growth, which demonstrated a great Zn fluctuation within the plant during the vegetative period. Yläranta et al.,[895] on the other hand, reported that the variation in the Zn content of wheat is surprisingly small and that the content increases slightly during the whole growth period. It has been calculated by Baumeister and Ernst[55] that up to 75% of the total Zn that is taken up is in the tops of young plants, whereas 20 to 30% occurs in the tops of old plants.

Roots often contain much more Zn than do tops, particularly if the plants are grown in Zn-rich soils. With luxury levels of soil Zn, this element may be translocated from the roots and accumulated in the tops of the plant. Zn is reported to be concentrated in chloroplasts, especially in those of some plants (e.g., spinach). This metal is also likely to be accumulated in vacuole fluids and in cell membranes.[798]

2. Biochemical Functions

Zn plays essential metabolic roles in the plant, of which the most significant is its activity as a component of a variety of enzymes, such as dehydrogenases, proteinases, peptidases, and phosphohydrolases (Table 37). Lindsay,[476] Price et al.,[630] and Shkolnik[718] have indicated that the basic Zn functions in plants are related to metabolism of carbohydrates, proteins, and phosphate and also to auxins, RNA, and ribosome formations. There is evidence that Zn influences the permeability of membranes and that is stabilizes cellular components and systems of microorganisms.[718,856] Zn is believed to stimulate the resistance of plants to dry and hot weather and also to bacterial and fungal diseases.

Plant species and varieties differ widely in their susceptibility to Zn deficiencies. Although these deficiencies are relatively common (Table 39), their diagnosis is rather complex, and the best diagnoses are obtained when based on visual symptoms, plant analyses, and soil testing together. It must be emphasized, however, that for certain crops and soil, two chelating extractants, DTPA and EDTA, give linear relationships between Zn in the plant and the soluble Zn pool in the soil.[476,797]

Nambiar and Motiramani[560] reported that Zn levels in tissues used for the prediction of its deficiency often fail as the diagnostic test and that tissue Fe to Zn ratios appear to be more promising for the prediction even of hidden Zn deficiency. The critical Fe to Zn ratio in maize was found to be around 6.0. Lindsay[476] extensively reviewed the patterns of Zn deficiency and its common occurrence throughout the world and listed the most important factors contributing to Zn deficiency as follows:

1. Low soil Zn content
2. Calcareous soils and pH above 7
3. Soils low in organic matter
4. Microbial inactivation of Zn in soil
5. Limited Zn uptake by roots due to restricted root zone and to cool spring seasons
6. Differential responses of plant species and genotypes
7. Antagonistic effects

Table 66 Zinc Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Country	Mean or Range in Content	Ref.
Old mining area	Great Britain	220–66,400	808, 915
	Great Britain	455–810	165
Nonferric metal mining	Great Britain	185–4500	165, 786, 1005
	U.S.	500–80,000	615, 1108
	Russia	400–4245	467, 567
Metal-processing industry	Canada	185–1397	363
	Belgium	66–180,000	1142
	Holland	915–3626	305
	Greece	550–16,000	559
	Japan	132–5400	891, 403, 926
	Poland	1665–13,800	224, 1015, 1526
	U.S.	155–12,400	365, 259
	Romania	3000	1126
	Zambia	180–3500	573
Urban garden and orchard	Canada	30–117	243, 848
	Great Britain	250–1800	956, 1190
	Poland	15–99	159
	U.S.	20–1200	628
Sludged farmland	Great Britain	217–525	59
	Great Britain	1097–7474	165, 166
	Hungary	100–360	1177
	Germany	190–1485	397, 176
	Holland	234–757[a]	314
	Sweden	369	24
	U.S.	345–764	964, 1186

[a] 6 and 16 tonnes dry matter sludge/ha/year, for 5 years.

Zn toxicity and Zn tolerance in plants have recently been of special concern because the prolonged use of Zn fertilizers, as well as its input from industrial pollution, is reflected in enhanced Zn content of surface soils (Table 66).

Several plant species and genotypes are known to have a great tolerance of Zn and a great selectivity in absorbing Zn from soils. Plants usually reflect changes in the Zn content of growth media and therefore are good indicators in biogeochemical investigations. Some genotypes grown in Zn-rich soils or in areas of heavy atmospheric Zn deposition may accumulate extremely large amounts of this metal without showing symptoms of toxicity. Petrunina[613] and Kovalevskiy[417] listed several species, particularly of the families Caryophyllaceae, Cyperaceae, and Plumbaginaceae, and also some trees, as extremely good Zn indicators that concentrate this metal in the range from about 0.1 to about 1% (DW). Tolerant species may reduce the effect of excessive Zn concentrations either by metabolic adaptation and complexing or by limiting the presence of the metal at cellular locations or by immobilization in storage tissues.

Most plant species and genotypes have great tolerance to excessive amounts of Zn. Chlorosis, mainly in new leaves, and depressed plant growth are the common symptoms of Zn toxicity (Table 40). An excess of Zn can be bound by phytic acid in roots of some crop plants (e.g., soybean, tomato, cabbage, wheat). This mechanism does not work, however, when there is also an excess of Cd.[1507]

Zn phytotoxicity is reported relatively often, especially for acid and heavily sludged soils. The physiology and biochemistry of the toxic effects of Zn in plants are likely to be similar to those reported for other heavy metals; however, Zn is not considered to be highly phytotoxic. The toxicity limit for Zn depends on the plant species and genotypes, as well as on the growth stage. Hence, about 300 ppm Zn is reported to be toxic to young barley, whereas about 400 ppm is toxic to oats at the beginning of tillering.[171,322] However, in root tissues, where Zn is immobilized in cell walls or complexed in nondiffusible Zn proteins, the critical concentration of Zn is much higher. Sensitive plant species are reported to be retarded in growth when their tissues contain 150 to 200 ppm Zn.[1052] Most commonly, however, the upper toxic levels range in various plants from 100 to 500 ppm (DW).[1081]

Some species are known to hyperaccumulate Zn, such as *Thlaspi caerulencens* or *Thlaspi ochroleucum*, and are recommended for *in situ* decontamination of polluted soils. The first species of *Thlaspi* appears to be more resistant to a very high concentration of Zn and to significantly higher accumulated amounts of Zn (up to 8000 ppm) than the second species (up to 2000 ppm). Both plants, however, accumulate more Zn in shoots than in roots.[1409] Mean extraction of Zn by these plants from soils contaminated with Zn (124–444 ppm Zn) was calculated at 14 to 57 kg ha^{-1}.[1407]

3. Interactions with Other Elements

Zn is relatively active in biochemical processes and is known to be involved in several biological and chemical interactions with several elements. Findings of Graham et al.[1013] supported earlier reports of Loneragan et al.[1074] that Zn deficiency interferes with the control of ion absorption, causing ions to accumulate to high levels in plant tissues. Thus, supplying Zn is expected to decrease the uptake of most nutrients. This was not observed for Fe, while the uptake of B and Mn was especially depressed. Graham et al.[1013] were the first to report that inadequate Zn content leads to increased uptake of B and S by barley.

Zn-Cd interactions appear to be somewhat controversial, since there are reports of both antagonism and synergism between the two elements in the uptake-transport processes. Kitagishi and Yamane[395] explained the observed synergism in rice plants in terms of Zn competition for the Cd sites, resulting in an increase in Cd solubility, and in Cd translocation from the roots to tops. Wallace et al.[846] reported a high Cd accumulation in roots of plants at a high Zn level and at a low pH of the solution. Earlier findings, well illustrated by those of Lagerwerff and Biersdorff,[449] however, show antagonism between these cations in the uptake-transport process. It may be stated that the ratio of Cd to Zn in plant media controls the occurrence of synergism and antagonism between these cations.

Zn-Cu antagonistic interactions have been observed in which the uptake of one element was competitively inhibited by the other. This may indicate the same carrier sites in absorption mechanisms of both metals.

Zn-Fe antagonism is widely known and its mechanism is apparently similar to the depressing effects of other heavy metals on Fe uptake. An excess of Zn leads to a marked reduction in Fe concentration in plants. Olsen[581] stated that Zn interfered more with the absorption and translocation of Fe than it did with Cu and Mn. There are two possible mechanisms of this interaction—the competition between Zn^{2+} and Fe^{2+} in the uptake processes, and the interference in chelation processes during the uptake and translocation of Fe from the roots to tops. Also, Fe decreases Zn absorption and the toxicity of Zn that was absorbed. Observed Zn-Fe synergism is reported to be linked with the P supply. It is suggested that at a relatively high accumulation of P and Zn in roots, the precipitation of $FePO_4$ in root tissues can account for the increase in Fe uptake.[1013]

Zn-As interaction was reported by Shkolnik[718] as a possible antagonism observed in the decrease of toxic effects of As excesses after Zn treatments. Similar interaction between Zn and Hg was also mentioned, although not described clearly.

Zn-P interaction has been widely observed and reported for many crops, especially after phosphate and lime applications.[491] Norvell et al.[1104] studied Zn-P interaction in alkaline soils and stated that the specific effects of P on the concentration of Zn^{2+} in the solution were small and observed only when the Zn^{2+} content was raised previously by Zn fertilizers. However, the addition of P also caused small decreases in the concentrations of other divalent cations in the solution. The P-Zn imbalance, resulting from excessive P accumulation, is known to induce Zn deficiency. This antagonism appears to be based to a large extent on chemical reactions in the root media.[581,675] However, Smilde et al.[738] stated that Zn-P antagonism could not be explained by only mutual immobilization and that this interaction is mainly a plant physiological characteristic. The specific mechanisms of Zn-P interaction are not yet known. Usually, the antagonistic effect of P on the concentration of Zn was more pronounced than that of Zn on P. The optimum P:Zn ratio for corn plants is 100. At lower and higher values, a steep decrease in yield is observed.[1542a] Synergism between P and Zn was also observed in some plants.[654] A balanced P and Zn nutrition was reported by Shukla and Yadav[722] to be essential for the proper activity of *Rhizobium* and N fixation.

Zn-N interaction is mostly a secondary "dilution" effect due to the increase of biomass because of the heavy N treatment. Olsen[581] also reported an enhancement of Zn in tops due to a higher bonding of Zn by proteins and amino acids in root tissues.

Zn-Ca and Zn-Mg interactions appear to vary for a given plant and media (Table 43). Apparently, several other factors, pH in particular, control the antagonistic and synergistic character of interactions between these elements. Olsen[581] stated that reactions which lowered Zn deficiency by Mg applications occurred within the plant rather than within the soil, but that competition between Mg and Zn in soil exchange sites cannot be precluded.

4. Concentrations in Plants

It is assumed that the Zn content of plants varies considerably, reflecting different factors of the various ecosystems and of the genotypes. However, the Zn contents of certain foodstuffs, cereal grains, and pasture herbage from different countries do not differ widely. Zn content ranged from 1.2 to 73 ppm (DW) in apple and lettuce leaves, respectively (Table 67). Chinese tea leaves contain Zn from 26 to 40 ppm, of which up to 50% is extracted by hot water. Tea drinks have from 0.08 to 0.17 ng Zn L^{-1}.[1550]

Mean values for Zn in wheat grains ranged from 22 to 33 ppm (DW) and did not show any clear differences in country of origin (Table 68). Rye seems to contain a little less, and barley somewhat more Zn than wheat. The geometric mean of Zn in 6500 samples of cereal grains (wheat and rye) collected from 1992 to 1995 from the whole territory of Poland is 33 ppm (Table 7), within the range from 0.3–298, and is very close to the mean values reported for worldwide cereals about two decades earlier (Table 68). The Zn mean content of over 5000 samples of potato tubers (washed, unpeeled) grown in Poland accounts for 20 ppm within the range from 1.2 to 150.[1514] The median Zn content ($N = 128$) in wheat grain grown in France is 15.5 ppm (range 7–43 ppm).[1213] A recent reference for food compositions in the U.S. gives the following values for Zn in some categories of plant food (ppm FW): (1) vegetables: range 0.7–8.0, the lowest value for celery root, and the highest for spinach; (2) fruits: range 0.4–3.0, the lowest value for grapes, and the highest for black

Table 67 Mean Zinc Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis		DW Basis			AW Basis	
		(574)	(395, 1187)	(705)	(852)	(381)	(705)	(852)
Sweet corn	Grains	—	18.5	25	36	—	980	1060
Bean	Pods	0.3	28.3	38	32	—	550	550
Cabbage	Leaves	0.6	2.2[a]	24	26	31	270	275
Lettuce	Leaves	0.1	11.7	73	44	—	520	240
Carrot	Roots	0.5	2.6	21	24	27	290	325
Beet	Roots	—	—	—	28	46	—	485
Onion	Bulbs	—	1.7	22	22	32	530	395
Potato	Tubers	0.3	3.4	14	10	26	340	310
Tomato	Fruits	—	1.4	26	17	—	220	235
Apple	Fruits	0.03	—	1.2	—	—	67	—
Orange	Fruits	0.09	0.9[b]	5.0	—	—	140	—
Tea	Leaves	—	—	34[c]	32[c]	32[c]	—	—

Note: References are given in parentheses.

[a] Pulses.

[b] *Citrus unshiu* (Satsuma orange).

[c] Tea from Japan, India, and China, respectively.[1032]

Table 68 Zinc Content of Cereal Grains from Different Countries (ppm DW)

Country	Cereal	Range	Mean	Ref.
Afghanistan	Barley	—	20	446
	Wheat	—	25	446
Australia	Wheat	16–35	22	867
Canada	Oats	—	37	514
Egypt	Wheat[a]	19–29	25	213
Germany	Wheat	6–40	23[b]	65
Finland	Wheat[a]	25–47	37	508
	Wheat[c]	27–35	32	508
Great Britain	Barley	16–49	30	783
Japan	Wheat (flour)	—	5[d]	395
	Brown rice	19–28	23	395
	Unpolished rice	—	21[d]	891
Norway	Barley	15–51	29	446
	Wheat	21–67	33	446
Poland	Wheat[c]	23–38	27	268
	Rye	14–73	31	424, 1045
	Oats	12–75	29	1045
	Triticale	—	22	667
Sweden	Wheat[c]	20–40	34[e]	26
U.S.	Barley	20–23	22	484, 710
	Wheat, soft	—	5	906
	Wheat, hard	20–47	28	906
	Rye	—	34	492
	Rice	7.2–21	14[d]	1187
	Triticale	—	26	492
Russia	Rye	—	19	501

[a] Spring wheat.

[b] Mean value calculated from the given range.

[c] Winter wheat.

[d] FW basis.

[e] Data calculated from the figures given.

Table 69 Mean Levels and Ranges of Zinc in Grass and Clover of Immature Growth from Different Countries (ppm DW)

	Grasses		Clovers		
Country	Range	Mean	Range	Mean	Ref.
Bulgaria	24–50	34	—	—	680
Czech Republic	15–35	25[a]	—	—	154
Germany	15–80	47[a]	20–50	24[b]	65
Germany	27–67	31[c]	—	—	596
Finland	28–39	32	—	—	388
Great Britain	22–54	33	—	—	165
Hungary	21–36	27	30–126	39	803
Japan	18–38	28	23–55	34	770
New Zealand	16–45	28	20–49	27	536
Poland	12–72	30[d]	16–86	37[e]	838, 1045
Russia	—	—	—	45	501
Yugoslavia	6–11		48–94	62	623, 755

[a] Mean value calculated from the given range.

[b] Alfalfa.

[c] Perennial rye grass and clover mixture.

[d] Orchard grass.

[e] White clover.

Table 70 Excessive Levels of Zinc in Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean, or Range of Content	Country	Ref.
Old mining area	Grass	65–350	Great Britain	165, 167
	Clover	450	Great Britain	513
Nonferric metal mining	Onion bulbs	39–710	Great Britain	169a
	Lettuce leaves	55–530	Great Britain	169a
Metal industry	Lettuce leaves	316	Australia	57
	Chinese cabbage leaves	1300	Japan	403
	Oat grains	132–194	Poland	224
	Potato tubers	74–80	Poland	224
	Lettuce leaves	213–393	Poland	224
	Carrot roots	201–458	Poland	224
	Blueberry tops	130–680	Poland	922
Urban garden	Radish roots	27–708	Great Britain	166, 167
	Leafy vegetables	35–470	U.S.	628
Sludged, irrigated or fertilized farmland	Grass	126–280	Holland	297
	Sudan grass	66–250	Hungary	1177
	Rice grains	21	Japan	395
	Rice roots	4510	Japan	395
	Oat grains	27–85	U.S.	726
	Soybean leaves	156	U.S.	126
	Soybean seed	114	U.S.	126
	Sagebrush	2600[a]	U.S.	278
	Potato tubers	36	Germany	176

[a] AW basis.

currant (European); (3) cereals: range 0.7–32.5, the lowest value for barley pearls (cooked), the highest for rye (whole grain); and (4) nuts: range 5–42.3, the lowest value for coconut (meat, fresh), and the highest for Brazil nuts (shelled).[1291]

Background content of Zn in grass and clover throughout the world is also relatively stable, and its mean levels in grasses ranged from 12 to 47 ppm (DW), and in clovers ranged from 24 to 45 ppm (DW) (Table 69).

The deficiency content of Zn in plants has been established at 10 to 20 ppm (DW) (Table 36). These values, however, may vary considerably because the Zn deficiency reflects both the requirements of each genotype and effects of the interactions of Zn with other elements within the plant tissues.

Environmental Zn pollution greatly influences the concentrations of this metal in plants (Table 70). In ecosystems where Zn is an airborne pollutant, the tops of plants are likely to concentrate the most Zn. On the other hand, plants grown in Zn-contaminated soils accumulate a great proportion of the metal in the roots. The reported Zn contents of plants from some contaminated sites have already reached the magnitude of 0.X% (DW) and are a real health risk.

VII. CADMIUM

A. Soils

There is growing environmental concern about Cd as being one of the most ecotoxic metals that exhibit highly adverse effects on soil biological activity, plant metabolism, and the health of humans and the animal kingdom. The behavior of Cd in the environment and related health aspects has recently been reviewed by Kabata-Pendias and Pendias[1357] and Stoeppler.[1506]

The abundance of Cd in magmatic and sedimentary rocks does not exceed around 0.3 ppm, and this metal is likely to be concentrated in argillaceous and shale deposits (Table 59). Cd is

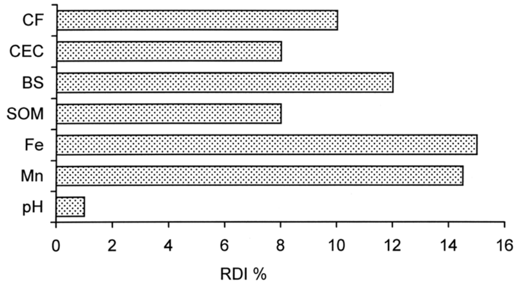

Figure 49 Relative explanation index (RDI) of statistically significant relationship between Cd and soil parameters in mineral soils at the 99% confidence level (N = 780). Soil parameters: CF, clay fraction <0.02 mm; CEC, cation exchange capacity; BS, base saturation; SOM, soil organic matter; Fe, total content; Mn, total content; pH, in water; soil:water ratio, 1:2.5.

strongly associated with Zn in its geochemistry, but seems to have a stronger affinity for S than Zn, and also exhibits a higher mobility than Zn in acid environments. Cd compounds are known to be isotypic with corresponding compounds of such cations as Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mg^{2+}, and, in some cases, of Ca^{2+}.

During weathering, Cd goes readily into solution and, although known to occur as Cd^{2+}, it may also form several complex ions ($CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdCl_3^-$, $CdCl_4^{2-}$, $Cd(OH)_3^-$, and $Cd(OH)_4^{2-}$) and organic chelates. However, the most important valence state of Cd in the natural environment is +2, and the most important factors which control Cd ion mobility are pH and oxidation potential. Under conditions of strong oxidation, Cd is likely to form minerals (CdO, $CdCO_3$) and is also likely to be accumulated in phosphate and in biolith deposits.

The main factor determining the Cd content of soil is the chemical composition of the parent rock. The average contents of Cd in soils lie between 0.06 and 1.1. ppm (Table 71) and seem not to correlate with the soil units, although its highest mean content is for histosols (0.78 ppm) and the lowest for podzols (0.37 ppm) (Table 9). This relationship is nicely illustrated by the Cd geometric mean contents increasing with the content of the soil clay fraction. Light sandy soils of Poland contain 0.22 ppm Cd, whereas light loamy soils contain 0.31, and heavy loamy soils contain 0.51 ppm (Table 20). Although clay fraction is not a major soil factor controlling the Cd distribution, it contributes up to 10% of all relationships (Figure 49). A stronger relationship is observed for Cd with Fe and Mn contents of soil. Oxides appear to be of minor importance in soil at low pH (<5.5). The calculated worldwide mean is 0.53 ppm Cd in surface soils, and apparently all higher values reflect the anthropogenic impact on the Cd status in topsoils. Surface soils from major agricultural production areas of the U.S. contain Cd within the range of <0.01 to 2.0 ppm Cd (geometric mean, 0.175).[1329] Govindaraju[1313] reported Cd contents in reference soils from different countries to range from 0.06 to 4.3 ppm. Soils from Sichote-Alin (remote region of Russia) contain Cd from 0.2 to 1.14 ppm, and the greatest concentration was noticed in flooded soils.[1428]

1. Reaction with Soil Components

The sorption of Cd species by soil components has recently been widely studied. Farrah and Pickering[228] stated that competitive adsorption by clays is the predominant process in Cd bonding. Also, findings of Tiller et al.[796] and Soon[747] support the opinion that adsorption, rather than precipitation, controls Cd concentrations in soil solutions until a threshold pH value is exceeded. The pH-solubility diagram (Figure 50) indicates that above pH 7.5, Cd sorbed in soils is not easily mobile; therefore, the solubility of $CdCo_3$, and possibly of $Cd_3(PO_4)_2$, would control the Cd mobility in soils. The solubility of Cd appears to be highly dependent on the pH; however, the nature of sorbent surfaces and of organic ligands is also of importance. As John[361] reported, the coefficient of bonding energy of the Cd adsorption was higher for organic matter than for soil clays. Abd-Elfattah and Wada[2] on the other hand, stated that Fe oxides, allophane, and imogolite reveal the highest affinity for the selective adsorption of Cd. Hydroxides appear to be of minor importance in soil at low pH (<5.5). Cd sorption in acid soil is highly influenced by composition of the liquid phase.[1233]

Table 71 Cadmium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Romania	0.2–2.7	0.9	1127
	Poland	0.01–0.24	0.07	378
	U.S.	0.08–0.47	0.21	1026
	Canada	0.10–1.80	0.43	243
	Russia	—	0.32	1031
Loess and silty soils	Poland	0.18–0.25	0.20	378
Loamy and clay soils	Poland	0.08–0.58	0.26	378
	Romania	0.5–1.6	0.9	1127
	Canada	0.12–1.61	0.64	243
	U.S.	0.13–0.55	0.27	1026
Soils on glacial till	Denmark	—	0.25	801
	Great Britain	0.49–0.61	—	353
	Poland	0.04–0.80	0.27	974
Fluvisols	Austria	0.21–0.52	0.37	6
	Great Britain	0.41–2	1.10	166, 353, 786
	Poland	0.24–0.36	0.30	378
	Bulgaria	0.42	—	612
Gleysols	Poland	0.14–0.96	0.50	378
Rendzinas	Poland	0.38–0.84	0.62	378
Brown soils	Austria	0.22–0.49	0.33	6
	Romania	0.3–1.4	0.7	1127
	U.S.	0.05–0.71	0.27	1026
Chernozems	Poland	0.18–0.58	0.38	378
	Bulgaria	0.55–0.71	0.61	612
	Russia	—	0.32	1031
Histosols and other organic soils	Denmark	0.8–2.2	1.05	1, 801
	Canada	0.19–1.22	0.57	243
	Great Britain	0.56	—	353
	U.S.	0.36–1.44	0.72	1026
Forest soil	U.S.	0.5–1.5	0.73	87
Yermosols	U.S.	0.17–0.71	0.35	1026
Various soils	Austria	0.19–0.46	0.29	6
	Denmark	—	0.26	801
	Great Britain	0.27–4	1.00	100, 353, 786, 818
	Germany	0.3–1.8	0.80	390
	Italy	0.07–0.89	0.44	946
	Japan	0.03–2.53	0.44	395
	Poland	0.1–0.6	0.41	1046
	Bulgaria	0.24–0.35	0.29	612
	Canada	—	0.56	243
	U.S.	0.41–0.57	—	396
	Russia	0.01–0.11	0.06	233, 1131

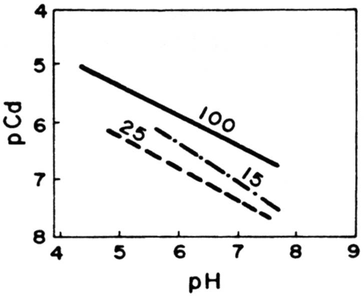

Figure 50 Solubility of Cd^{2+} in soils as a function of soil pH. Equilibration with 15, 25, and 100 μg Cd per 2 g of soil.[747]

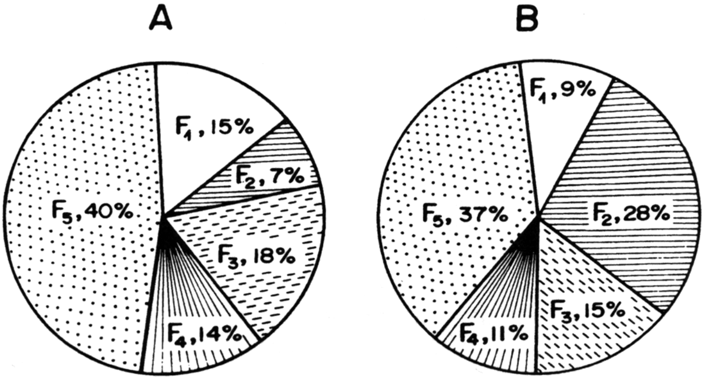

Figure 51 Variation in Cd species in soils under sludge application: (A) unsludged soil, (B) sludged soil. Cd species: (F_1) easily soluble; (F_2) exchangeable; (F_3) associated with hydrous oxides; (F_4) bound to organic matter; and (F_5) residual.[985]

Recently, Cd adsorption to organic matter as well as to Fe and Mn oxides has been widely studied by Gadde and Laitien,[253] Forbes et al.,[240] and Street et al.[761] All the findings lead to some generalizations: in all soil, Cd activity is strongly affected by pH; in acid soils, the organic matter and sesquioxides may largely control Cd solubility, and that in alkaline soil, precipitation of Cd compounds is likely to account for Cd equilibria. The amount of Cd bound to organic matter and in residual fraction seems to be relatively stable in the soil, while its exchangeable forms increase significantly under sludge application (Figure 51).

Soil microbial activity is also believed to play a significant role in the Cd behavior in soils. Chammugathas and Bollag[962] observed both binding of Cd and its subsequent release from soils under the influence of soil microorganisms. The rate and degree of these processes depend upon soil parameters of which the Eh-pH system is of greater importance. Isenbeck et al.[1033] reported that the carbonate concentration in the soil solution leads to total Cd precipitation, and that no other soil factors are so active in Cd immobilization. This observation is also supported by recent findings of Fic[992] and Christensen.[967]

Cd is most mobile in acidic soils within the range of pH 4.5 to 5.5, whereas in alkaline soil Cd is rather immobile. However, as the pH is increased in the alkaline range, monovalent hydroxy ion species are likely to occur (e.g., $CdOH^+$), which could not easily occupy the sites on cationic exchange complexes. The sorption of Cd is known to be the fast process. Christensen[967] found that 95% of the Cd sorption takes place within 10 minutes, reaching equilibrium in 1 hr and that the soil has very high affinity for Cd at pH 6. In the pH interval from 4 to 7.7, the sorption capacity of the soil increases approximately 3 times for a pH increase of one unit.

Cd concentration in the soil solution is relatively low and is reported to range from 0.2 to 6 μg L^{-1}. The much higher value (300 μg L^{-1}) reported by Itoh and Yumura[342] presumably indicates contaminated soil and corresponds to the value (400 μg L^{-1}) given by Kabata-Pendias and Gondek[379] for contaminated soil. The solubility of Cd is closely related to the acidity of the soil solution (Figure 14). The critical acidity in mineral soils is within the pH range of 4.0 to 4.5, at which a drop in pH of merely 0.2 units results in a 3 to 5 times increase in the Cd concentration.[938] Asami[924] found that a half or more of the total Cd in paddy soils is readily extractable by 0.05 M $CaCl_2$. Among the other trace metals, Cd is known to be most mobile under conditions of different soils. Lodenius[1071] studied the mobilization of Cd in sand and peat soils under leaching with artificial acid rain (pH 3.6 and 5.4) and with salt solution (pH 7.0). In each case, the strongest leaching was achieved by a neutral solution containing Ca^{2+}, K^+, NO_3^-, and SO_4^{2-} ions. This supports Laxen's conclusion[1057] that as alkalinity increases, Cd adsorption decreases, probably due to the competition from Ca^{2+} and Mg^{2+} ions. These findings have important implications for the development of realistic reclamation techniques for the management of Cd-enriched soils.

Table 72 Cadmium Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Maximum or Range of Content	Country	Ref.
Mineralized bedrock and mining area	0.6–468	Great Britain	166, 808. 915
	2–336[a]	Great Britain	959
	2–144	Belgium	728
Metal-processing industry	3.2–1781	Belgium	1142
	2–5	Bulgaria	611
	2–36	Canada	363
	9–33	Holland	305
	1.8–88	Japan	336, 403, 891, 926
	6–270	Poland	224, 871, 1015
	12	Romania	1126
	26–1500	U.S.	233, 1108
	0.6–46	Zambia	573
Urban gardens	1–17	Great Britain	959
	0.08–61	Poland	159, 1173
	0.02–13.6	U.S.	127, 628
	10–100[b]	U.S.	1073
	3.9	Germany	1046
Sludged, irrigated, or fertilized farmland	7.3–8.1	Canada	243
	1.5–167	Great Britain	959, 987
	15–57[c]	Holland	314
	2.5–5.6	Hungary	1177
	2.2–7.5[d]	Japan	924
	0.4–107	Poland	1173
	2.6–8.3	U.S.	964, 1186
Vicinity of highways	1–10	U.S.	705a

[a] Zn mining area.

[b] Soils sludged since 1964.

[c] 6 and 16 t dry matter sludge/ha/year, for 5 years.

[d] Paddy soils.

In soils developed under the influence of humid climate, migration of Cd down the profile is more likely to occur than its accumulation in the surface horizon; thus, the enrichment in Cd content observed so commonly in topsoils should be related to contamination effects.

2. Contamination of Soil

Soil contamination with Cd is believed to be a most serious health risk. Under man-induced conditions, Cd is likely to build up in surface soils (Tables 18 and 72). However, elevated levels of Cd in soils can also be of lithogenic (geogenic) origin. This is reported by Čurlik and Forgač[1267] for alluvial soils derived from pyritized quartzes and from hydrothermally altered pyritized andezine in Slovakia (area near Banska Stavnica) in which a high concentration of Cd up to 222 ppm is observed at a depth of 100 to 120 cm. This phenomenon is due to the redeposition of sulfide materials which absorb some metals mobilized during weathering. Natural Cd anomalies have also been detected by Baize et al.[1214] in France. These Cd-contaminated soils are derived from Jurassic or Cretaceous limestones. The Cd content of Jurassic rocks ranges broadly from 0.02 to 8.15 ppm.

The present concentration of Cd in topsoils is reported to be very high in the vicinities of Pb and Zn mines and, in particular, smelting operations (Table 72). Sewage sludges and phosphate fertilizers are also known as important sources of Cd, and there are several comprehensive reviews of this subject, as given by Fleischer et al.,[233] Williams and David,[878,879] Street et al.,[761] Chaney and Hornick,[129] von Jung et al.,[372] and Andersson and Hahlin.[22] Poelstra et al.[1121] calculated the accumulation of Cd in soils due to the application of sewage sludges. The permissible level

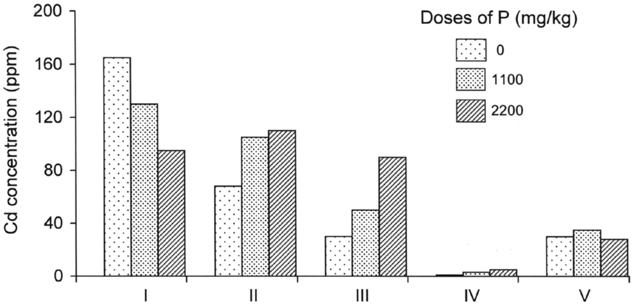

Figure 52 Influence of KH_2PO_4 on Cd fractionation in soil contaminated with Cd (370 ppm), soil pH 7.0 after $CaCo_3$ amendment. Fractions of Cd (after Tessier et al.[1162]): I, exchangeable; II, carbonate; III, oxide; IV, organic; V, residual, (With permission from the authors.[1328])

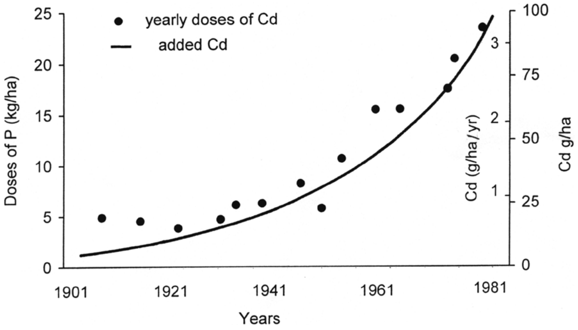

Figure 53 Cd input in Swedish agricultural soils with phosphate fertilizers. (Modified from Gunnarson.[1320])

of Cd (i.e., 22 kg ha^{-1}) from this source will be reached, in different periods, depending upon soil variables and, in particular, upon the adsorption coefficient. The significant increase of weakly bound and exchangeable species of Cd in the sludged soils will affect its phytoavailability (Figures 51 and 55).

Jones et al.[1044] gave an excellent example for the Cd long-term increase in the soil plow layer in the Rothamsted Experimental Station, England. Both the Cd atmospheric deposition and fertilizers (farmyard manure or phosphate fertilizers) resulted in Cd increases. Changes in soil Cd levels in untreated plots were from 0.51 to 0.77 ppm over a period of about 40 years. Even in the forests of remote regions in various countries, with the exception of one site in Sweden, the atmospheric input of Cd exceeded the output of this metal from the soil profile (Table 17). In France, some highly polluted soils are reported to contain over 100 ppm Cd.[1214]

In recent years, a decrease of Cd emissions from anthropogenic sources has been noted in some countries. For example, in Finland, the Cd emission decreased from 6.3 tonnes in 1990 to 1.1 tonnes in 1997.[1433]

A significant source of Cd in soils is phosphate fertilizers (Table 23). However, phosphate added to soils immobilizes the Cd. As Hettiarachchi et al.[1328] reported, the mobility of Cd in phosphorus-amended soil is significantly reduced. The exchangeable fraction of Cd decreases with the presence of phosphate in soils, while carbonate and oxide fractions increase (Figure 52). Phosphate fertilizers are a continuous source of Cd in soils. The highest content of Cd, up to >100 ppm, is reported to be in raw phosphates from the U.S. (Idaho), and the lowest, below 3 ppm, in phosphate rocks of igneous origin mined in Russia (Kola mine) and in Finland (Siilinjärvi).[1420] Gunnarson[1320] calculated the added Cd to soils in Sweden since 1901 (Figure 53). Recent data[1044,1257] have also shown a significant increase in Cd concentration in agricultural soils (Figure 54). Similar results were

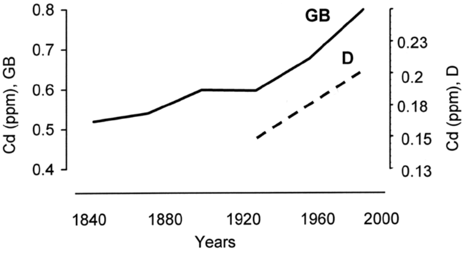

Figure 54 Changes in soil Cd levels in unfertilized plots of long-term experiments in Great Britain and Denmark. (Modified from Jones et al.[1044] and Christensen and Tjell.[1257])

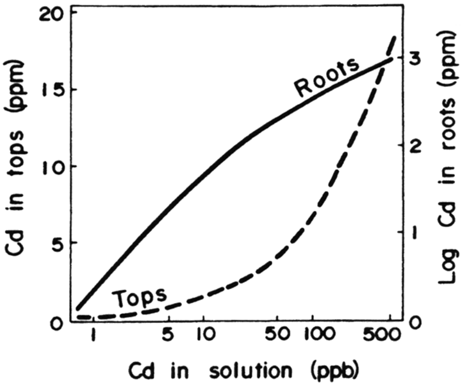

Figure 55 The effect of Cd concentration in the culture solution on Cd uptake by grass *Bromus unioloides*.[1045]

presented by Sillanpää and Jansson[1491] for worldwide soils (N = 1823). The Cd contents of soils and of crop plants increased from 0.04 to 0.1 ppm and from 0.04 to 0.12 ppm, respectively, with increasing fertilization from 5 to 70 kg P ha^{-1}. The prediction presented by Stigliani[1508] indicates that due to the continuous increase of Cd in soils and decrease of soil pH, the transfer of Cd to the food chain will grow significantly with time. In the year 2010, the crop from acid soils (pH 5.0) can increase the PTWI doses up to 1200 μg Cd, which is several times higher than the dose accepted as the health-related limit for Cd intake by humans.

Because of the environmental significance of the Cd accumulation in soil, several techniques for the management of Cd-enriched cropland have been investigated. Similarly, as in the case of Zn-contaminated soils, these techniques are based on increasing the soil pH and CEC. Although liming generally is expected to decrease Cd absorption by raising the soil pH, it is not effective for all soils and plants. Kitagishi and Yamane[395] reported that the best and most reliable results in reducing Cd availability was the layering of unpolluted soil over polluted soil to a depth of 30 cm. The maximum permissible rate of Cd addition to soil should depend strongly on the soil pH. Escrig and Morell[1295] reported that a tenfold increase in Ca concentration in soil reduced the Cd adsorption capacity by approximately three times.

B. Plants

1. Absorption and Transport

Although Cd is considered to be a nonessential element for metabolic processes, it is effectively absorbed by both the root and leaf systems, and is also highly accumulated in soil organisms (Table 28). In almost every case, a linear relationship between Cd in plant material *vs*. Cd in growth medium is reported (Figures 55 and 56). Nevertheless, several soil and plant factors affect the plant uptake of Cd. The variable ability of plants to take up Cd from a calcareous soil treated with 0.1 and 5 mg Cd kg^{-1} soil in sewage sludge is presented by McGrath[1406] (after Bingham). While field

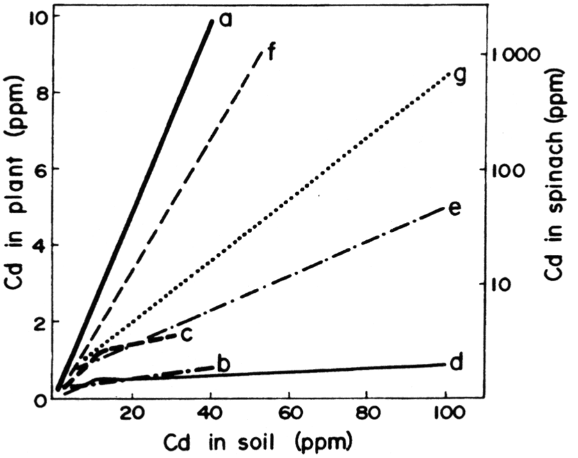

Figure 56 Cd uptake by plants from soil contaminated by this metal. (a) Potato stalks, (b) potato tubers, (c) wheat grains, (d) brown rice, submerged during growth period, (e) brown rice, drained after tillering stage, (f) barley grains, value in ng g^{-1}, (g) spinach leaves, data for 0.1 *N* HCl-soluble Cd in soil.[22,176, 336, 342]

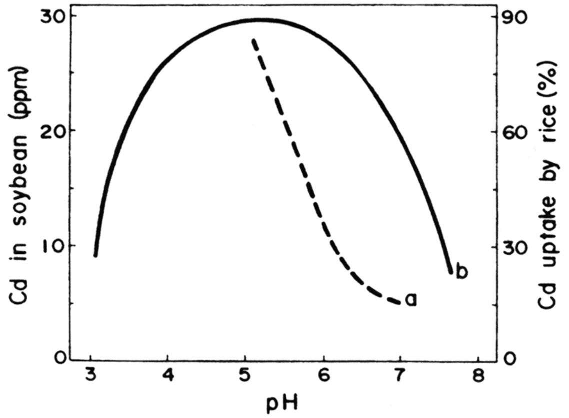

Figure 57 (a) Effect of soil pH on Cd content of soybean leaves and (b) effect of solution pH on relative Cd absorption by rice seedlings.[129,395]

bean contents of Cd (ppm in edible tissue) were at levels <0.1 and 0.4, carrot contained 0.9 and 8.2, lettuce contained 1.4 and 21, and spinach contained 3.6 and 91, respectively.

In nearly all the publications on the subject, soil pH is listed as the major soil factor controlling both total and relative uptake of Cd (Figure 57). Kitagishi and Yamane[395] reported results of their experiment, indicating that the relative uptake of Cd by rice seedlings was the greatest within the pH range of 4.5 to 5.5. Bingham et al.[77] also found that the Cd content of rice grain is highly dependent upon the soil pH and is highest at pH 5.5. However, there are contradictory results which show that when Cd becomes more mobile in alkaline soil due to the formation of complexes or metal chelates, the plant uptake of Cd may be independent of the pH.[41,129] Kitagishi and Yamane[395] described that when the redox potential of soils decreases to about −0.14 V, the proportion of soluble Cd decreases, corresponding to the reduction of sulfate to sulfides. This is well-illustrated in the much lower uptake of Cd by rice grown on submerged soil than on soil drained after the tillering stage (Figure 56).

Even at the high soil pH (7.2–7.8), Cd uptake by barley was a function of its content in soil. The rapid increase in the Cd concentration in straw at the 0.5-ppm level, and in grain at the 0.3-ppm level (Figure 58) is most probably related to a break of the physiological barrier controlling a metabolic

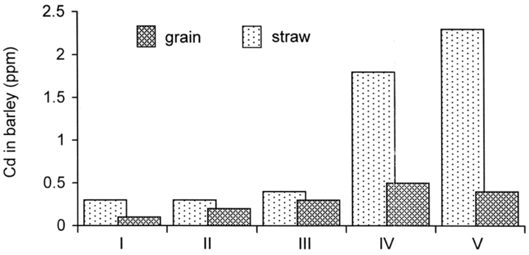

Figure 58 Impact of Cd added, as Zn and Pb smelter flue-dust, to the soil on the concentration of Cd in spring barley grain and straw. Cd levels in soils (ppm): I, 0.7 (blank); II, 3.7; III, 7.7; IV, 50.7; V, 100.7.[1357]

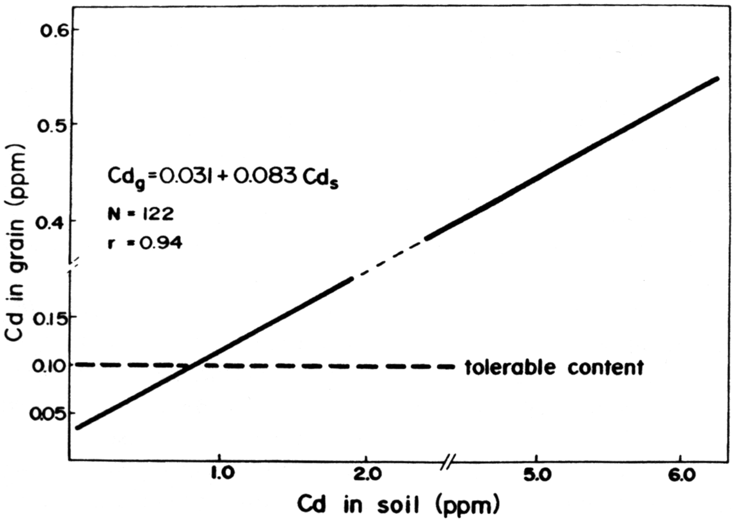

Figure 59 Relation between the Cd content of wheat grain (Cd_g) and the total content of Cd in soil (Cd_s). (Modified from Hornburg and Brümmer.[1029])

absorption of this metal. The influence of low-molecular-weight organic acids present in the rhizosphere of durum wheat on the mobility of particulate-bound Cd and on metal phytoaccumulation is reported by Cieoeliñski et al.[1262]

Although soil characteristics other than the pH can also cause differences in the Cd absorption by roots, it may be stated that soluble species of Cd in soil are always easily available to plants. Poelstra et al.[1121] described that the calculation of the uptake of Cd by vegetation from soils of variable conditions is difficult and uncertain. Findings of Hornburg and Bümmer,[1029] however, indicated that the Cd concentrations in wheat grains increase linearly with the total Cd content of soils (Figure 59). Also, a worldwide experiment carried out in 30 countries with young wheat (N = 1723) and young corn plants (N = 1892) indicates that plant-Cd is a function of soil-Cd.[1491] The content of clay fraction proved to be the most important factor, among six investigated soil parameters, controlling the Cd uptake by plants. In some cases, however, soil pH and carbonates also influenced the Cd phytoavailability. The frequency distribution of Cd contents of both plants indicated the most common (ca. 15%) concentrations ranging from 0.03 to 0.1 ppm. Results of this research program clearly indicated the effect of phosphorus fertilization on increased levels of plant-Cd and soil-Cd. Effects of the phosphate application rates of 3 years prior to sampling were as follows: at 10 kg P ha^{-1} rate, plants contain 0.06 ppm Cd; and at 50 kg P ha^{-1}, 0.1 ppm Cd. Effectiveness of liming to minimize uptake of Cd by cereals has also been reported.[1444] However, the response was variable, and in some cases raising soil pH to 6.0 was not sufficient to decrease the Cd concentration in grain below 0.05 ppm (MAC), and would not be considered economically acceptable in several areas.

Mench[1413] reviewed changes in Cd availability in relation to major long-term changes in the agronomy system, and concluded that cropping systems and fertilizing affect Cd concentrations in potato tubers and cereal grains, which are the major plant-derived diet of the European population.

Some plants reveal a great affinity to absorb Cd from growth media. Lepp et al.[1060] gave as an example the mushroom (*Amanita muscaria*), growing in unpolluted woodland in soil with a relatively low Cd content (total Cd 0.34 ppm DW), and containing 29.9 ppm Cd. Nuorteva[1104a] reported high Cd contents (12 to 24 ppm DW) of fruitbodies of some mushrooms also growing in unpolluted forest in Finland. The origin of the Cd is an additional important factor controlling its solubility and phytoavailability. Grupe and Kuntze[1019] have shown that oats absorbed a much higher proportion of the anthropogenic Cd (added as Cd oxide) than that of the lithogenic origin (Figure 2). Filipiński[993] calculated that spinach uptakes about three times more Cd from the anthropogenic source than from the pedogenic one. Although an appreciable fraction of Cd is taken up passively by roots, Cd is also absorbed metabolically.[737]

Some soil variables are known to affect Cd phytoavailability. McLaughlin et al.[1411] reported that plants, especially sunflowers and potatoes, take up significantly more Cd from salt-affected soils. Chloride forms strong complexes with Cd (e.g., $CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, and $CdCl_4^{2-}$) and therefore mobilizes and increases its phytoavailability. Data from several experiments indicate that soil salinity effects may dominate soil pH effects on the Cd uptake by plants, which is especially observed in potato tubers. A reported increase of Cd content in sunflower seeds was from 0.41 ppm on control soils to 1.12 ppm on soils with increased levels of Cl.[1388] The Cd contents increased up to 2.3 ppm and 2.8 ppm in winter and spring wheat grain, respectively, when grown on soil with KCl addition (control value, 0.18 and 0.16 ppm); whereas this increase was up to 2.03 and 1.49 ppm on soil amended with K_2SO_4 (control value, 0.10 and 0.16 ppm).[1510] A remarkable increase in Cd concentration in soil solution affected by NaCl is responsible for high Cd uptake by crop plants.[1502] Peat and phosphate amendments are known to inhibit the Cd uptake by crop plants.[1235] On the other hand, an increased Cd availability to crops on a sewage-sludge amended soil does not indicate an immobilization of Cd under influence of increased organic matter content.[1517] Results of the experiment carried out by Singh and Myhr[1497] have not shown any significant effect on its concentration in barley grain when Cd was applied to a soil in various forms.

Chaney and Hornick[129] reviewed plant response to increased levels of Cd in soil and showed a great difference in the ability of various plant species to absorb this metal. The difference in Cd content of crops grown on the same soil containing 10 ppm Cd exceeded 100-fold; the lowest concentration was in rice plants, Sudan grass, and clover, and the highest was in spinach and turnip. Also, the distribution of Cd within plant organs is quite variable and clearly illustrates its rapid transport from roots to tops and, in particular, to leaves (Figure 60). The Cd distribution in

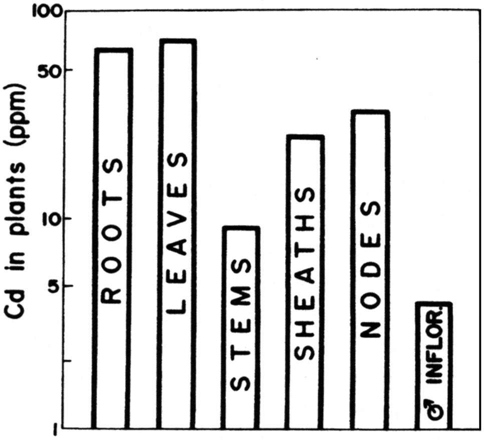

Figure 60 Distribution of Cd in corn plants grown in the soil with 15 ppm Cd.[1045]

strawberries indicates a rather low rate of transport from roots to above-earth parts of plants. The following Cd concentrations were found in strawberries grown on soil with 60 ppm Cd and neutral pH; roots 191–509 ppm; leaves 3.7–8.9 ppm; and fruits 0.15–0.7 ppm.[1261]

Tiffin[789] found the ^{109}Cd concentration in tomato xylem exudates to be from 1.5 to 3.5 μM after treatment with this radionuclide. This suggests that Cd, as other heavy metals, can be easily transported within a plant in the form of metallo-organic complexes.

Mechanisms of the long distance transport of Cd^{2+} have not yet been presented, but Cd most likely would be transported by the carrier mechanisms similar to those of Zn translocation. Cunningham et al.[155] reported that increased Cd^{2+} treatment progressively suppressed the proportion of Cd translocation to epigeal parts of young leaves and that Cd was localized mainly in roots, with lesser amounts in stem nodes, petioles, and major leaf veins.

A great proportion of the Cd is known to be accumulated in root tissues, even when Cd enters the plant via foliar systems.[376] This, however, was not reported for rice plants when ^{109}Cd was applied to the leaves.[395] When the amount of Cd is increased in the growth medium, the concentration of this metal in roots exceeds its content in the tops by about 100 times (Figure 55).

It may be concluded that the Cd in plants is relatively very mobile, although the translocation of Cd through the plant tissues may be restricted because Cd is easily held mainly in exchange sites of active compounds located in the cell walls.

2. Biochemical Roles

The most important biochemical characteristic of Cd ions is their strong affinity for sulfhydryl groups of several compounds (Cd complexes with metallothionein-like protein are already known). In addition, Cd also shows an affinity for other side chains of protein and for phosphate groups.

Dabin et al.[161] and Braude et al.[102] reported that Cd is likely to be concentrated in the protein fractions of plants. This fact is very important in food production problems.

There are no known enzymes that depend on Cd for their normal activity. Roucoux and Dabin[666] reported that Cd specifically induced cysteine and methionine synthesis in soybeans, depending on the degree of plant resistance to increased Cd levels. Cd is considered to be a toxic element to plants, and the basic cause of its toxicity lies in its disturbing enzyme activities. Cunningham et al.[155] and Baszynski et al.[54] reported inhibition of the formation of anthocyanin and chlorophyll pigments in plants that were treated with Cd. The amount of chlorophyll was found to be a function of the Cd concentration in plant tissues and has been proposed as an indicator of the upper critical Cd level in plants.[958] Kloke et al.[1052] estimated the phytotoxic concentrations of Cd to be 5 to 10 ppm (DW) in sensitive plant species, while Macnicol and Beckett[1081] gave the range of 10 to 20 ppm (DW) as critical Cd levels (Tables 36 and 42).

The response of bean plants to Cd in growth media depends on the age of plants and time of Cd action. With plant aging, their sensitivity to Cd increases and is more related to the functioning of the photosynthetic apparatus than to growth parameters. As Skórzynska-Pilot and Baszyñski[1499] reported, in young plants big changes in growth parameters are observed but photosynthetic activity is almost unchanged. Elevated concentrations of Cd in the rooting medium of barley affected the increase of shoot thionein mRNA, which is similar to the effect of a pathogen attack.[1378]

In general, overt symptoms induced by elevated Cd contents of plants are growth retardation and root damage, chlorosis of leaves, and red-brown coloration of leaf margins or veins. The phytotoxicity of Cd, beyond interfering with normal metabolism of some micronutrients, shows inhibitory effects on photosynthesis, disturbs transpiration and CO_2 fixation, and alters the permeability of cell membranes. The excess Cd has a complex inhibitory impact on the Calvin cycle, and especially disturbs a function of the key enzyme, ribulose diphosphate carboxyhydrazine. Photochemical activities of chloroplasts are significantly reduced at Cd concentrations of 50 to 75 $\mu M\ L^{-1}$ in the nutrient medium.[1523] Cd is also known to inhibit the DNA-mediated transformation in microorganisms and to interfere with symbiosis between microbes and plants, as well as to increase plant predisposition to fungal invasion. McKenney and Vrisacker[1090] found that Cd is an effective and specific inhibitor of the biological reduction of NO_2^- to NO. However, even at a high Cd content of soils, a slow adaptation of some streptomycetes species was observed.[1049]

The Cd content of plants is, however, of great concern as a Cd reservoir and as the pathway of Cd to man and animals. Thus, tolerance and adaptation of some plant species to higher Cd levels, although important from an environmental point of view, create a health risk.

3. Interactions with Other Elements

Plants are simultaneously exposed to a variety of pollutants, and thus their integrated effects most often are different from the effect of Cd only. Several elements are known to interact with Cd in both the element uptake by plants and in biochemical roles.

Cd-Zn interactions are commonly observed, but findings appear contradictory, since both depressing and enhancing effects of each have been reported (Chapter 7, Section VI.B.3). The interaction of Cd and Zn has received much study, and all findings may be summed up by stating that, in most cases, Zn reduces the uptake of Cd by both root and foliar systems. Chaney and Hornick[129] suggested that when the Cd:Zn ratio in plant tissues is limited to 1%, the Cd content is restricted to below 5 ppm, thus below its phytotoxic level (Table 36). Babich and Stotzky[41] described the double antagonistic interactions between Cd-Zn and Cd-Mg in microorganisms.

Cd-Cu interactions are also complex (Chapter 6, Section V.B.3). The inhibitory effect of Cu on Cd absorption is reported most often. Interactions of Cd with other heavy metals such as Mn and Ni are also often reported and appear to be related to their replacement by Cd during the uptake processes.

Cd-Fe interactions are related to disturbances in the photosynthetic apparatus. Only a moderate excess of Fe has a detoxificatory influence on Cd-treated plants, while a higher dose is toxic. Effects of Cd-Fe interaction on photosynthesis is most probably of an indirect nature.[1489]

Cd-Se mutual antagonistic effects were observed in certain crops. Cd-P interaction is exhibited in the P effects on Cd uptake by plants. Both increased and decreased contents of Cd under phosphate treatment are reported. Apparently, these reactions take place in the root media, and thus, the influence of the P supply on soils may differ for various soils and crops. It is most likely that Cd-P interactions may be similar to those in the Zn-P relationship.

Cd-Ca relationship seems to be highly cross-linked with variation in the soil pH. It cannot be precluded, however, that Ca^{2+} cations are able to replace Cd^{2+} in the carrier mechanism and thus Cd absorption by plants may be inhibited by an excess of Ca^{2+} ions. Cd uptake-translocation mechanisms are reported to be influenced by the supply of other nutrients such as K, N, and Al, but the results are not clear at this time and may be related to some secondary effects.

Interactions of Cd with several other essential elements (e.g., Mg, Mn) are observed and may be related to an impaired effect of Cd on the cell membrane, which disturbs their uptake and transport within plant organs. An antagonistic impact of Cd on P absorption by plants is significant for plant growth and agricultural practices. P uptake by plants can be reduced up to 40% of control values.

4. Concentrations in Plants

In man and animal nutrition, Cd is a cumulative poison; therefore, its content in food and feed plants has been widely studied. A comparison of the Cd contents of plant foodstuffs produced under uncontaminated conditions of various countries shows the highest Cd concentration in spinach leaves (0.11 ppm, FW) and lettuce leaves (0.66 ppm DW, 3.00 ppm AW) (Table 73). When plants are grown on contaminated soil, however, Cd is very likely to also be concentrated in roots (Table 74). This clearly confirms the statement that leafy vegetables such as spinach, and root vegetables such as turnips, carrots, and potatoes, should be considered to be the main routes of Cd supply to man. The highest contribution of Cd in the diet in Germany is calculated, in % of Recommended Dietary Allowance (RDA), for cereal bread as 13.3%, and for potatoes as 5.7%.[1247] In Japan, rice is the major source of Cd in the diet.

Table 73 Mean Cadmium Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis			DW Basis			AW Basis
		(569, 1187),	(395, 891)	(704, 705)	(233)	(497, 852)	(430)	(704, 705)
Sweet corn	Grains	0.012	—	0.007	0.1	—	0.06	1.00
Bean	Pods	—	0.02[a]	0.024	—	0.29[b]	—	0.34
Cabbage	Leaves	0.05	0.02	0.05	0.05	—	—	—
Lettuce	Leaves	—	0.11[c]	0.42	0.4	0.66	0.12[c]	3.00
Carrot	Roots	0.09, 0.03	0.05	0.15	<0.35	0.24	0.07	2.10
Onion	Bulbs	0.011	0.01	0.05	—	—	0.08	1.20
Potato	Tuber	0.001–0.09	0.02	0.08	0.05–0.3	0.18	0.03	1.80
Tomato	Fruits	0.02	—	0.11	—	0.23	0.03	1.00
Apple	Fruits	0.008	0.003	0.03	—	—	0.05	0.19
Orange	Fruits	—	0.002	0.005	—	—	—	0.14

Note: References are given in parentheses.

[a] Pulses.

[b] Soybean seeds.

[c] Spinach.

The background levels of Cd in cereal grains, as well as in common feed plants that are reported for various countries are fairly low and surprisingly similar (Tables 75 and 76). Thus, grand mean values for all cereal grains range from 0.013 to 0.22 ppm (DW), grasses range from 0.07 to 0.27 ppm (DW), and legumes range from 0.08 to 0.28 pm (DW). Recent data (1998) for cereals grain in Poland gave the mean Cd content as 0.06 ppm (Table 7), and similar values were obtained in monitoring during the period 1995 to 1997: mean Cd in wheat grain 0.09 ppm, and in rye grain 0.05 ppm.[1416,1514] The range for Cd in wheat flour in Poland is 0.001 to 0.1 ppm (average, 0.04 ppm).[1402] The median ($N = 128$) Cd concentration in wheat grain grown in France is 0.045 ppm (range, 0.015–0165 ppm).[1213] The average Cd concentration in wheat grain collected in Germany from 1989 to 1993 was 0.057 ppm (FW).[1247] Wheat grain of the U.S. has an average Cd concentration of 0.03 ppm (FW).[1549] The maximum limits for Cd in wheat grain established in various countries range from 0.05 to 0.1 ppm.

Potato stalks and tubers are especially susceptible to increased levels of Cd and potatoes are considered a major source of Cd in diets of several human populations.[1455] Therefore, the Cd concentration in potatoes is monitored in some countries. Potato tubers (washed, unpeeled) sampled from the whole territory of Poland from 1995 to 1998 contained a Cd average of 0.11 ppm (DW), and 0.02 ppm (FW).[1416,1357] Potato tubers collected in Germany (1989–1993) had 0.108 ppm.[1247] A median value for Cd in potato tubers on a state basis for the U.S. is 0.028 ppm (FW) (which roughly corresponds to 0.15 ppm DW).[1411] Potatoes sampled a decade earlier were reported to have a similar level of Cd, mean 0.03 ppm (FW).[1549]

At the present time, special attention is being given to the Cd content of carrot roots, which have a major use in baby foods. Usually, carrot fields are highly fertilized with phosphates. The average Cd concentrations in commercially grown carrots in different countries is (ppm FW): Sweden 0.32; Romania (industrial region) 0.23; Poland (industrial region) 0.20 and (rural region) 0.04.[1357]

Because Cd is readily available to plants from both air and soil sources, its concentration rapidly increases in plants grown in polluted areas. Data collected for several countries show that both industrial and agronomic practices may create a significant Cd supply to plants (Table 74). The highest concentrations of Cd in polluted plants were always reported for roots and leaves, whereas Cd seems to be excluded from seed crops. The highest Cd values reported for wheat grains (14.2 ppm) and brown rice (5.2 ppm) were less than the amounts of the metal accumulated in the root and leaf tissues of these plants. At present, Cd levels in cereal grains are of special interest as a potential significant source of this metal in the human diet. Despite considerable seasonal differences in the Cd uptake by cereals, the long-term experiment showed a general upward trend in the Cd content of grains grown on plots receiving

Table 74 Excessive Levels of Cadmium in Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean or Range in Content	Country	Ref.
Ancient mining area	Grass tops	1.0–1.6	Belgium	728
	Lichens	11–22	Belgium	728
	Brussels sprouts	0.10–1.77	Great Britain	168
	Grass tops	1.1–2.0	Great Britain	513
	Clover tops	4.9	Great Britain	513
Metal-processing industry	Lettuce leaves	45	Australia	57
	Silver beet leaves	0.04–0.49[a]	Australia	793a
	Turnip leaves	0.5	East Germany	430
	Grass, tops	8.2	Great Britain	1005
	Brown rice	0.72–4.17	Japan	395, 891
	Lettuce leaves	5.2–14.1	Poland	224
	Carrot roots	1.7–3.7	Poland	224
	Spinach leaves	6.4	Zambia	573
	Wheat grain	0.22–0.47	Poland	1510
	Mushrooms[d]	3–56	Finland	1069
Lignite coal-fired power station	Grass tops	1.1	Czech Republic	655
Urban garden	Brussels sprouts	1.2–1.7	Great Britain	786
	Cabbage outer leaves	1.1–3.8	Great Britain	786
	Lettuce leaves	0.9–7.0	U.S.	627
Sludged, irrigated, or fertilized farmland	Cereal grains	0.1–1.1	Finland	748
	Brown rice	5.2 (max.)	Japan	336
	Sudan grass, tops	0.3–2.9	Hungary	1177
	Lettuce[b]	70	U.S.	789
	Lettuce leaves	8–37	Germany	947
	Corn[b]	35	U.S.	789
	Lettuce leaves	0.5–22.8	U.S.	127
	Carrot roots	0.2–3.3	U.S.	127
	Soybean seeds	2.3	U.S.	102
	Cabbage leaves	130	Russia	826
	Wheat grains	5.5–14.2[c]	Russia	338
	Wheat leaves	19–47[c]	Russia	338
	Wheat roots	397–898[c]	Russia	338
Airborne contamination	Lettuce leaves	5.2	Denmark	625
	Spinach leaves	3.9	Denmark	625
	Carrot roots	3.5	Denmark	625

[a] FW basis.

[b] Diagnostic leaf.

[c] Pot experiment.

[d] *Boletus edulis.*

NPK fertilizers.[1044] Hornburg and Brümmer[1029] found also that the Cd content of wheat grain is highly correlated with the Cd concentrations in plow layer (Figure 59).

The maximum allowable limit of Cd in plant foodstuffs has been widely discussed and should always be calculated on the basis of daily metal intake by a given population group.[395,404] The threshold concentrations in feed plants may be a bit higher than those established for food plants and may differ for each kind of animal. However, in view of variable and secondary effects of Cd in the food chain, it is desirable to minimize its concentrations in crops.

The distribution of Cd in forest ecosystems is of special environmental concern. Cd is likely to be concentrated in the outer parts of conifer trees (spruce and pine), phloem, and bark (up to 1.3 ppm), which leads to its accumulation in wood ash up to 30 ppm. In the wood ash of willow, Cd contents can reach 70 ppm.[1391]

Table 75 Cadmium Content of Cereal Grains from Different Countries (ppm DW)

Country	Cereal	Range	Mean	Ref.
Australia	Wheat	0.012–0.036	0.022	878
Canada	Oats	—	0.21	497
Denmark	Oats	—	0.03[a]	625
Egypt	Wheat	0.01–0.09	0.05	213
Germany	All cereals	0.02–0.06	0.05	430, 488
Germany	Various cereals	0.01–0.75	0.22	55
	Barley	0.01–0.02	0.02	577
	Wheat	0.03–0.04	0.04	577
Great Britain	Wheat	0.03–0.06	0.04	1254
	Oats	0.02–0.03	0.02	577
Japan	Rice, unpolished	0.01–0.11	0.07	395, 891
	Wheat (flour)	—	0.03[a]	395
Norway	Barley	0.006–0.044	0.022	446
	Wheat	0.008–0.260	0.071	446
Poland	Oats	0.03–1.3	0.11	1045
	Wheat	—	0.056	1045
	Rye	0.03–0.25	0.08	1045
Sweden	Barley	—	0.013	22
	Wheat	—	0.06	18
U.S.	Rice	<0.001–0.23	0.012[a]	1187
	Wheat	0.07–0.13	0.10	906
	All cereals	0.1–0.5	—	704
Russia	Wheat	0.06–0.07	—	338

[a] FW basis.

Table 76 Mean Levels and Ranges of Cadmium in Grasses and Legumes at the Immature Growth Stage from Different Countries (ppm DW)

	Grasses		Clovers		
Country	Range	Mean	Range	Mean	Ref.
Canada	—	0.21	—	0.28[a]	497
Czech Republic	—	0.6	—	—	655
France	—	0.16	—	0.11[a]	577
Germany	0.05–1.26	0.27	0.02–0.35	0.16	430, 488
Germany	0.03–0.14	0.07	0.04–0.18	0.08[a]	577
Iceland	0.07–0.14	0.10	—	—	577
Poland	0.05–1.25	0.32[b]	0.07–1.0	0.46[c]	1045
U.S.	0.03–0.3	0.16	0.02–0.2[a]	—	330a, 704
Kazakhstan	0.1–0.55	0.22	—	—	1131

[a] Alfalfa.

[b] Orchard grass.

[c] White clover.

VIII. MERCURY

A. Soils

In all types of magmatic rocks, the Hg content is fairly low and does not exceed the order of XO ppb (Table 59). Initial estimation of the Clarke value for Hg varies from 50 to 77 ppb. Recently, there is a tendency to lower, by about half, the Hg Clarke value. Thus, Hg abundance in the Earth's crust is still uncertain (Table 59). A much higher concentration of this metal is reported for sedimentary rocks, argillaceous sediments and, in particular, organic-rich shales (common range, 40 to 400 ppb).

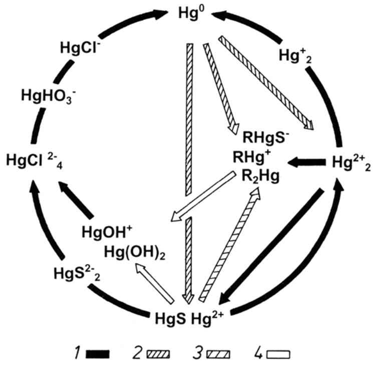

Figure 61 Ionic species and transformations of mercury compounds in soils. (1) Reduction; (2) oxidation; (3) formation of organic compounds; (4) hydration; R: CH_3,CH_3CH_2,C_6H_5.

The most important geochemical features of Hg are:

1. Affinity to form strong bonds with S (e.g., cinnabar, HgS, is the most common Hg mineral)
2. Formation of organomercury compounds that are relatively stable in aqueous media
3. Volatility of elemental Hg

Hg occurs in several minerals, but the only frequent one is cinnabar, HgS. This mineral is not easily altered and is seldom found as detrital material. Although Hg may form several ionic species (Figure 61), it is not very mobile during weathering (Table 10). As Jonasson,[367] Shcherbakov et al.,[715a] and Landa[458] have reported, Hg is likely to be strongly bound when added to soils as elemental Hg or as cationic or anionic complexes. Mercuryl ions (Hg_2^+) generally form weaker complexes than do mercury ions (Hg_2^{2+}). Hg is retained by soils mainly as slightly mobile organocomplexes. The behavior of Hg in soils depends highly on its form, which is a function of several soil parameters, and of initial Hg concentration in soil solution, as well as of other ions (e.g., Cl).[1562] Easily volatile fractions are, for example, Hg^0 and $(CH_3)_2Hg$; easily soluble are $HgCl_2$, $Hg(OH)Cl$, and $Hg(OH)_2$; and slightly mobile are mainly organic complexes (CH_3Hg^+ and CH_3HgS^-). Simple cations of Hg dominate in aerobic soil conditions. Complex anions of Hg with S are likely to occur in anoxic soil conditions, while methylated Hg compounds predominate in soils of intermediate redox states.

A broad review of Hg in soil, its distribution, speciation, and biological effects is presented by Rundgren et al.[1473] and Ebinghaus et al.[1284] The findings of Hem[312] and of Farrah and Pickering[229] clearly indicate that $Hg(OH)_2$ is likely to predominate over other aqueous species at a soil pH near or above neutrality. Some investigators believe, however, that $Hg(OH)_2$ is the preferred sorbed species.[948] The presence of an excess of Cl^- ions in soils appears to decrease the sorption of Hg^+ onto both mineral particles (including Mn oxides) and organic matter, because the highly stable Hg-Cl complexes are rather poorly sorbed.[948] The sorption of Hg by clays in soil seems to be relatively limited and to vary only a little with pH. However, in acid gley soils, the formation of HgS and even of metallic Hg may take place. The accumulation of Hg in soil is, therefore, controlled mainly by organic complex formation and by precipitation. Thus, the mobility of Hg requires dissolution processes and biological and chemical degradation of organomercury compounds.

Investigations carried out by Yin et al.[1562] show that less than 4% of the total Hg content could be adsorbed via electrostatic interaction, and it is not a major driving force for Hg adsorption by soil particles. The data of these authors clearly indicate the importance of soil organic matter in the adsorption and desorption of Hg^{2+}. However, the adsorption and desorption isotherms do not follow the same track. Anoshin et al.[1203] studied Hg behavior in the environment of western Siberia, and also emphasized the significant role of organic matter in its distribution within soil profiles and indicated different cyclings of Hg in forest ecosystems and steppe ecosystems. The studies of Malinina et al.[1398] indicate that suspension forms of Hg are mainly responsible for its migration in various soils of semi-humid and humid zones in Russia.

The transformation of organomercury compounds, especially the methylation of elemental Hg, plays the most important role in the Hg cycle in the environment. The mechanism of methylation has recently been the subject of many studies because methylated Hg is readily mobile and easily taken up by living organisms, including some higher plants.[58,359,470,856] Humic substances are known to mediate the chemical methylation of inorganic Hg by releasing labile methyl groups. On the other hand, a rapid conversion of organic Hg and Hg^{2+} ions to the elemental state (Hg^0) in contact with humic substances is also reported.[1064] The mechanism of the methylation of Hg is still not fully understood. It can occur abiotically; also, a vast number of organisms (especially microorganisms) may carry out these reactions. The methylation processes evidently have been involved in environmental catastrophes of Hg poisoning.

Several types of bacteria and yeasts have been shown to affect the reduction of cationic Hg^{2+} to the elemental state (Hg^0); thus, the result of these processes is the volatilization of Hg from the medium. The oxidation of elemental Hg to its cationic form can also be mediated by microorganisms.

The Hg content of virgin soil profiles is inherited mostly from the parent material; however, because Hg is easily volatile, some additional natural sources, such as degassing and thermal activity of the earth, cannot be precluded. The accumulation of Hg is related to the organic C and S levels in soils and is distributed in the surface soils at several times the concentration in the subsoils. Generally, organic soils have a higher Hg content than mineral soils. This is mainly due to a great capacity of humus, especially raw humus, for binding Hg. Johansson et al.[1041] reported high Hg concentrations in raw humus, often exceeding 0.3 ppm (DW). These authors assumed that the original level (baseline) was about 0.1 ppm, and they related this increase of Hg mainly to atmospheric fluxes of the metal. The sorption of Hg varies with pH, the highest being at pH from 4 to 5.[1143,1163] Although soils have greater capacity for organic Hg than for $HgCl_2$, the sorption of all Hg compounds is positively correlated with the organic C and CEC of the soils.

Background levels of Hg in soils are not easy to estimate due to widespread Hg pollution. Nevertheless, data reported for various soils on a worldwide basis show that mean concentrations of Hg in surface soils do not exceed 400 ppb (Table 77). The highest mean levels of Hg were reported for histosols of Canada (400 ppb) and for paddy soils of Japan (350 ppb) and Vietnam (300 ppb). Similarly, in organic and clay soils of the U.S., the highest average concentrations were found to be 280 ppb in histosols and 130 ppb in loamy soils. Apparently, the organic soils and paddy soils are likely to retain more than any other soils, the Hg resulting from vegetable decay and absorption from the atmosphere. The range of Hg in reference soils of China is from 15 to 294 ppb (mean, 142 ppb).[1313] The mean content of total Hg in agricultural surface soils and forest soils of Poland is estimated at 61 ppb, within the range 3.4 to 284.4 ppb, with the highest concentration in forest soils near the Nitrogen Fertilizers Works.[1274] The range for urban soils in Poland is 130 to 500 ppb.[1297] Thus, Hg contents exceeding these values should be considered contamination from anthropogenic or other sources.

1. Reactions with Soil Components

In soils, the migration processes involving Hg are rather limited; therefore, the Hg content of surface soils is slowly built up, even under a low input of this metal.[205] However, Landa[459] reported Hg losses by volatilization from soils, which increased with higher soil temperature and with higher soil alkalinity, and Kulikova and Nurgaleyeva[438] described a short life of Hg residues in chernozems from Hg seed dressing. As reported by Lodenius,[1071] a strong affinity of Hg to organic matter seems to increase with increasing soil acidity. Even in sandy soil, Hg is strongly adsorbed, and the addition of acid rain or salt solution does not increase its solubility. The Hg leaching from the soil may be stimulated by factors increasing the leaching of organic matter. Recent studies conducted on a large scale in Sweden showed a relative mobility of Hg in soils, especially of the Hg fraction which is bound to organic matter.[1064] Thus, Hg is leached out from the soil profiles in an acid environment in a form bound to organic compounds; and in neutral and slightly alkaline soils, it is leached out in an inorganic active fraction. Wallschläger et al.[1536] have shown that only a small part (about 1%) of the total Hg present in

Table 77 Mercury Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Holland	—	0.04	223
	Canada	0.01–0.70	0.06	243
	U.S.	0.01–0.54	0.08	706
	Poland	0.05–0.95	0.05	1390
Desert sands	Israel	0.008–0.03	0.02	724
	U.S.	0.02–0.32	0.06	218, 219
Cambisols, luvisols, and other loamy soils	Holland	0.45–1.1	—	223
	Egypt	0.012–0.03	—	990
	Canada	0.02–0.78	0.13	243
	U.S.	0.01–0.90	0.13	706
Soils on glacial till	Canada	0.02–0.10	0.05	368
	U.S.	0.02–0.36	0.07	706
Gleysols	Canada	0.018–0.22	0.05	520
Rendzinas	U.S.	0.01–0.50	0.05	706
Histosols and other organic soils	Canada	0.05–1.11	0.41	243
	U.S.	—	0.28	706
	Switzerland	0.04–0.11	0.08	637
Chernozems	U.S.	0.02–0.53	0.10	706
Forest soils	Norway	0.02–0.55	0.19	447
	Japan	0.02–0.20	0.07[a]	395
	U.S.	0.02–0.14	0.06	218, 219
	Yugoslavia	0.08–0.58	0.23	413, 754a
	Switzerland	0.073–0.10	0.08	637
	Russia (Asia)	0.12–0.35	0.19	1197
Paddy soils	Japan	0.15–0.76	0.35[a]	395
	Japan	0.13–0.46	0.27	277
	Vietnam	0.02–1	0.3	8
Volcanic soils	Italy (Etna)	0.03–0.101	0.08	931
Various soils	Canada	0.005–0.10	0.06[b]	521
	Great Britain	0.01–0.09	0.03	164a
	Greece	0.033–0.101	—	1022
	Japan	0.08–0.49	0.28	395
	Norway	0.02–0.35	0.19	367
	Poland	0.02–0.16	0.06	162
	Spain	0.03–0.37	0.15	929
	Sweden	0.004–0.99	0.06	19
	Germany	0.025–0.35	0.09	390
	U.S.	0.02–1.50	0.17	706
	Russia (Europe)	0.04–5.8	—	8
	Former S.U. (Asia)	0.01–0.29	0.08	1131, 1197, 1396
	Poland (peats)	0.05–1.4	0.09	1390

[a] Calculated from the histogram.

[b] Data for whole soil profiles.

contaminated soils can be mobilized by water, and entirely in the form of a complex bound to humic acids. Fulvic acids and particulates do not seem to contribute to this process. In contrast to other trace metals, the amount of mobilized Hg decreases at pH < 3 and at pH > 12, due to the extremely high buffering capacity of humics, both in acidic and alkaline states. Mou et al.[1429] estimated that the maximum Hg capacity of soil minerals and humus is in the range of 106 to 474 ppm, and 322 to 889 ppm, respectively. The humus-Hg is more easily released through evaporation and leaching than mineral-Hg. Johansson et al.,[1041] observed that the largest amounts of Hg are transported in the autumn and spring when the water discharge is high and the Hg content and acidity of the water are elevated. They calculated the flow rate between 1 and 6 g Hg km^{-2} per year. The Hg leached from soils, together with the Hg transported from the soil with runoff and direct aerial

Hg deposition onto the lake surface, have created complex and serious environmental problems.[1041,1064] Lodenius[1070] reported, however, that increased acidity of the eluent enhances the sorption of Hg to the humic substances, and thus decreases the leaching of Hg. Therefore, Hg is likely to be relatively strongly bound to organic compounds in acid soil conditions, and thus the Hg in acidified lakes of Scandinavian countries does not seem to be caused by an increased leaching of Hg from the soil.

The affinity of Fe oxy-hydroxides to bind Hg results in a concentration of this metal in the ferralitic soils, rich in ferruginous nodules. In these types of soils, Hg distribution is associated with Fe compounds rather than with organic matter. Increased levels of Hg are observed in Amazonian soils with horizons enriched in Fe oxides.[1300] Under processes of the reduction of Fe-oxides and the podzolization, Hg trapped by Fe-compounds is released into aquatic systems. Such behavior of Hg is likely to occur in soils of an aridic climatic zone.

Kot et al.[1371] measured Hg forms in soils and bottom sediments and concluded that the most mobile fraction of Hg bound to fulvic acids is present mainly in urban soils (up to 7% of total contents) and in bottom sediments (up to 14% of total contents). Predominating fractions of Hg, however, are those trapped by humic acids (26–59% of total contents) and fixed as not-hydrolyzing residue (17–66% of total contents).

The behavior of Hg in contaminated soils is of great interest since the ready bioavailability of this metal creates an important health hazard. Kitagishi and Yamane[395] have widely reviewed this topic, giving special concern to paddy soil. It can be generalized that inorganic compounds of Hg added to soils are likely to be absorbed well by humus and partly by clays. Various organic compounds of Hg (methyl, ethyl, and phenyl) added to soil are partly decomposed or adsorbed by soil constituents. However, all these compounds, having a relatively small degree of dissociation and adsorbability, are readily taken up by plants. The authors reported that methyl-Hg was the most available, while phenyl- and sulfide-Hg were the least available to plants and that residue of organomercuries varied, being the highest for phenyl-Hg and methyl-Hg iodide. Compared with methylation, demethylation is a much slower process, although both biological and chemical demethylations of methyl-Hg are reported.[948] Inverfeldt et al.[1342] reported that the rate of methyl-Hg production decreases with time, indicating that the added inorganic Hg is immobilized and unavailable for methylation a few months after addition. The net production of methyl-Hg is much faster in wetlands than in dry soil (up to 20 times). Thus, it is difficult to calculate the net production of methyl-Hg considering the total Hg pool of soils. Wallschläger and Bloom[1535] estimated that dimethyl-Hg contributes between 1 and 15% of the total Hg emissions from wetlands. Thus, dimethyl-Hg can be considered a "carrier species" in the transport of Hg from the soil to the atmosphere, but due to a rapid decomposition cannot serve as a simple indicator of the total Hg emission from soils.

The potential for microbial methylation of Hg by bacteria and fungi exists under both aerobic and anaerobic soil conditions. Soil contamination with Hg itself is usually considered not to be a serious problem, although there is the possibility that a large amount of methyl-Hg will result. Nevertheless, even simple Hg salts or metallic Hg create a hazard to plants and soil biota from the toxic nature of Hg vapor. The volatilization of Hg from Hg-polluted soils can also have an adverse effect on human health when exceeding the EPA inhalation reference concentration of 300 ng Hg m^{-3}.[1326]

Lagerwerff[447a] stated that Hg uptake by plant roots may be minimized by neutralizing the soil pH with lime. Also sulfur-containing compounds and rock phosphates have been proposed to inactivate mercurial fungicides or elemental Hg in soils. Sorterberg,[748] in contrast, reported that heavy liming was ineffective in reducing toxic effects of Hg excesses in the soil. Also, studies conducted by Oberländer and Roth[1105] with labeled Hg (^{203}Hg) showed that plants took up several times more Hg from the calcareous soil than from the acid soil. Stankheev et al.[1503] studied Hg flow in the soil gas in earthquake areas and have stated that the increase of the flow of Hg-vapors corresponds to the intensity of earthquakes.

2. Contamination of Soil

Sources of contamination of soil with Hg are related mainly to base metal processing industries and some chemical works (chloralkali, in particular), as well as due to earlier use of fungicides containing Hg (although these have not been used in most countries for the last 20 years). Worldwide occurrence and problems related to Hg-contaminated sites (Table 78) are discussed in a recent publication edited by Ebinghaus et al.[1284] Increased levels of Hg are also observed around coal power stations and metallurgic plants; in Poland, Hg contents of surface soils in such areas are up to 0.4 and 7.55 ppm, respectively.[1390] Extremely high concentrations of Hg were found in soils at a former battery recycling facility.[1326]

In the last few decades, Hg has been used in the gold amalgamation process in gold mines in Brazil (Amazon region) and in Siberian regions. The emission of Hg in one Hg mining area in central Brazil during the 1980s was estimated at about 80 t year^{-1}.[1467] Mallas and Benedicto[1082] estimated Hg losses to be 1.32 kg per kilogram Au. The amount of Hg used for gold mining in Brazil calculated for 50 t in 1985 was increased to 5000 t in 1995. Yagolnister et al.[1559] estimated that 210 t Hg remain in the Siberian environment annually. Such amounts of Hg added to the environment create a great risk of its transfer to the food chain. An increased load of Hg is an especially serious threat in the Amazonian region due to specific climatic conditions in which Hg becomes extremely mobile. The impact of Hg released into the atmosphere and into rivers and on

Table 78 Mercury Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Maximum or Range of Content	Country	Ref.
Ancient mining area, Hg mining or ore deposit	0.21–3.4	Great Britain	164a, 165
	0.2–1.9	Canada	368
	0.09–0.22	Brazil	1467
	54	Czech Republic	1114
	0.6–4.2	Yugoslavia	413, 414
	2.6–2.9	France[c]	1463
	8.2–40	U.S.	79, 703
	0.1–5.6	Former S.U.	198, 1396
Chloralkali or chemical works	3.8	Great Britain	111
	0.32–5.7	Canada	776
	0.06–0.495	Egypt	990
	0.10–0.43	Switzerland	637
	0.08–0.26	France	1463
Urban garden, orchard, and park	0.03–1.14	Canada	243
	0.25–15.0	Great Britain	488a, 850
	0.6	Great Britain	634
	0.6	U.S.	208
	0.04–0.08	Israel	724
	0.06–0.24	Japan	277
Sludged or irrigated farmland	10.0[a]	Holland	223
	0.03–0.15	Hungary	1177
	0.43–24	Germany	205, 947, 1023
	0.29–0.71	Japan	395
	0.8	Sweden	25
	0.68–1.43[b]	U.S.	1186
	0.12–0.35	Poland	162
Application of fungicides	9.4–11.5	Canada	498
Volcanic area	0.041–7.450	Italy (Etna)	931
	0.0014–0.0232	U.S. (Mt. St. Helens)	1146

[a] Soil flooded by Rhine River water.

[b] Nine years after sewage sludge application at rate 33 and 180 t ha^{-1}, respectively.

[c] Alluvial soils downstream from the ancient industrial Hg pollution.

plants and soils of this region, as well as in the Siberian subregion, has been extensively investigated in recent years.[1203,1284,1293,1559]

Although the physical sorption of Hg predominates in soils, in areas close to Hg ore deposits, sulfur compounds of Hg are frequently found.[1513] The dredging of sediments could mobilize Hg in aquatic systems since dissolved oxygen increases the amount of Hg^{2+} and methyl-Hg in solution.[948]

B. Plants

1. Biochemical Roles

The information on the biochemistry of Hg is concerned mainly with biological transformation of Hg compounds, but it is not yet clear which processes are most important in the cycling of Hg in the environment. Doelman,[982] Jernelöv,[359] Johansson et al.,[1041] and Weinberg[856] reviewed all topics related to Hg transformation and to Hg resistance in microorganisms. There is an assumption that microorganisms produce methyl-Hg for the purpose of detoxifying the metal, but at the same time methylated Hg being readily absorbed through cell membranes is highly biotoxic.[1171]

Plants seem to take up Hg easily from solution culture (Figure 62). There is also much evidence that increasing soil Hg generally causes an increase in the Hg content of plants. The rate of increase of the Hg content in plants when the soil was the only source of this metal was reported to be highest for roots, but leaves and grains also accumulated much Hg.[321,481,748] These findings show that Hg is easily absorbed by the root system and is also translocated within the plants. Blanton et al.,[79] on the other hand, reported that Hg levels in plants bear little relationship to the Hg content of soils from an Hg mining district and that this reflects strong Hg bonds to soil components. Also, in the official report on Environmental Mercury and Man,[214] it was stated: “For most plants, even when grown on soils having much higher concentrations of mercury, there is very little additional uptake.” Malikova et al.,[1397] however, have stated that the Hg content of the roots of *Artemisia* species is a function of its soil granulometric fraction of less than 0.1 mm, and increasing up to 0.15 ppm at about 1 ppm Hg in the soil fraction. Fine, hairy roots contain more Hg than coarse roots.

Plants are known to directly absorb Hg vapor. Browne and Fang[107] reported that the rate of Hg vapor uptake is particularly influenced by illumination, but is unaffected by ambient temperature. Thus, soil Hg is not only directly absorbed by plants, but also indirectly absorbed from Hg vapor

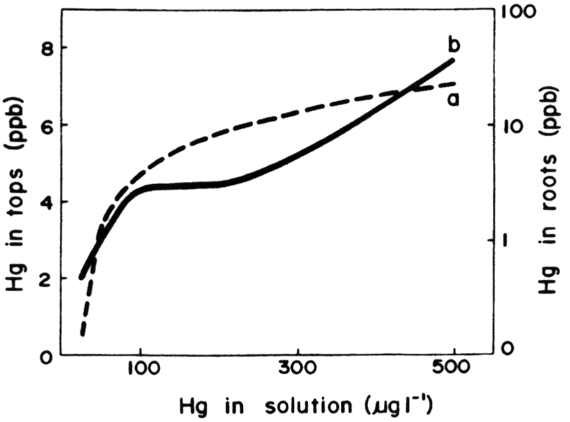

Figure 62 Uptake of Hg by 7-day-old oat seedlings from the culture solution of $HgNO_3$ concentration. (a) Tops; (b) roots.[735]

gradually released in soils. The soluble Hg forms in aerosols are easily adsorbed by pine needles and transported inside plants.[1319]

Translocation of Hg occurs in various plant tissues, including apple leaves to fruits, from potato leaves to tubers, from rice leaves to grains, and also from the wheat and pea seed treated with mercurial fungicides into the first-generation seed.[447a] The content of Hg in rice grains harvested from plants treated with phenylmercuric acetate was reported to be the highest in bran but the fraction of Hg accumulated in whole grains apparently was associated mainly with gluten.[395] The Hg content of grains is shown to be correlated with the ash content of grain fractions. Since bran is the richest and flour is the poorest in ash, the Hg content of bran is about three times higher, on average, than the Hg content of flour.[1105]

Although Hg is known to bind strongly to the amino acid S atoms contained in many proteins and enzymes, this metal seems to be relatively easily transported in plants. The Hg affinity to sulfhydryl groups apparently is the key reaction in disrupting metabolic processes of plants.

Toxic effects in young barley were observed at an Hg level of 3 ppm (DW), and Hg at a concentration of 0.01 ppm (AW) was reported to be severely toxic.[171,710] The toxicity of volatilized elemental Hg and of some methylated compounds is known to be the most serious for plants. Siegel et al.[1145] suggested that Hg vapor accelerates senescence-related processes via elevated ethylene production and that the most active toxicant is elemental Hg—not ionic Hg. They found that young plants are more sensitive to Hg-saturated air than mature plants. Kloke et al.[1052] reported the retardation of growth of sensitive plant species at an Hg content ranging from 0.5 to 1 ppm (DW), whereas Macnicol and Beckett[1081] established the critical level of Hg from 1 to 8 ppm (DW) (Table 42). Mhathre and Chaphekar[1092] observed damage to plants even at 1 ppb Hg concentration in the nutrient solution. They reported that Hg impact should be considered in the event of failure of various metabolic processes like photosynthesis, chlorophyll manufacture, exchange of gases, and respiration.

The symptoms of Hg toxicity are, most commonly, stunting of seedling growth and root development and inhibition of photosynthesis and, as a consequence, a reduction in yield. Hg accumulated in root tissue inhibits K^+ uptake by plants, although the stimulating effect of low Hg concentration on K^+ uptake was also reported by Hendrix and Higinbotham.[315]

The resistance to Hg compounds in fungi and bacteria has received extensive study, as it is of practical importance. Weinberg[856] reviewed results and demonstrated that in most cases the resistant strain was capable of volatilizing Hg. Plasmids are believed to carry determinants for the Hg resistance.

Particularly resistant to high Hg concentrations is the transgenic *Arabidopsis thaliana* with the genes for mercuric ion reductase (reduction of toxic Hg^{2+} to the relatively inert Hg^0).[1407] This plant (as probably others with such a gene) is believed to be useful as a phytoextractive plant to grow on the contaminated sites. The tolerance to Hg in higher plants has also been reported, and although the mechanism of the physiological barrier is not known, it is most probably related to the inactivation of Hg at the membrane sites. The affinity of Hg to form insoluble compounds with S-rich proteins was reported for several plant species.

Some chemical fertilizers are known to affect Hg uptake in roots. Their impact, however, differs with soil characteristics and amount of Hg. Most commonly, ammonium sulfate and calcium phosphate decrease the Hg uptake in corn roots and increase the amount of Hg volatilizing from soil with high Hg contents.[1558]

2. Concentrations in Plants

The distribution of Hg in plants has recently received the most study because of the Hg pathway into the food chain. Therefore, most information is at present related to the Hg content of plant foodstuffs. The background levels of Hg in vegetables and fruits vary from 2.6 to 86 ppb (DW) and from 0.6 to 70 ppb (FW) (Table 79). Vegetables from western Siberia contain from 5 to 36 ppb Hg (FW), and the highest concentrations were in cucumbers.[1203] Potato tubers collected in Poland have

Table 79 Mean Mercury Content of Plant Foodstuffs (ppb)

Plant	Tissue Sample	FW Basis	DW Basis	Ref.
Sweet corn	Grains	—	4.6, 3	126, 705
	Corn Products	—	11	1136a
Bean	Pods	70, 17	3, 11	163, 373, 395, 705
Beet	Roots	3	—	776
Carrot	Roots	—	86, 5.7	496,705
Lettuce	Leaves	<0.6	8.3	705, 776
Cabbage	Leaves	10	6.5	395, 706
Potato	Tubers	3, 12	47, <10	163, 496, 705, 710
	Potato products	—	26	1136a
Onion	Bulbs	7	<10	163, 705
Cucumber	Unpeeled fruits	1,11	—	163, 776
Tomato	Fruits	1	34, 3.1	496, 705, 776
Apple	Fruits	10	<10	163, 705
Orange	Fruits	—	2.6	705
Lemon	Fruits	43	—	163
Mushroom	Caps and stalks	—	3.5	754a
Tea	Leaves	—	34–46	1032

Table 80 Mercury Content of Cereal Grains from Different Countries (ppb DW)

Country	Cereal	Range	Mean	Ref.
Canada	Barley	5–17	12	279[a]
	Oats	4–19	9	279[a]
	Wheat	7–15	11	279[a]
Egypt	Wheat	11–28	21	213
Germany	Wheat	—	<10	400
Japan	Wheat (flour)	—	20[a]	395
	Buckwheat (flour)	—	10[a]	395
Norway	Barley	0.2–17.2	3.4	446
	Wheat	0.2–2.7	0.9	446
Poland	Barley	7–82	19	373
	Oats	7–42	20	373
	Rye	3–18	9	373
	Wheat	4–33	13	373
	Wheat (flour)	0.8–17	4.2	1136a
Sweden	Oats	<4–45	14	748
Switzerland	Wheat	6–10	7	637
U.S.	Barley	—	19	110
	Oats	—	12	110
	Wheat	10–16	14	110, 447a
Russia	Wheat	7–12	10	163
	Various grains	12–18	15	1197

[a] FW basis.

from 3 to 45 ppb Hg (FW). The highest Hg concentrations were always found in crops grown in industrial regions.[1245]

Gracey and Stewart[279a] reported Hg to average 39 ppb (DW) in alfalfa; Rovinskij et al.[1130] gave the range from 10 to 160 ppb Hg (DW), average 50 ppb, in grasses of northern Kazakhstan; and other observations[1045] show that natural Hg levels in grass and feed legumes do not exceed 100 ppb (DW). The Hg contents of cereal grains seem to be fairly similar for various countries and for certain kinds of cereals, with mean values ranging from 0.9 to 21 ppb (DW) (Table 80). However, grain crops from land where mercuric compound dressings of seeds were used show some elevation (up to 170 ppb DW) in the Hg content.[162] A similar statement was made by Kulikova and Nurgaleyeva,[438] although without analytical data. The latter reports do not support the earlier findings indicating that the use of Hg in the U.K. for the treatment of cereal seeds had very little effect on Hg levels in the grains.[214]

Plants differ in their ability to take up Hg and can also develop a tolerance to high Hg concentrations in their tissues when grown in soils overlying Hg deposits. Shacklette et al.[710] reported Hg to range from 0.5 to 3.5 ppm (DW) in trees and shrubs from areas of Hg mineralization. In general, Hg content of plants is high when the Hg content of soils is also high, but this relation does not always hold. Siegel et al.[1147] discussed this problem and stated that several data support the hypothesis that specific local environmental factors strongly influence the accumulation of Hg in plants, even when the immediate soil concentrations are the same.

Plants grown in contaminated sites may accumulate much higher than normal amounts of Hg (Table 81). Certain plant species—lichens, carrots, lettuce, and mushrooms in particular—are likely to take up more Hg than other plants grown at the same sites. Also, some parts of plants have a greater ability to adsorb Hg, as is the case of apple flesh and apple pips. Extremely high Hg content (from 72 to 200 ppm [DW]) was found by Lodenius and Herranen[1072] in mushrooms (*Agaricus* species) that occur in the immediate vicinity of the chloralkali plant in Finland (Table 81). Nuorteva[1104a] described a high accumulation of Hg by various species of mushrooms in Finland and gave, after

Table 81 Mercury Content of Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Maximum or Range of Content	Country	Ref.
Mining area and metal-processing industry	Edible mushrooms	37.6	Yugoslavia	414
	Boletus edulis	0.3–1.5	Finland	1069
	Carrot, roots	0.5–0.8[a]	Yugoslavia	116
	Apple, flesh	0.04–0.13[a]	Yugoslavia	116
	Apple, pips	0.33–1.32[a]	Yugoslavia	116
	Pine needles	0.2–11.4	Italy	931
	Labrador tea, stems	1–3.5	U.S.	703
Chloralkali or chemical works	Lettuce, leaves	0.09–0.35	Egypt	990
	Lettuce, leaves	0.15–0.36	Switzerland	637
	Spinach, leaves	0.11–0.59	Switzerland	637
	Corn, grains	0.074–0.136	Switzerland	637
	Radish, roots	0.032–0.29	Egypt	990
	Lettuce, leaves	0.1[a]	Canada	776
	Festuca rubra	4.0	Great Britain	111
	Lichens	36.0	Finland	485
	Edible mushrooms	72–200	Finland	1072
Urban vicinity and parks	Edible mushrooms	33.6	Switzerland	635
	Bryophytes	1.4	U.S.	893
Sludged or irrigated farmland	Bromegrass, tops	0.09–2.01[b]	Canada	321
	Sudan grass, tops	0.04–0.06	Hungary	1177
	Brown rice, grains	4.9	Japan	336
Application of fungicides or Hg salts	Potato, leaves	1.1–6.8	Canada	585
	Lettuce, leaves	0.1–0.3	Canada	496
	Oat, grains	0.63[b]	Sweden	748
	Oat, straw	99[b]	Sweden	748
	Wheat, grains	0.05–0.17[c]	Poland	162
Volcanic areas	Lichens	0.102–0.213	Italy (Etna)	931
	Pine needles	0.007–0.027	Italy (Etna)	931
	Pine needles	0.031–0.330	U.S. (Hawaii)	931
	Horsetail	0.002–0.045	U.S. (Mt. St. Helens)	1146

[a] FW basis.

[b] Pot experiment.

[c] After Hg treatment of seeds.

Autio, the Hg range from 1.1 to 4.7 ppm (DW) for edible *Boletus edulis* growing in sites with no local pollution sources. Thus, mushrooms as well as rootless mosses and lichens are known to be suitable bioindicators for Hg in the ecosystems. Pine needles are also most often reported as sensitive Hg environmental biomonitors[931] (Table 81).

Several authors have made an attempt to estimate a permissible limit for Hg in food plants and have proposed 50 ppb (FW), although the background Hg levels for plants have been estimated by Kosta et al.[415] to range from 1 to 100 ppb DW. The baseline Hg in indicator plants selected by Nuorteva[1104a] for the forest ecosystems in Finland is within the range of 10 to 330 ppb (DW). The allowable limit of Hg in plant foodstuffs should always be calculated on the basis of daily Hg intake by a given population group.

CHAPTER 8

Elements of Group III

I. INTRODUCTION

Geochemical and biochemical properties, as well as the abundance in the biosphere, of all the trace and rare elements of Group III (new group 13) are highly divergent. The geochemistry of Group IIIa elements is especially complicated, reflecting a wide range in occurrence and behavior from B, the lightest nonmetal, to amphoteric Al, which is one of the basic constituents of the lithosphere. Ga, In, and Tl (the latter two being widely distributed elements in the lithosphere and biosphere) also belong to this group. A strong affinity for oxygen and the predominant +3 state are common characteristics of these elements. In Group IIIb (new group 3) Sc and Y are very rare in the environment. Other rare elements are subdivided into the lanthanides and actinides, of which many are natural or artificial radionuclides.

II. BORON

A. Soils

B, the only non-metal among the elements of Group III, is not uniformly distributed in the Earth's crust. The B content of magmatic rocks increases with the acidity of the rocks; while in sedimentary rocks, the element is associated with the clay fraction (Table 82). B is known to be associated with organic matter and is enriched in some carboniferous sediments. This indicates that B may be preferentially fixed in some kind of organic substances, and its concentrations are elevated in some coals.[1357] The largest quantities of B are concentrated in marine evaporites and in marine argillaceous sediments; therefore, their B content can serve as a paleosalinity indicator. It should be emphasized, however, that the geochemistry of B is characterized by an abnormally large range of variation in its concentration in rocks. In the terrestrial environment, B is likely to occur in chemical combination with oxygen and is known to form several minerals, mainly hydroxides and silicates, of which the tourmaline group is the most common in soils.

During chemical weathering of rocks, B goes easily into solution, forming several anions such as BO_2^-, $B_4O_7^{2-}$, BO_3^{3-}, $H_2BO_3^-$, and $B(OH)_4^-$. Although B is likely to be retained by clays (illitic minerals in particular and also by sesquioxides and organic substances), its concentration in soil solutions in relatively high, ranging from 67 to 3000 μg L^{-1} (Table 16). The most common forms of B in soil solutions are, apparently, its undissociated acid H_3BO_3 and, in part, $B(OH)_4^-$. Only at pH above 7 are other anions such as $H_2BO_3^-$ and $B_4O_7^{2-}$ likely to occur in soil solutions.

Table 82 **Boron, Aluminum, Gallium, Indium, Thallium, Scandium, and Yttrium in Major Rock Types (values commonly found, based on various sources)**

Rock Type	B (ppm)	Al (%)	Ga (ppm)	In (ppb)	Tl (ppm)	Sc (ppm)	Y (ppm)
Magmatic Rocks							
Ultramafic rocks: dunites, peridotites, pyroxenites	1–5	0.45–2.0	1–3	10–60	0.05–0.2	5–15	0.5
Mafic rocks: basalts, gabbros	5–20	7.8–8.8	15–20	20–220	0.1–0.4	20–35	5–32
Intermediate rocks: diorites, syenites	9–25	8.8	15–24	40–130	0.5–1.4	3–10	20–35
Acid rocks: granites, gneisses	10–30	7.2–8.2	16–20	40–200	0.6–2.3	3–14	30–40
Acid rocks (volcanic): rhyolites, trachytes, dacites	15–25	6.9–8.1	20	30–150	0.5–1.8	3–8	28–44
Sedimentary Rocks							
Argillaceous sediments	120	7.2–10.0	19–25	70	0.5–1.5	12–15	25–35
Shales	130	7.8–8.8	15–25	50	0.5–2.0	10–15	30–40
Sandstones	30	2.5–4.3	5–12	XO	0.4–1.0	1	15–50
Limestones, dolomites	20–30	0.43–1.30	1–3	XO	0.01–0.14	0.5–1.5	4–30

The behavior of B in soils has been widely studied, and the basic results have been summed up by Ellis and Knezek[207a] and more recently reviewed in a book edited by Gupta.[1320a] It has been shown that B is sorbed more strongly by soils than are other anions (e.g., Cl^- and NO_3^-), and the manner of B sorption by the clay surface is somewhat similar to that of cations rather than anions. B may be entrapped in the clay lattice by substitution for Al^{3+} and/or Si^{4+}.[427] Thus, B-silicate compounds (minerals) are likely to occur in soils. Adsorbed B on soil minerals is rather easily leachable; however, irreversibility of B sorption has also been observed. The variable fixation of B is due to different mechanisms of B-anion sorption, including ligand exchange, formation of surface complexes, and incorporation into clay mineral lattices.

In general, retention of B is greater on sesquioxides than on clay minerals, and the hydrous oxide of Al is more effective than that of Fe. Lindsay[475] stated that B adsorption on oxides of Fe and Al is believed to be an important mechanism governing B solubility in soils. Čumakov[973] observed the decrease in the solubility of B in soils heavily fertilized with K. This might be a secondary effect of the B affinity to illites or K-montmorillonites, which are known to be formed in soils enriched in K. Organic matter also exercises a powerful influence on B mobility and availability, particularly in acid soils.[166] Soil organic matter adsorbs more B than mineral soil constituents. B adsorption on a soil humic acid increases with increasing pH, up to a maximum near pH 9, and decreases at $pH > 9$. Ligand exchange is a possible mechanism for B sorption by organic matter.

There are several descriptions in the literature of mechanisms of B reactions with soil components; however, the nature of B adsorption in soils is still not well-understood. These reactions are highly pH dependent, with the maximum always occurring at pH above 7. The B adsorption by oxy and hydroxy bonds by surface coatings and by incorporation into interlayer or structural positions of aluminosilicates are the mechanisms likely to predominate in acid and neutral soils. Jin et al.[1040] found the highest amount of B occluded in crystalline Al and Fe oxyhydroxides (up to 74% of the total soil B), and a smaller amount occluded in amorphous Al and Fe oxyhydroxides (up to 34%). On the other hand, in arid-zone soils, B is likely to be coprecipitated with Mg and Ca hydroxides as coatings of soil particles, and B may also occur as Na-metaborate. In sodic soils, tourmaline is reported to be the major source of B.[72]

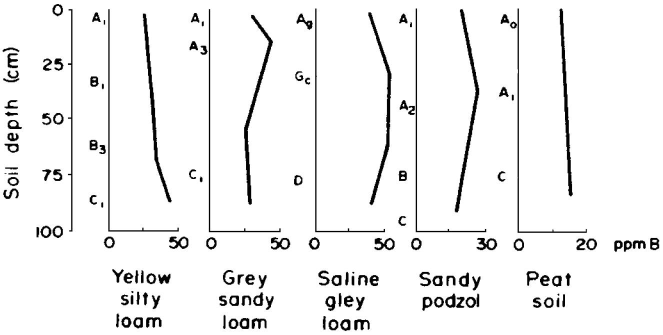

Figure 63 Distribution of B in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

In soils, B is considered to be the most mobile element among the micronutrients, although its water-soluble fraction is relatively low and varies from 3.2 to 5.3% of the total content.[973] Thus, B movement in soils follows the water flux, and in cool humid-zone soils B is leached downward in soil profiles, whereas in soils of warm humid, or arid and semiarid regions, B is likely to concentrate in surface horizons (Table 14). B may also be concentrated in other soil horizons that are enriched in illitic clays or sesquioxides (Figure 63).

The B status of arable soils has been extensively investigated throughout the world. The total B content in surface soil ranges from 1 to 467 ppm, and its average content ranges from 9 to 85 ppm. The lowest amounts of B were found in sandy and loamy soils of Poland and New Zealand, while the highest concentrations were reported for lateritic soils of India, for solonchaks of Russia, and for calcareous soils of Israel (Table 83). On a world scale, total B contents are lower in podzols and histosols than in other soil units, and average 35 ppm for all soils (Table 9). Levels of total B reported for soils of the U.S. seem to be fairly stable, with calculated means from 20 to 55 ppm.[219,706] It should be pointed out, however, that due to the low detectability of the analytical method that was used, some values of B in soils could be overestimated.

Although B is a rather deficient micronutrient in most soils, some soils of arid or semi-arid regions and soils overfertilized with B may contain hazardous amounts of this element. Some sewage sludges and fly-ash may also be significant sources of B contamination of soils.

B-rich soils are known to cause B toxicity in the field, as well as decreased crop yields in different regions of the world. This is primarily associated with soils developed on marine argillaceous sediments and with man-induced contamination; for example, in sewage wastewaters, up to 40% of B is from a detergent source. The yearly input of B in surface waters in the U.S. is calculated at 32,000 t, and this creates both environmental and agricultural problems in some areas. The amelioration of high-B soils is very difficult.[1440]

Light acid soils with an excessively high level of B are easily improved by irrigation. The B hazard in sodic soils is proposed by Bhumbla and Chhabra[72] to be ameliorated by the addition of gypsum, which converts readily soluble Na-metaborate to sparingly soluble Ca-metaborate. Also, phytoamelioration has been recently reviewed as a promising practice. B-tolerant grass species and some *Brassica* are suitable for phytoremediation because these plants can extract B from soils and decrease soil total B by about 7% compared with the control. As McGrath[1407] stated, such a decrease—especially in extractable and leachable species of B in soils—can alleviate two problems: toxicity to subsequent crops and the potential toxicity of drainage water. Heavy applications of $Ca(H_2PO_4)_2$ also resulted in a lower availability of B, especially in acid soils. As Prather[626] reported, sulfuric acid can effectively aid in reclaiming soil high in B, but the enhanced desorption of B by silicate ions is believed to be the main soil reaction.

Table 83 Boron Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Israel	29–43	—	644
	New Zealand	1–56	15.5	865
	Poland	5–134	9	91, 382
	U.S.	<20–100	35	706
	Russia	—	15.5	912
Loess and silty soils	China	48–128	88	1068
	New Zealand	—	37	865
	Poland	14–48	35	91, 382
	U.S.	<20–70	40	706
Loamy and clay soils	New Zealand	<1–32	10.5	865
	Poland	3–75	15	91, 382
	U.S.	7–70	50	250, 706
Fluvisols	India	4–9	—	772
	Israel	50–85	—	644
	Czech Republic	48–75	61	973
	New Zealand	14–37	29	865
Gleysols	New Zealand	13–60	31	865
Rendzinas and other calcareous soils	China	20–210	97	1124
	Israel	100–145	—	644
	Poland	1–194	25	91, 382
	U.S.	<20–70	35	706
	Russia	—	10.5	912
Kastanozems and brown soils	China	31–92	61	1068
	New Zealand	11–70	34.5	865
	Russia	—	40.5	912
Ferrasols	China	5–300	60	1068
	India	14–467	—	772
	Israel	30–60	—	644
Solonchaks and Solonetz	India	12–81	34[a]	772
	New Zealand	28–67	44	865
	Russia	49–105	85	12, 351, 912
Chernozems	Czech Republic	42–64	54	973
	U.S.	<20–70	35	706
	Russia	47–68	52	4, 351, 912
	Yugoslavia	—	32	412
Prairien and meadow soils	China	32–72	54	1068
	Russia	27–50	38.5	12
	Yugoslavia	—	38	412
Histosols and other organic soils	New Zealand	4–15	8.8	865
	Poland	17–48	—	91, 382
	U.S.	<20–100	30	706
	Russia	8–47	26.5	912
Forest soils	China	—	46	225
	U.S.	30–70	35	218, 219
	Russia	—	32	4, 912
Various soils	Czech Republic	54–76	65	973
	Great Britain	4.7–21	13	818
	New Zealand	2.5–47	15.5	865
	Romania	21.5–68.5	43	43
	U.S.	<20–150	45	706

[a] Data for alkaline, saline, and calcareous alluvial soils.

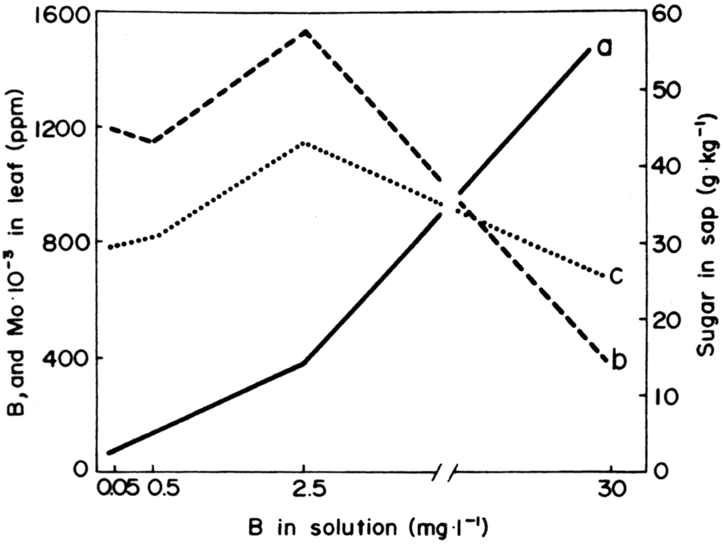

Figure 64 The effect on sugar beet of B levels in the nutrient solution. (a) B concentration in leaves; (b) Mo concentration in leaves; (c) sugar content of sap.[90]

B. Plants

B is important in plants metabolically and is believed to play the most significant role in the translocation of sugars because the borate-polyhydric complex is more mobile than polar sugar molecules. Most studies have been done on the effects of B on the metabolism of sugar beet, and it has been shown that adequate B supply is necessary for sugar synthesis (Figure 64).

1. Absorption and Transport

Soluble forms of B are easily available to plants which can take up undissociated boric acid as well as other B species present in the ambient solution. The property of boric acid to complex with polysaccharides is believed to play an important role in passive sorption.[531]

There is still controversy as to the extent to which the uptake process is either passive or active. From several reviews presented by Moore,[548] Price et al.,[630] Shkolnik,[719] and Loneragan,[489] it may be concluded that B uptake by roots consists of different phases. Moore[548] described three processes, whereas Bowen[95] observed six phases of B absorption by barley roots. The metabolically controlled process seems to be relatively minor; the B absorption mainly follows water flow through the roots. The B uptake is, therefore, proportional to its concentration and to the water flow. Indeed, Jin et al.[1040] reported that B concentration in corn tissues correlates positively with four easily soluble species of B; for example, water soluble, sorbed (either specifically or nonspecifically), and occluded in Mn oxyhydroxides. The sum of these four B species accounts for only 0.4 to 2.0% of the total B in soils. Szabo[1158] reported that the B uptake by plants increases with its content of nutrient solution, and that is far greater than physiological needs. A relatively close relationship was observed between citrus leaf B and hot-water-soluble B in soil in several studies.

Hu and Brown[1337] have reviewed the mechanisms of B absorption by plant roots; B is absorbed from soil solution mainly as undissociated boric acid, which theoretically should be membrane permeable. Thus, it can be predicted that B absorption is primarily determined by the B concentration in the nutrient solution and the transpiration rate of the plants. However, B uptake differs between species, genotypes, etc. Also, the range of genotypic variation in plant response to a low B level in soil is very large. B uptake in higher plants is most probably a passive process related to the external boric acid concentration and to the transpiration rates, but it is under the control of membrane permeability and internal complex formation. There is ample evidence that B nutrition has marked effects on proton secretion and creation of an electrical potential gradient across the membranes. Thus, the B supply may stimulate proton-pumping activity of membranes, resulting in an increased driving force for ion influx (uptake). On the other hand, B deficiency results in an increase in membrane permeability of leaf cells. As compared with B-sufficient leaves (of sunflower), B-deficient leaves net efflux was 35-fold higher for K^+, 45-fold higher for sucrose, and sevenfold higher for phenolic and amino acids.[1248]

Soil pH is one of the most important factors affecting the availability of B to plants. The lowest ratio of B uptake occurs when the soil pH is approximately 7. In alkaline soils, the availability of B increases with an increase in soil pH. This affects B hazard problems, particularly in irrigated saline-alkaline soils.[72] The absorption of B is temperature dependent and increases during warm periods.

B is relatively immobile in plants; but because it is translocated mainly through the xylem, it is largely accumulated in old leaves in which the highest B content is in the tips and margins.[1158] Epigeal parts of plants usually contain more B than do roots. Although B is easily retranslocated in phloem, the mobility of B in plant tissues is restricted. This phenomenon has implications in the diagnosis of B imbalance in crops. The foliar application of B has not been widely used in agriculture as it was believed that the immobility of B would limit its effectiveness. Recent findings, however, have shown that foliar application of B can supply B to flower and fruit tissues, and at any time to functional leaves. However, after foliar B fertilization, there was no corresponding effect on fruit yield (orange juice) or on chemical characteristics.[1232]

Van Goor[820a] compared the B concentrations in phloem exudate ($10\ \mu g\ g^{-1}$) and in leaf tissue ($34\ \mu g\ g^{-1}$) and showed that B content relative to other micronutrients is higher. This may indicate that the absorption of B during its transport within veins is less than that of other elements. Although B may become quite immobile within plant tissues, there are indications that B can be transported from leaves to developing fruits and seeds.

2. *Biochemical Functions*

The physiological role of B differs from other micronutrients in that this anion has not been identified as a component of any specific enzyme. Despite the essentiality of B for higher plants, the biochemical role of this element is still not well-understood. There have been many physiological experiments, usually with B-deficient plants, and the results are extensively reviewed by Price et al.,[630] Shkolnik,[719] Jackson and Chapman,[348] and Mengel and Kirkby.[531]

The *Symposium on Boron in Soils and Plants* held in Thailand (Chiang Mai) in 1997 highlighted recent research activities and results, mainly on B deficiencies. Crop responses to B are highly variable on plant species and genotypes, as well as on growth conditions. Recent research of the biochemistry of B has emphasized the particular importance of B interactions with biological membranes, and with a variety of biomolecules. The deficiency of B in the field reveals an impaired sexual reproduction, marked seed yield reduction, and low male fertility. However, there is a great diversity of effects of low B on reproductive growth among species. As Dell and Huang[1275] stated, much of the data on severely B-deficient plants require reevaluation. However, positive responses to B application have been reported in over 80 countries, where soil parent material and texture are major factors controlling the B status of soils (Table 39).

The functions of B are related to some basic processes such as:

1. Carbohydrate metabolism and transport of sugars through membranes
2. Nucleic acids (DNA and RNA) and phytohormone syntheses

3. Formation of cell walls
4. Tissue development (involvement in a messenger role in plants is suggested)
5. Formation of stable complexes with compounds having *cis*-hydroxyl groups
6. Formation of B complexes with the constituents of cell walls and plasma membranes

Although B is well-known to be essential for plants, the primary functions of B are still not fully understood. B seems to be of crucial importance for the structural integrity of plasma membranes. As Matoh[1403] described, it is now clear that boric acid links some cell wall components, but it is not clear yet whether there is a structural requirement for B in cell wall function.

B deficiency in several plant species is common on a worldwide scale (Table 39), and its deficiency in some commercial crops such as sugar beet and mangels, celery, sunflower, legumes, and apples is of great agronomic concern. Specific symptoms of B deficiency (Table 38) first appear as retarded and abnormal development of growing points, blue-green color of young leaves, and impairment of fruit formation. Jackson and Chapman[348] reported that there is a general similarity of B deficiency symptoms and the response of plant tissue to treatment with growth hormones (e.g., auxin, gibberellic acid). Cakmak and Römheld[1248] reported after Dugger that the enhancement in concentration of phenolics in B-deficient tissues is a result of either stimulation of the pentose phosphate pathway or restriction in biosynthesis of phenolic alcohols. This is less pronounced in monocots as compared with the dicotyledons. Also, the concentration of ascorbic acid is reported to be substantially decreased in plant tissues in response to B deficiency.[1393] Apparently, the biosynthesis of ascorbic acid was reduced and the consumption (oxidation) of ascorbic acid was stimulated during B deficiency. In return, B fertilization (potato experiment) increases the concentration of ascorbic acid in plant tissues.[1248] In B-deficient leaves, impaired photosynthesis and enhanced phenol oxidation is associated with photooxidative damage to membrane and chlorophyll. B is required to detoxify the phenolics produced at higher light intensities, which can increase plant sensitivity to B deficiency.

Strangely, B seems not to be essential for some fungi and algae, although this element was reported to stimulate N fixation by bacteria.[504,630] Bonilla et al.[1235a] reported that nodules from plants (*Phaseolus vulgaris*) grown without B in the nutrient solution were smaller and had lower weights than controls. Thus, B is an obligatory requirement for normal nodule development and functioning. On the other hand, exudation of B complexing agents into the rhizosphere restricts B uptake from the soil. A great difference (three- to tenfold) is observed in the root B-adsorption capacity between dicots and graminaceous monocots. Hu and Brown[1337] suggested that more B is required by dicots than graminaceous monocots because of the higher pectin content in the dicots. Mycorrhizal plants have a greater need for a B supply than do nonmycorrhizal plants.[457] The beneficial impact of B on nodule formation and nitrogenase activity in pea roots is reported by Bolanos et al.[1234] A recent report by Dixon[1277] has indicated a beneficial effect of B on the resistance mechanism of *Brassicas* against clubroot (*Plasmodiophora brassicae*), a soil-borne fungi pathogen that affects crops on a worldwide scale.

The assessment of B availability and its requirement by plants have been extensively studied and it has been found that analysis of water-soluble B in soils and plant tissue tests are adequate for the diagnosis and prediction of B deficiency (Table 39). Some plant species have a low B requirement and may also be sensitive to elevated B levels even only slightly above those needed for normal growth. Therefore, toxic effects of B are likely to arise by excessive use of B fertilizers. The toxicity is usually more common in arid and semiarid regions on soils with naturally high levels of B. Sensitive crop plants (e.g., cereals, cotton) may be affected by a B concentration in soil solutions as low as 1 mg L^{-1}, but 5 mg L^{-1} may be tolerated by various plant species, whereas 10 to 15 mg L^{-1} was toxic to tolerant plants.[11,90,648] The increased B content of irrigation water may be especially toxic to crops grown in an arid region.[133,674]

Diagnosis and prediction of B deficiency for plant production has been widely reviewed by Bell.[1220] The author emphasizes that one of the major difficulties with B deficiency diagnosis is that environmental factors such as low soil water, low temperature, high light, and low vapor pressure can induce a temporary B deficiency.

If there is an excess of B, a very high concentration (1000 to 1500 ppm) of this element often occurs in leaf tips or margins. These parts of leaves become necrotic, while at the early stage of B toxicity the leaves are dark green and wilted. The growing points of such plants become dark and decay.

There is a narrow range of toxic and deficient B levels to plants. However, due to a great species variation, toxic symptoms are observed at very different B concentrations in plant tissues. For example, B toxicity occurs in cotton at tissue concentrations of 422 ppm and in kenaf at 222 ppm; both plants were grown in soil with 45 ppm B content.[1407] For animal nutrition, B above 150 ppm in fodder is not recommended.

3. Interactions with Other Elements

Interactions of B in the uptake of other nutrients by plants are apparently related to changes in membrane permeability and in the status of cell colloids. Physiological mechanisms of these reactions are, however, still not well-understood.

Several interactions reported for B and other trace elements, as shown in Figure 30, have not yet been confirmed. The possible antagonisms with Cu, Cr, Mo, and Mn may be effects of indirect influence through the increase of growth, hence increased demands for a given micronutrient. However, Lambert et al.[457] reported that B-deficient alfalfa also contained a lower amount of Cu. Leal et al.[463] explained Fe-B antagonism as a result of increased B accumulation in roots with a higher soil supply of Fe. B-Si antagonism is an effect of possible competition by silicate ions for adsorption sites of B, and this reaction has been observed in both soil environments and root tissues. Graham et al.[1013] demonstrated that both low Zn and high P supplies increase the accumulation of B in barley plants. Thus, the B uptake to toxic levels in plants may be expected in soils with a low level of available Zn, a high B level in the rooting zone, and a high P fertilization rate. Findings of these authors show that at the excessive B concentrations, the toxicity symptoms first appeared on low-Zn plants, which suggests a partial protective effect of Zn against toxic levels of B in the rooting zone.

The B-Ca interrelationship is reported most often. Plants grow normally if a certain balance exists in the intake and in the tissue concentrations of Ca and B. Lime-induced B deficiency has frequently been observed in acid soils. However, it has also been shown that at equivalent amounts of Ca, tissue B concentrations are much higher if $CaSO_4$, rather than $CaCO_3$, is applied to the soil.[626,772] Liming is believed to result in decreased B adsorption; thus, toxic effects of B may be reduced or prevented by adding Ca to soils. These phenomena have been ascribed both to reactions within soil media and to metabolic processes. The B-Mg synergic interrelationship is observed at combined fertilization of barley.

B and P have similar reactions with OH^- groups; thus, the uptake of these elements by plants is likely to follow similar patterns.[52] The uptake and distribution of P are reported to be dependent on B concentrations because B increases P immobilization in roots.[463] B-P interactions in soils are related to the interference of phosphate ions with B mobility. Graham et al.[1013] described that interactions between P and B are not yet fully understood; however, these two elements influence the integrity of cell membranes, and imbalances in these nutrients could lead to aberrations in ion uptake. These interactions are cross-linked with Zn functions in the absorption and transport of nutrients in plants. Other effects of nutrients, such as K and N, on the B content of plants are, presumably, secondary results of increased plant growth or of some physiological disorders.

B is reported to have beneficial effects on Al toxicity on plant growth. However, the ameliorative effect of B is related rather to root activity under Al stress, and not directly to Al toxicity involved in the ascorbate metabolism.[1393]

High salinity levels of some coastal soils (e.g., in Chile) due to Na and Cl can reduce increased levels of B in crop plants.[1299]

Table 84 Boron Content of Grasses and Legumes (ppm DW)

Country	Grasses		Clovers		Ref.
	Range	Mean	Range	Mean	
Great Britain	—	26[a]	—	—	112
Czech Republic	14–30	22[a]	—	—	154
Finland	3.9–6.3	4.9	—	—	590
Germany	—	—	20–50[b]	—	65
	—	—	20–60	—	65
Germany	—	—	30–100[b]	—	65
Hungary	1.0–7.9	5.8	20–35	33	803, 804
Japan	1.6–12	4.9	12–35	21	770
Poland	1.0–15.6	5.6	11.3–16.5	14	1045
New Zealand	1.7–10.0	5.2	6–120	26[b]	865
U.S.	<5–20	7.4	10–70	22[c]	710
Russia	2–10	5	32–50	40[b]	337
	—	—	10–40	26	337
Yugoslavia	—	—	70–97	78	623

[a] Pasture herbs.

[b] Alfalfa.

[c] Calculated from AW basis.

Table 85 Mean Boron Content of Plant Foodstuffs (ppm)[381,710]

Plant	Sample	DW Basis	AW Basis
Sweet corn	Grains	1.5	58
Bean	Pods	13	180
Cabbage	Leaves	14	140
Lettuce	Leaves	1.3	93
Carrot	Roots	9.9	140
Onion	Bulbs	10	250
Potato	Tubers	6.1	58
Tomato	Fruits	6	84
Apple‘	Fruits	8.3	455
Orange	Fruits	9.4	260

4. Concentrations in Plants

The B content of plants grown under natural conditions is widely varied for plant species and kinds of soil. In general, however, dicot plants have a higher B requirement and thus a higher B content than do monocot plants. The average B content of forage plants from various countries supports this statement (Table 84). This table gives the average B concentration in grasses as 5.7 ppm, whereas the content of alfalfa and clover is 37 ppm. Using these averages, the ratio of B in dicots to monocots is 6.5, which is higher than that calculated by other authors.[166]

The range of the B content in vegetables and fruits is 1.3 to 16 ppm (DW) or 58 to 455 ppm (AW) (Table 85). Shacklette et al.[710] reported that trees and shrubs (B content, 50 to 500 ppm AW) generally contain 2 to 10 times as much B as do vegetables. The lowest B amounts, however, have always been found in seeds and grains, cereal grains in particular (Table 86). The highest B level was found in leaves of sugar beets (Figure 64). The general trend in the B distribution among different crop plants is illustrated in Figure 65.

It has been relatively easy to establish the critical B levels in plant tissues as 5 to 30 ppm (DW) (Table 33). The toxic B contents, on the other hand, have been reported as follows: John et al.[362] found that spinach, although with reduced yield, could grow when containing 348 to 990 ppm B, whereas corn could tolerate a content of 1007 to 4800 ppm; Chapman[131] reported toxic concentrations

Table 86 **Boron Content of Cereal Grains from Different Countries (ppm DW)**

Country	Cereal[a]	Range	Mean	Ref.
Canada	Oats	—	0.7	293
Great Britain	Barley	—	3.4	112
	Oats	—	3.3	112
Poland	Oats	1.9–2.3	2.0	1045
	Rye	1.1–1.6	1.3	1045
	Wheat	0.3–1.5	0.8	267
Finland	Barley	0.7–1.1	1.0	829
	Oats	0.9–1.3	1.2	829
	Wheat	1.1–1.2	1.2	829
U.S.	Barley	0.9–2.3	1.6	200
	Oats	1.6–3.8	2.2	200
	Wheat (s)	0.8–4.3	1.9	200
	Wheat (w)	0.8–3.5	1.8	200
Russia	Barley	5–9	6.6	337
	Oats	5–8	6.8	337
	Rye	5–12	7.3	337
	Wheat	1–15	6.8	337

[a] Spring, s; winter, w.

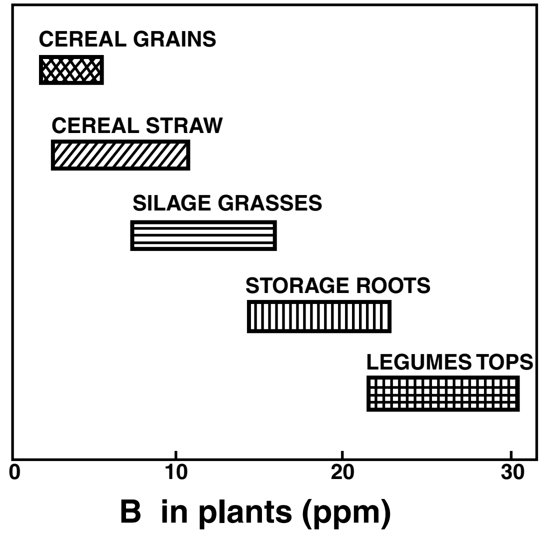

Figure 65 Distribution pattern of B in different crop plants. (Modified from Yläranta and Sillanpää.[1191])

for alfalfa to be from 283 to 333 ppm; Alikhanova[11] observed B toxicity in cotton at 283 to 333 ppm; and Davis et al.[171] stated that 80 ppm B is toxic to barley seedlings. Cole crops are known to be very resistant to high B concentrations in plant tissues. Gupta et al.[1020] found the B as much as 123 and 161 ppm (DW) in brussels sprouts growing in soils with 7.6 and 91 ppm B (hot water soluble), respectively, and no symptoms of toxicity were observed. Ryegrass grown in the soil amended with fly-ash (enriched in easily soluble B) contained up to 430 ppm (DW) B and did not show toxic symptoms.[1045] In orchards where citrus trees showed some toxicity symptoms, about 14% of leaf samples had B greater than 200 ppm, and only 18% had B less than 100 ppm.[1210]

The B toxicity in some crops (commonly in cereals and sunflower) occurs most often on soil contaminated with B due to: (1) irrigation with treated municipal wastewaters or with B-enriched river waters in aridic climatic zones, (2) amendment with fly-ash, and (3) foliar application of B on citrus and/or apple orchards. In plants grown in saline soils, foliar levels of B may be reduced because high soil salinity reduces plant water uptake.[1299] Plants that exhibit salt tolerance are usually also sufficiently tolerant of B elevated concentration in growth media. Thus, plant species such as *Astragalus* are considered to be B tolerant.[1450]

III. ALUMINUM

A. Soils

As one of the main constituents of the Earth's crust, Al in rocks commonly ranges from 0.45 to 10% (Table 82). The only stable and frequently occurring ion, Al^{3+}, is known to coordinate with oxygen-bearing ligands.

During weathering of primary rock minerals the series of Al hydroxides of variable charge and composition, from $Al(OH)^{2+}$ to $Al(OH)_6^{3-}$, are formed and they become the structural components of clay minerals. Some Al silicates (e.g., imogolite) are believed to be the principal dissolved Al species in podzols, while in some sulfate- and acid-spoiled soils, the Al solubility is governed mainly by Al sulfate.[1102] In general, the solubility of Al hydroxides is low, especially in the pH range 5 to 8, and solubility decreases with aging. Freshly precipitated solid Al hydroxide species and colloidal species have a potential for anion adsorption, as well as the ability to flocculate negatively charged particles. Thus, Al hydroxides contribute greatly to various soil properties.

The important results related to Al species and Al toxicity in soil and water are reviewed by Klöppel et al.[1366] Depending on the properties of both environmental compartments, a variety of Al complexes and species can occur, as well as free $Al(H_2O)_6^{3+}$, which is regarded as the most toxic to biota. However, when Al products are exposed to environmental media, the toxic Al species are not significantly increased.

Al ions in soil solutions depend on the pH. Al^{3+} predominates at pH 4 to 5, $Al(OH)^{2+}$ and $Al(OH)_2^+$ at pH 5.5 to 7, and $Al(OH)_4^-$ at pH 7 to 8. Organic compounds, both high and low molecular weight (e.g., humic acid, citric acid), decrease soil acidity and therefore decrease free Al ion contents. Al is known to form several polynuclear species in aqueous environments. The tridecameric (Al_{13}) species, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$, is the primary proposed model of polynuclear species in soil-water systems. The Al_{13} polynuclear species is believed to be important in the behavior of Al in soils and aquatic systems, and is known to reveal a complexing ability to immobilize some free cations.[1211] Berth and Parker[1224] reported that polynuclear Al_{13} and Al-montmorillonite immobilize Cd and Zn in polluted soils. The binding of Zn and Pb by the clay mineral montmorillonite is stimulated by Al hydroxides and low-molecular-weight acids.[1344]

The total Al content of soils is inherited from parent rocks; however, only that fraction of Al which is easily mobile and exchangeable plays an important role in soil fertility.[528] In acid soils with pH below 5.5, the mobility of Al increases sharply and very actively competes with other cations for exchange sites. A sudden increase of the Al solubility is observed mainly in the narrow pH range from 4.5 to 4.0. The solutions of neutral soils contain Al on the order of about 400 $\mu g\ L^{-1}$ (Table 16); while in the soil solution at pH 4.4, Al concentration was reported to be 5700 $\mu g\ L^{-1}$.[279] Nilsson and Bergkvist[1102] studied Al chemistry in a Swedish podzol and found higher Al concentrations (ranging from 95 to 115 $\mu M\ L^{-1}$) in leachates collected below the B horizon than below the upper A_0 and A_2 horizons. These investigators emphasized a significant contribution of the organic Al species to Al solubility. They stated that DOC (probably FA) affects the Al release through the complex formation in the upper soil layer, while the other types of mechanisms are operating in the lower B horizon. Also, soil acidification due to the atmospheric deposition of S (mainly SO_2) increases the Al solubility in soils, possibly by the formation of soluble $Al(OH)SO_4$. With sulfides (e.g., pyrites) present in soils, oxidation produces H_2SO_4, which interacts with other minerals to yield Al ions which then occupy exchange sites.[1118] The mobile Al in acid soils can be taken up rapidly by plants and it creates a problem of chemical stress in the plants. Foy[998] reported that Al toxicity in subsoils is particularly harmful because it causes shallow rooting, drought susceptibility, and poor use of subsoil nutrients.

B. Plants

Al is a common constituent of all plants and is reported to occur in higher plants in the range X0 to X00 ppm (DW). However, the content of this element in plants varies greatly, depending on soil and plant factors (Table 87). Some species of Al-accumulating plants may contain more than 0.1% (DW) of Al.

The physiological function of Al in plants is not clear, although there is some evidence that low levels of Al can have a beneficial effect on plant growth, especially in Al-tolerant plant species.[141,241] Small quantities of Al are believed to activate some enzymes and to control physical properties of plasma and membrane permeability. According to Ślaski,[1500] Al ions interact with root tips of cereals sensitive to an excess of Al in mobile forms. Roots of cereals tolerant to the Al excess (e.g., wheat, sp. *Atlas*) exclude phosphate compounds, increasing pH at the rhizosphere and complexing Al^{3+} ion, and limiting its uptake.[1451] Al injury or toxicity is often reported for plants grown in acid soils. Several recent reviews have been published on this subject, which emphasized that a high availability of Al in acid soils is one of the limiting factors in the production of most field crops.[44,241,646,998] In fact, the reduced yield of crops as well as forest decline on acid soils is often due to increased availability of Al rather than high H^+ concentrations.

Plant species and even cultivars of the same species differ considerably in their ability to take up and translocate Al, which affects the tolerance of plants to excesses of Al. In most plants, the symptoms of Al injury first appear in the roots, and Al is likely to be concentrated in the roots of several plant species. The amount of Al passively taken up by roots and then translocated to tops reflects the Al tolerance of plants, but the ability to accumulate Al in roots is not necessarily associated with Al tolerance. Tea bushes grow mainly in very acid soils and therefore accumulate much Al. The median content of tea leaves from plantations of various countries is 2969 ppm.[1334] Chinese tea has from 676 to 1875 ppm Al, of which about 35% is extracted to hot water. Wong et al.[1550] reported that tea drinks contain from 2.1 to 2.5 mg Al L^{-1}.

Table 87 Aluminum Content of Food and Forage Plants (ppm)[15,55,113,484,536,547,590,705,1104a]

Plant	Tissue Sample	FW(a) Basis	DW Basis	AW Basis
Barley	Grains	—	135, 10	—
Oats	Grains	—	82	—
Sweet corn	Grains	—	2.6	100
Cabbage	Leaves	1.5	8.8	95
Spinach	Leaves	—	104	—
Lettuce	Leaves	0.1	73	520
Carrot	Roots	0.4	7.8	110
Onion	Bulbs	—	63	1500
Potato	Tubers	3.8	76, 13	310
Tomato	Fruits	—	20	170
Apple	Fruits	0.9	7.2	400
Orange	Fruits	1.4	15	430
Legumes	Tops	—	85–3470	—
Grass, timothy	Tops	—	6.5–23.5	—
Grasses[a]	Tops	—	60–14,500	—
Grasses	Tops	—	50–3410	—
Mushrooms[b]	Fruitbodies	—	25–130	—

[a] Sample from grass tetany pasture.

[b] *Suillus variegatus.*

As Foy et al.[241] stated, the physiological mechanisms of Al toxicity are still debated; however, they are related mainly to impaired nutrient uptake and transport and to an imbalanced ratio of cations to anions. The Al excess in plants is also likely to interfere with cell division and with properties of the protoplasm and cell walls. Al is known to form organic complexes and therefore to precipitate nucleic acids. Taylor[1161a] reviewed recent findings on Al phytotoxicity which is related to several effects, mainly reductions in root elongation and root biomass production, reduction in membrane fluidity, and changes in DNA synthesis. The most significant mechanisms of Al tolerance depend upon: (1) exclusion of Al at the root-soil interface, (2) plant-induced pH barrier in the rhizosphere, (3) Al immobilization at the cell wall and binding by proteins, and (4) evolution of enzymes.

The complex physiology of Al toxicity in plants is reflected in several interactions with the uptake of nutrients such as P, Ca, Mg, K, and N. In general, cation uptake by plants is reduced with an excess of Al. Al toxicity is also frequently associated with increased levels of Fe and Mn, and possibly other heavy metals, which are readily available in acid soils. However, Al-induced chlorosis due to impaired Fe metabolism in some plants and Fe deficiency were also reported by Foy et al.[241] It is to be expected that the toxicity would be accompanied by lower levels of Ca and Mg in both soils and plants.

The interaction of Al and P is related to the formation of sparingly soluble Al phosphates in soils and to other coreactions of internal adsorption or precipitation of Al and P, as well as to Al interference with normal P metabolism, mainly in root tissues. Jarvis and Hatch[1036] observed that the effects of Al^{3+} at low concentrations were related to the reduced uptake of P and NO_3^- by white clover. Hence, Al toxicity is often manifested as a P deficiency, and P is an effective agent for detoxifying excess Al. Also Si is known to play a significant role in detoxifying Al.[241,998]

Al excess in plants is known to induce Ca deficiency or reduce Ca transport. Also, the Mg content of plants is greatly decreased by Al, and this decrease in Mg may be an important response of plants sensitive to Al. The addition of both Ca and Mg to soil greatly reduces Al toxicity. Al tolerance in plants seems to be associated with NH_4 tolerance because nitrification is strongly inhibited in acid soils. The mechanisms of Al tolerance in plants are known to be genetically controlled; therefore, the selection of plants having genetic adaptability may be a solution to the problem of Al stress for crops grown in acid soils. Al toxicity is one of the major growth-limiting factors in many acid soils. Foy[241,998] discussed differences in plant tolerance to the Al excess in acid soils, and the effective use of genetic diversity to solve some of the problems of the acid soil fertility.

IV. GALLIUM

A. Soils

Ga is distributed rather uniformly in the major types of rocks and its common values in both magmatic and sedimentary rocks range from 5 to 25 ppm; but in ultramafic and calcareous rocks, the concentration of this metal is about 3 ppm (Table 82). Ga is a widely dispersed element in many minerals, usually in the 5 to 200 ppm range and mainly in sulfides and hydroxides. The highest concentration of Ga, up to about 2%, is found in the mineral germanite, $Cu_3(Fe, Ge, Zn, Ga)S_4$. Elevated content of this metal is reported in micas, especially in muscovite, and also in feldspars and amphiboles.

In weathering, Ga behaves like Al and is usually strongly associated with Al minerals (e.g., bauxites). This general tendency of Ga is reflected in the fact that in soil profiles Ga is positively correlated with the clay fraction. The distribution of Ga in soils also shows a relation to Fe and Mn oxides.

The ionic form of this element in natural environments is Ga^{3+}, but the low solubility of $Ga(OH)_3$ seems to be most responsible for its limited migration. Ga is likely to be accumulated in the organic

Table 88 Gallium Content of Surface Soils of the U.S. (ppm DW)[145,706,1012]

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<5–30	11.0
Light loamy soils	5–50	20.5
Loess and soils on silt deposits	5–30	16.5
Clay and clay loamy soils	5–70	18.5
Alluvial soils	5–30	18.0
Soils over granites and gneisses	15–50	29.5
Soils over volcanic rocks	15–30	22.5
Soils over limestones and calcareous rocks	<5–30	12.0
Soils on glacial till and drift	7–30	15.0
Light desert soils	7–30	17.0
Silty prairie soils	10–20	14.5
Chernozems and dark prairie soils	7–30	15.0
Organic light soils	<5–50	13.5
Forest soils	<5–50	17.0
Various soils	<5–50	12.0
Various soils (of Alaska)	<4–32	15.0

matter of soil. Moreover, the higher concentrations of Ga are reported for bioliths, but whether Ga forms organometallic complexes has not been confirmed.[855]

The Ga status in soils has not been intensively studied. The data summarized by Wedepohl[855] for soils from various countries show that the Ga content ranges from 1 to 70 ppm and that the grand mean content is 28 ppm. Wells[863] reported Ga for soils derived from basalts and andesites of New Zealand to range from 16 to 48 ppm, and Gribovskaya et al.[283] gave the range from 6 to 17 ppm in various soils of Russia. The British standard soil sample contained 21 ppm Ga, as reported by Ure and Bacon.[818] Also, for calcareous soils of China, the average Ga concentration was given as 21 ppm (DW), with the highest value 50 ppm.[1124]

Average Ga content has been calculated for different soils of the U.S. to range from 11 to 30 ppm, being the lowest in sandy and calcareous soils and the highest in soils derived from granitic and volcanic rocks (Table 88). Govindaraju[1313] reported recent results for Ga in reference soils from different countries that ranged from 10 to 40 ppm in soils from China, and from 6.4 to 24.3 ppm in soils from the U.S.

Ga as a pollutant is emitted from aluminum works and during coal combustion. However, elevated concentrations of Ga in surface soils has not yet been reported. Asami et al.[1209] studied soils from sites both polluted and unpolluted by metals in Japan, and did not notice any significant difference. Ga content of both kinds of soils range between 13 and 16 ppm.

B. Plants

There is insufficient evidence to demonstrate either the necessity for or the toxicity of Ga in plants, although some earlier studies suggested a beneficial role of this element in the growth of microorganisms. Nevertheless, Ga is commonly found in plant tissues, and its concentration is reported to range from 3 to 30 ppm (AW) in a variety of native species from the U.S., as reported by Shacklette et al.,[710] and from 0.02 to 5.5 ppm (DW) in native herbage from the (former) Soviet Union as described by Gribovskaya et al.[283] and Dvornikov et al.[199] The highest Ga contents were given by Wedepohl[855] and Bowen[94] for lichens (2.2 to 60 ppm, DW) and bryophytes (2.7 to 30 ppm, DW). A higher ratio of Ga to Al in land plants than in the soils in which the plants grow can reflect the selective uptake of Ga by plants.

V. INDIUM

A. Soils

The geochemistry of In is not well-known. Concentrations of In in magmatic rocks exceed its occurrence in sedimentary deposits by about ten times (Table 82). The grand mean In content of rocks is 0.1 ppm. It exhibits a chalcophilic behavior in the Earth's crust and therefore forms mostly sulfide minerals, but selenide and telluride minerals are also common. Most recent geochemical studies of In have been made because it seems to be associated with base metal deposits. The current information on In in the environment has been extensively discussed by Smith et al.[742] During weathering, In oxidized to In^{3+} follows Fe^{3+}, Mn^{4+}, and, partly, Al^{3+}, and usually precipitates under conditions which form hydrous Fe oxide. The concentration of In up to X0% has been reported, as found in some Fe oxides as a result of their sorption capacity.

Indium in acid solutions may form several ionic species (e.g., $InCl^{2+}$ and $In(OH)^{2+}$), which are precipitated in the pH range of 5 to 9. Above pH 9.5, the anion $In(OH)_4^-$ is likely to occur.

Indium is commonly found in coals and crude oil and is reported to be combined with organic substances. In soils, In also seems to be associated with organic matter and therefore its concentration is increased in surface-soil horizons. This concentration may also reflect pollution.

Natural In content of various soils in the U.S. range from <0.2 to 0.5 ppm (average, 0.2 ppm), whereas in soils of other countries, In is reported to average 0.01 ppm. Chattopadhyay and Jervis[132] reported that the In content of cultivated surficial organic soil increased up to 2.6 ppm. The natural concentration of In in soils of Japan is reported to range from 0.02 to 0.08 ppm, whereas soils polluted with metals contain from 0.107 to 1.92 ppm In.[1209] Govindaraju[1313] reported results for In in reference soils from China to range from 0.03 to 4.1 ppm (average, 0.675). Somewhat elevated concentrations of In (up to 4.2 ppm) in the topsoil near Pb and Zn works are described by Smith et al.[742] Some sewage sludges may also be a source of In.[249]

B. Plants

In is known to be readily available to plants, although it is not significantly concentrated by most plants. Physiological effects on plants are reported mainly in relation to In-induced toxicity in roots, which were described by Smith et al.[742] to occur in various plants at 1 to 2 ppm In concentrations in culture solutions. More results were obtained from studies of the effects of In on microorganisms, which reveal a greater resistance to In concentrations in solution than do higher plants. However, concentrations of 5 to 9 ppm In were reported to inhibit activity of nitrate-forming bacteria in soil.

A few data collected by Smith et al.[742] show that the In content of vegetation from unpolluted sites ranged from 30 to 710 ppb (FW) (mean, 210 ppb); whereas in unwashed plants (chiefly grass) from the industrial region, these values were 0.008 to 2.1 ppm (FW). Furr et al.[249] gave the range of In in beets grown in soil amended with sewage sludge to be 80 to 300 ppb (DW). Much lower values reported for In content (0.64 to 1.8 ppb DW) of the standard samples of orchard and tomato leaves show that either the In content of plants is highly variable or that determinations are not very precise.

VI. THALLIUM

A. Soils

The distribution of Tl in the Earth's crust shows that its concentration seems to increase with increasing acidity of magmatic rocks and with increasing clay content of sedimentary rocks (Table 82). Common Tl contents of mafic rocks range from 0.05 to 0.4 ppm, and in acid rocks from 0.5 to 2.3 ppm. Calcareous sedimentary rocks contain as little as 0.01 to 0.14 ppm Tl.

In geochemical environments, Tl is known to occur in three oxidation states, +1, +2, and +3. The cation Tl^+ is highly associated with K and Rb, and also with several other cations. It behaves like a lithogenic and a chalcophilic element and is incorporated into various minerals, mainly sulfides. Geochemical behavior of Tl is analogous to that of K. Tl reveals a great affinity to micaceous minerals and inhibits the activation energy of K released from these minerals.[999]

During weathering, Tl is readily mobilized and transported together with alkaline metals. However, Tl is most often fixed *in situ* by clays and gels of Mn and Fe oxides. The sorption of Tl by organic matter, especially under reducing conditions, is also known.

Smith and Carson[740] widely reviewed environmental occurrences of Tl and cited its concentration to range from 0.02 to 2.8 ppm in surface soils of the U.S. and enriched contents of Tl (up to about 5 ppm) in soils over sphalerite veins. Dvornikov et al.[199] reported the Tl content of soil within an Hg mineralization area in Russia to be 0.03 to 1.1 ppm. In garden soil analyzed by Chattopadhyay and Jervis,[132] Tl occurred in concentrations from 0.17 to 0.22 ppm, with the highest value in the surface samples. Ure and Bacon[818] found 0.27 ppm Tl in the standard soil sample. Lukaszewski[1076] gave the range of Tl from 0.014 to 0.405 ppm in topsoils of Poland, with the lowest contents in sandy soils. Recent data given by Govindaraju[1313] for Tl in reference soils, indicate the range in Chinese soils to be from 0.21 to 2.4 ppm (average, 0.98 ppm); and in soils from the U.S., from 0.18 to 0.64 ppm (average, 0.41 ppm).

The largest anthropogenic source of Tl is related to coal combustion, but also heavy metal smelting, the cement industry, and refining processes may release some amounts of Tl into the environment. Asami[926] cited that soils around abandoned Hg mines in China contain Tl within the range of 20 to 80 ppm (DW), and Schoer[1141] reported the range 3 to 6 ppm (DW) in soils in the vicinity of a cement plant. Anthropogenic Tl in soils seems to be easily soluble and thus readily available to plants. Highly elevated Tl levels, from 8.8 to 27.8 ppm, are also reported for soils in the vicinity of Pb and Zn mines in Germany.[1520] The highest Tl concentrations, however, were found in soils around old Zn mines (maximum, 73 ppm; mean, 15 ppm) and in surroundings of cement plants (maximum, 15 ppm; mean, 1.4 ppm).[1474] In general, Tl soil contents above 1 ppm indicate pollution and this concentration is proposed as the MAC value for agricultural soils. However, a lithogenic increase in Tl level, up to 40 ppm, has also been observed.[1520]

B. Plants

The Tl content of plants seems to be a function of Tl concentrations in soils, as illustrated in Figure 66. Herbage and woody plants apparently contain higher amounts of Tl than do other plant species. Dvornikov et al.[199] found Tl in herbage to range from 0.02 to 1.0 ppm (DW), and Shacklette et al.[710] cited Tl for pine trees to range from 2 to 100 ppm (AW), being higher in needles than in stems. Smith and Carson[740] gave Tl levels in edible plants to range from 0.02 to 0.125 ppm (DW), in clover from 0.008 to 0.01 ppm (DW), and in meadow hay from 0.02 to 0.025 ppm (DW). Rape seed can accumulate large amounts of Tl, up to 33 ppm, when grown in soils enriched in this metal.[1521] High Tl concentrations, up to 5.5 ppm, are sometimes observed in mushrooms. Reference content of Tl in plants has been calculated by Markert[1399a] at 0.05 ppm.

There is an assumption that some plants, especially of the *Cruciferae* (Brassica) and *Gramineae* families, can serve as hyperaccumulators for phytoremediation of contaminated soils. Some species of the *Cruciferae* family can accumulate Tl above 2000 ppm from soils with about 40 ppm of this metal. McGrath[1407] reported that there are programs for screening plants (e.g., *Brassica* sp.) for their ability to phytoextract Tl from soils impacted by a cement factory.

Źyka[909] analyzed herbaceous plants grown in soil over Tl mineralization and showed accumulations as high as 17,000 ppm (AW) in flowers of *Galium* sp. (Rubiaceae family), while other plants accumulated Tl in leaves and stalks at about 100 ppm (AW).

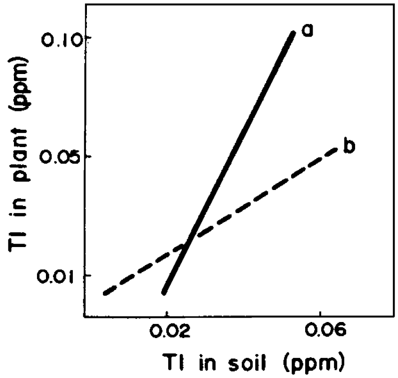

Figure 66 Tl content of two herbs, (a) wormwood and (b) euphorbia, as a function of its concentrations in soil.[199]

Increased Tl levels in plant tissues are highly toxic to both plants and animals. The concentration of 5 ppm Tl in the solution decreased by 50% the length of roots of collard and wheat, with no visual symptoms of Tl toxicity.[1009] Some plant species (e.g., wormwood [*Artemisia* sp., Compositae family]) are likely to accumulate Tl, and the concentration factor may be high. As Smith and Carson[740] described, at potash fertilizer works and smelter and bituminous coal plant sites, plants contained elevated Tl amounts. In industrial regions, Tl can be easily absorbed by plants from aerial deposits. Plants grown around coal power plants and cement factories are most likely to have elevated levels of Tl; for example, *Cruciferae* species accumulated up to approximately 450 ppm Tl near a cement plant in Germany.[1407]

Tl is easily available to plants, and when concentrated in roots up to about 2 ppm, can inhibit the germination, plant growth, and chlorophyll content. Plants especially sensitive to increased levels of Tl are the Leguminosae species, cereals, tobacco, and buckwheat. Microorganisms are reported to be relatively sensitive to Tl, and therefore the inhibition of nitrate formation in Tl-polluted soils may have an agronomic impact. There is also an opinion that Tl is likely to be involved in microbial cycling by possible methylation.[856]

VII. SCANDIUM

A. Soils

The lithospheric abundance of Sc presented in Table 82 shows that the element is likely to be enriched in mafic rocks and also in argillaceous sediments, whereas the Sc content of sandstones and limestones is low. Sc is known to occur in natural environments as Sc^{3+} which can substitute for Al^{3+}, Fe^{3+}, Y^{3+}, and also Ti^{4+}; thus, the element is mainly associated with ferromagnesian minerals and biotite. However, the simple Sc^{3+} ion probably does not exist in solutions. The complexes such as $Sc(H_2O)_6^{3+}$ and $Sc(H_2O)_5OH^{2+}$ are likely to occur in aqueous environments. Sc shows also an affinity for complexing with PO_4, SO_4, CO_3, F, and amines. PO_4 especially is most effective in the precipitation of Sc compounds; thus, its enrichment in phosphorites can be expected (Table 5).

The Sc content of surface soils ranges from 0.5 to 45 ppm (Table 89A). Erdman et al.[218] calculated the mean Sc content of uncultivated soils in the U.S. to be 7.1 ppm and in cultivated soils to be 5.1 ppm. Laul et al.[462] gave the range of Sc concentration in soils as 2.9 to 17 ppm.

The soil Sc content is governed mainly by the parent material, and its lowest concentrations are reported for sandy and light organic soils, whereas somewhat higher amounts have been found in soils derived from granitic and volcanic rocks. Waganov and Nizharadze[1184] gave 5 ppm for the mean Sc concentration in deep loess deposits of the European part of Russia. On a world scale, the mean contents of Sc range from 5 to 10 ppm, the lowest for podzols and highest for kastanozems and

Table 89 A. Scandium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols	Czech Republic	5.1–14	10	938
	Poland	0.8–3.5	1.5	1045
	U.S.	<5–30	5	145, 706
Loamy and clay soils	Bulgaria	11.7–13.9	12.9	558
	Poland	2.4–3.5	3	1045
	U.S.	<5–20	10	145, 706
Fluvisol	Bulgaria	—	7.6	558
	Poland	—	3.1	1045
Andosols	Japan	25.8–30.5	—	1192
Black earth	Poland	—	2.3	1045
Rendzinas	Poland	—	5.8	1045
	Czech Republic	—	11	938
Chernozems	Bulgaria	10.9–13.7	12	558
	Czech Republic	8.5–12.6	9.5	938
Forest soils	Bulgaria	4.2–24.8	12.5	558
	U.S.	5–20	7	145, 706
Various soils	Bulgaria	3.4–46.4	16.6	558
	Czech Republic	5.1–12.6	9.5	938
	Canada	4.9–17.8	10.5	409
	Great Britain	—	12.7	818
	Japan	14.9–22.2	—	1192
	Germany	0.5–9.0	4.3	325
	U.S.	5–30	11	145, 706
	U.S. (Alaska)	<2–39	13	1012

B. Yttrium Content of Surface Soils of the U.S. (ppm DW)[145,706]

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<10–100	22
Light loamy soils	10–70	29
Loess and soils on silt deposits	10–50	27
Clay and clay loamy soils	10–100	28
Alluvial soils	10–50	23
Soils over granites and gneisses	10–150	30
Soils over volcanic rocks	10–70	33
Soils over limestones and calcareous rocks	<10–70	27
Soils on glacial till and drift	10–20	16
Light desert soils	10–100	31
Silty prairie soils	10–30	20
Chernozems and dark prairie soils	10–70	24
Organic light soils	<10–50	21
Forest soils	<10–150	25
Various soils	10–150	26

chernozems (Table 9). Recent data for Sc in reference soils from China gave a range of 5 to 28 ppm (average, 15 ppm); and in soils from the U.S., a range of 5 to 18 ppm (average, 11 ppm).[1313]

Wedepohl[855] reported that the ash residues of some peats, coal, and crude oil carry significant amounts of Sc (5 to 1000 ppm, AW); therefore, environmental enrichment of Sc due to coal and oil combustion processes should be expected.

B. Plants

There is a paucity of data on Sc distribution in plants. Connor and Shacklette[145] gave the mean content of Sc in some shrubs and trees as <5 ppm (AW) and reported that in about 3% of the analyzed samples Sc was at detectable concentrations. Duke[197] gave the Sc range for several plant foods of tropical forest Indians to be 0.002 to 0.1 ppm (DW). Laul et al.[462] found 0.005 ppm Sc in vegetables and 0.07 ppm in grass. Sc content of mosses from Scandinavia varies from 0.16 to 0.25 ppm (DW), with the lowest from Sweden and the highest from Denmark.[1135] Yoshino and Goto[1192] found 0.174 ppm (DW) Sc in rice straw and 0.998 ppm Sc in manure produced from that straw.

Ozoliniya and Kiunke[588] reported high concentrations of Sc in barley roots (up to 0.63 ppm DW) and observed that the greatest amounts of Sc were taken up by plants from sandy soils. The Sc content seemed to be higher in old leaves than in young leaves, and its highest concentrations (0.014 to 0.026 ppm DW) were reported for flax plants, while in lettuce leaves Sc ranged from 0.007 to 0.012 ppm. Relatively high levels of Sc were found by Inarida et al.[1032] in tea leaves from different countries within the range 0.013 to 0.14 ppm (DW), with an average of 0.037 ppm. Bowen[94] reported the range of Sc in lichens and bryophytes to be from 0.3 to 0.7 ppm (DW), whereas in fungi the amounts of Sc were lower (<0.002 to 0.3 ppm).

VIII. YTTRIUM

A. Soils

The occurrence of Y in the Earth's crust is relatively common, and its abundance does not show any great differences between various rock types (Table 82). Ultramafic rocks contain somewhat smaller amounts of Y (0.5 to 5 ppm) than acid rocks and sandstones (28 to 50 ppm).

Geochemical properties of Y are similar to those of the lanthanides. Y is known to be incorporated mainly as Y^{3+} into several minerals, of which silicate, phosphate, and oxide forms are most frequent. The Y content of coal (range, 7 to 14 ppm) does not indicate its sorption by organic substances.

Soils have not often been analyzed for Y. The most comprehensive data are reported for Y in the soils of the U.S. (Table 89B). The Y content of these soils ranged from <10 to 150 ppm and averaged 25 ppm. Erdman et al.[218] gave the mean Y content of uncultivated soils as 23 ppm and of cultivated soils as 15 ppm. Gough et al.[1012] found Y in various soils of Alaska to range from <4 to 100 ppm (DW), with a mean of 14 ppm. Similar values for Y in soils are given by Ure and Bacon[818] for Great Britain (22 ppm), by Duddy[196] for Australia (17 ppm), and by Dobrowolski[181] for Poland (10 ppm in sandy soil). Yoshino and Goto[1192] found Y within a range of 5.3 to 17.1 ppm (DW) in Japanese soils. Govindaraju[1313] has reported results for Y in reference soils of China that range from 11 to 39 ppm (average, 22 ppm), and of the U.S., from 16 to 40 ppm (average, 24 ppm). The Y content of nitrogen fertilizers is given in a range of 2 to 4 ppm.[1362]

B. Plants

The most data for the Y content of plants are given by Connor and Shacklette[145] and Shacklette et al.[710] These authors found Y at detectable levels in about 10% of the plants studied. In edible plants, the Y content ranged from 20 to 100 ppm (AW), the highest amount being reported for cabbage. Duke[197] gave the range from 0.01 to 3.5 ppm (DW) for the Y content of food plants from a tropical forest region. Yoshino and Goto[1192] found Y in rice straw at the level of 0.061 ppm (DW), while in manure produced from that straw, Y content increased up to 0.73 ppm. The reference content of Y in plants is calculated at 0.02 ppm.[1399a]

Woody seed plants can accumulate Y to as much as 700 ppm (AW). Data collected by Bowen[94] show that lichens accumulated Y in the range of 0.2 to 2 ppm (DW), whereas bryophytes concentrated 1.3 to 7.5 ppm (DW). Erämetsä and Yliroukanen[217] gave the range in Y contents in mosses and lichens as 2 to 200 ppm (DW).

IX. LANTHANIDES

A. Soils

Lanthanides, also called rare earth metals or more commonly rare earth elements (REE), comprise a group of 15 elements, of which one, promethium (Pm), does not occur naturally in the Earth's crust (it has not yet been detected), while the others occur in all types of rocks (Tables 90 and 91). The terrestrial abundance of the rare earth metals shows a general peculiarity; their contents decrease with an increase in atomic weights, and, according to the Oddon-Harkins rule, the element with the even atomic number is more frequent than the next element with an odd atomic number (Figure 67 and Table 92).

The geochemical properties of the lanthanides are fairly similar—they occur mainly as +3 cations, show an affinity for oxygen, and are likely to be concentrated in phosphorites and in argillaceous sediments. The common mineral monacite ($CePO_4$) is often associated with other REE, and thus is often presented as (Ce, La, Y, Th)PO_4. Apparently, Ce^{4+} oxygenated form is likely to occur in soil and is less available to plants than other REE. Most often, their lowest concentrations are reported for ultramafic and calcareous rocks. Two subgroups of lanthanides are distinguished: the first, composed of the more basic and more soluble, light metals from La to Gd, and the second, composed of less basic and less soluble metals from Tb to Lu. During weathering processes, the REE are fractionated. Their relative enrichment in weathered material is relatively high, especially for the light REE subgroup.[196]

Brookins[952] studied the behavior of fissiogenic REE at the natural reactor which occurred in the U ores in Oklo Mine, Gabon, and observed a relatively low mobility with retention in host pitchblende and in gangue minerals. He concluded that a chemically reducing environment of the U-ore shales results in long-term storage of the REE. A baseline survey of REE in soils was presented by Barnard and Halbig[932] for the island of Hawaii. They stated that REE concentrations in the soils are moderately enriched, up to two times greater than in common sedimentary rocks worldwide.

Table 90 Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, and Gadolinium in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock Type	La	Ce	Pr	Nd	Sm	Eu	Gd
Magmatic Rocks							
Ultramafic rocks Dunites, peridotites, pyroxenites	0.X–1.8	0.X–3.3	0.6	0.X–2.4	0.X	0.01–0.X	0.X
Mafic rocks Basalts, gabbros	2–27	4–50	1–15	5–30	0.9–7.0	0.8–3.5	2–8
Intermediate rocks Diorites, syenites	30–70	60–160	7–15	30–65	6–18	1.3–2.8	7–18
Acid rocks Granites, gneisses	45–60	80–100	7–12	33–47	8–9	1.1–2.0	7.4–10.0
Acid rocks (volcanic) Rhyolites, trachytes, dacites	30–150	45–250	6–30	18–80	6–11	1.0–1.9	4.3–8.7
Sedimentary Rocks							
Argillaceous sediments	30–90	55–80	5.5–9.5	24–35	6.0–6.5	1.0–1.8	6.4–7.4
Shales	34–50	30–90	5–10	18–41	5–7	1.0–1.4	5.0–6.5
Sandstones	17–40	25–80	4–9	16–38	4–10	0.7–2.0	3–10
Limestones, dolomites	4–10	7–20	1.0–2.5	4.7–9.0	1.3–2.1	0.2–0.4	1.3–2.7

Table 91 **Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium in Major Rock Types (ppm) (values commonly found, based on various sources)**

Rock Type	Tb	Dy	Ho	Er	Tm	Yb	Lu
Magmatic Rocks							
Ultramafic rocks Dunites, peridotites, pyroxenites	0.X	0.05–0.95	0.X	0.X	0.X	0.X	0.X
Mafic rocks Basalts, gabbros	0.5–1.2	0.9–6.9	1.0–1.5	0.9–3.9	0.2–0.6	0.8–3.4	0.2–0.6
Intermediate rocks Diorites, syenites	1.1–2.8	6–13	1.5–3.5	3.9–7.0	0.6	3.8–7.0	0.6–2.0
Acid rocks Granites, gneisses	1.0–2.5	5–7	1.3–2.0	3.5–4.2	0.3–0.7	3.5–4.3	0.5–1.2
Acid rocks (volcanic) Rhyolites, trachytes, dacites	1.0–1.2	5–8	1.3–1.7	3.1–4.6	0.5–0.7	2.9–4.6	0.7
Sedimentary Rocks							
Argillaceous sediments	0.9–1.1	4.6–5.4	1.0–1.6	2.5–3.8	0.2–0.6	2.6–3.6	0.7
Shales	1	4.0–5.8	1.0–1.8	2.5–4.0	0.6	2.2–3.9	0.2–0.8
Sandstones	1.6–2.0	2.6–7.2	2	1.6–4.9	0.3	1.2–4.4	0.8–1.2
Limestones, dolomites	0.2–0.4	0.8–2.1	0.3	0.4–1.7	0.04–0.16	0.3–1.6	0.2

Table 92 **Concentrations of Lanthanides in Soils, as Given by Various Authors (ppm DW)**

Element	(818)	(94)	(462)	Mean[a]	(1313)[b]	(1577)[c]	(1566)[d]
La	33.5	40	29.5	26.1	35.1	35.2	8.53–31.4
Ce	48.5	50	29.5	48.7	71.1	97.4	15.8–64.4
Pr	7.7	7.5	6.7	7.6	5.4	8.4	1.84–5.01
Nd	33.0	35	27.9	19.5	30.6	29.3	7.69–28.6
Sm	6.1	4.5	5.1	4.8	6.7	5.5	1.75–3.98
Eu	1.9	1	1	1.23	1.2	0.8	0.44–1.43
Gd	3.0	4	4.7	6.03	3.2	4.8	1.77–5.54
Tb	0.63	0.7	0.7	0.71	0.85	0.58	0.27–0.82
Dy	3.8	5	—	3.65	4.3	2.9	1.68–4.67
Ho	0.38	0.6	1.1	1.08	0.96	0.51	0.36–0.95
Er	2.0	2	2.8	1.58	2.6	1.4	1.08–2.72
Tm	0.16	0.6	0.4	0.46	0.34	0.19	0.16–0.40
Yb	2.3	3	3.1	2.06	2.4	1.1	1.11–2.64
Lu	0.34	0.4	0.3	0.34	0.39	0.16	0.16–0.40

Note: References are given in parentheses.

[a] Mean values calculated from data presented in Tables 93 to 102.

[b] Mean values for reference soils.

[c] Mean values for 27 soils of China.

[d] Mean values for various soils of Japan. The lowest values are for sand dunes and peat soils, the highest for red soils and gray lowland soils.

The REE contents of different soils in various countries are fairly similar, with the exception of dune sands and some peat bogs, shown in Tables 93 to 102. The grand means for REE calculated by various authors (Table 92) clearly indicate the general decrease in abundance with increasing atomic number in both even-numbered and odd-numbered sequences. The values of mean concentrations of REE in soils (Table 92) fairly correspond to their contents in sedimentary rocks, with

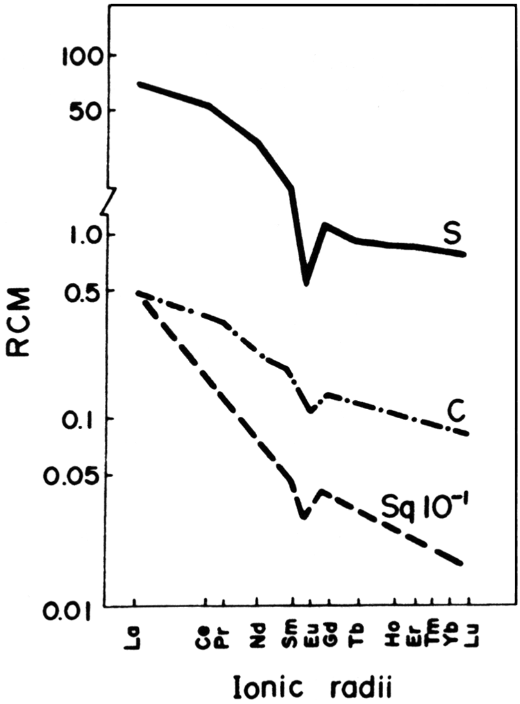

Figure 67 The relative occurrence of rare earth elements in surface soil and plants as a function of their ionic radii and expressed as a ratio (RCM) of the abundance in samples to the content of chondrite meteorites. S, soil; C, cheatgrass; Sq, squash.[462]

the exception of calcareous rocks (Tables 90 and 91). Thus, presented data show that the enrichment in REE in soils occurs mainly with respect to the calcareous parent rocks.

Zhu et al.[1577] reported significant differences in REE concentrations among different soil types in China. The sum of total REEs ranges from 88.9 to 469 ppm; the sum of LREEs range from 76.2 to 447.7 ppm; and the sum of HREEs ranges from 9.2 to 55.2 ppm. The REEs are slightly mobile in soils. Their solubility in acid extractants varies from about 5% of total contents to about 10% when extracted with 0.1 M HOAc-NaOAc (pH 4.2) and with NH_4Ac and EDTA (pH 4.7), respectively.[1556,1577] The relative highest extraction was observed for Sm, Eu, Tb, and Nd. However, during a longer period of time, the mobility of REEs can affect their distribution. Öhlander et al.[1446] reported that since the last glaciation period (about 8700 years ago), up to 84% of LREEs and 79% of HREEs were leached down from soil derived from glacial till. Although the solubility of soil REEs in water is very small (usually hundreds of times smaller than their total contents), on a longer time scale, it should not be ignored as an available pool of REEs to crop plants.

There are scanty data on individual REEs in soils. All REEs are, however, reported to be concentrated more in alkaline soils than in acid soils, probably due to the easy removal of their hydroxide complexes. La, Ce, Pr, Nd, Sm, and Y in fluvisols in Poland (central Vistula valley) reveal a strong positive correlation with amounts of fine granulometric fractions (<0.002 and <0.02 mm).[1256]

Lieth and Markert[1063] compared the chemical composition of peats and nearby mineral soils and estimated the range for lanthanides from 0.X to X0 ppm (DW) in both kinds of soils. Most of these elements are ten times more abundant in peats than in mineral soils. Markert[1085] found that the distribution pattern of the REE in both soils follows that in geological samples and concluded that the Earth's crust is the original source of these elements in soils. The observed higher total REE contents of Swedish mineral soil compared to that of German mineral soil (Tables 93 to 102)

Table 93 Lanthanum (La) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Bulgaria	34.4–49.2	40.2	558
	Czech Republic	—	20.5	938
	Sweden	—	34	1085
	Germany[b]	—	5.4	1085
Andosols	Japan	22.4–23.4	—	1192
Loess	Poland[c]	—	21	1027
Fluvisols	Bulgaria	—	20.1	558
Chernozems	Bulgaria	19.5–35.8	30.2	558
	Czech Republic	—	34	937
Peat bog	Sweden	—	1.4	1085
	U.S. (Hawaii)	4.6–16.2	9.2	932
	Germany	—	1.9	1085
Forest soils	Bulgaria	17.9–72.0	39.1	558
Various soils	Brazil	92; 231[d]	—	1065
	Bulgaria	13.9–56.3	34.5	558
	Canada[c]	46–48	—	972
	Czech Republic	—	37	937
	Japan	14.1–30.9	—	1192
	Sweden	—	32	1084
	U.S.	16.2–54.6	36	409
	U.S. (Hawaii)	31.6–89.7	55.3	932
	U.S. (Alaska)	<2–120	19	1012

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

[d] Two single analyses of soils near REE ore body.

are apparently related to the various geological origins and mineral composition of the sand dune (in Germany) and of the sand podzol (in Sweden).

Elevated concentrations of some lanthanides (La, Ce, Sm, Eu, and Tb) found in the air of industrial and urban areas (Table 3) indicate that these elements are likely to be released into the environment mainly from coal burning and nuclear energy materials processing. The radionuclide ^{144}Ce, which has a high probability of release during a reactor accident, is potentially hazardous because of its soil-crop pathways, although the root uptake of Ce is rather limited.[1016] Municipal sewage sludges and farm manure contain, in most cases, REE at levels found in soils (Table 103), and therefore are not considered to be a significant source of these elements in soils.

B. Plants

Neither the distribution of lanthanides in plant tissue nor their physiological functions have received much attention until the past decade. Recently, more environmental studies on lanthanides have been performed.[1446,1554–1556,1576] Robinson et al.[1129] reported one of the first high concentrations (up to 2300 ppm DW) of the total REE in hickory trees and pointed out the similarity in the proportion of REE in tree leaves and in the content of exchangeable REE in the soil. Laul et al.[462] calculated the relative abundance of lanthanides in both soil and plants and showed that the concentrations of these elements in plants followed their occurrence in soil (Figure 67). Orders of the contents of lanthanides in plants decrease with increase in the atomic number (Tables 104 and 105). Woody plants seem to have the highest ability to absorb lanthanides, and hickory trees are most often reported as lanthanide-accumulating plants (Table 104). Concentrations of REE in plants vary within a broad range, from below 1 ppb to above 15,000 ppb (DW) (Table 105).The distribution

Table 94 **Cerium (Ce) Content of Surface Soils of Different Countries (ppm DW)**

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Australia	—	21	196
	Bulgaria	49.4–85.3	63	558
	Czech Republic	—	44	938
	Sweden	—	56	1085
	Germany[b]	—	8.4	1085
Andosols	Japan	42.1–46.8	—	1192
Loess	Poland[c]	—	44.2	1027
Fluvisols	Bulgaria	—	31.9	558
Chernozems	Bulgaria	41.3–68.8	57.3	558
	Czech Republic	—	75	937
Peat bog	Sweden	—	2.1	1085
	U.S. (Hawaii)	31.1–58.6	42.3	932
	Germany	—	2.7	1085
Forest soils	Bulgaria	29.9–94.1	61.5	558
Various soils	Brazil	517; 944[d]	—	1065
	Bulgaria	21.2–75.7	48.1	558
	Canada[c]	111–112	—	972
	Czech Republic	—	81	937
	Japan	43.3–69.1	—	1192
	Sweden	—	62	1084
	U.S. (Hawaii)	54.4–225	146.1	932
	U.S. (Alaska)	<5–180	28	1012

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

[d] Two single analyses of soils near REE ore body.

Table 95 **Neodymium (Nd) Content of Surface Soils of Different Countries (ppm DW)**

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Australia	—	7	196
	Bulgaria	—	21.4	558
	Czech Republic	—	18.7	938
	Sweden	—	26	1085
	Germany[b]	—	3.6	1085
Andosols	Japan	19.9–23.6	—	1192
Loess	Poland[c]	—	18.2	1027
Fluvisols	Bulgaria	—	14.9	558
Chernozems	Bulgaria	17.9–47	24.3	558
	Czech Republic	—	30.5	937
Peat bog	Sweden	—	1	1085
	Germany	—	1.2	1085
Forest soils	Bulgaria	7.9–38.7	20.2	558
Various soils	Bulgaria	8.6–35	19.5	558
	Canada[c]	—	57	972
	Czech Republic	—	36	937
	Japan	10.4–27.2	—	1192
	Sweden	—	27.7	1084
	U.S.	16.5–56	36.1	409
	U.S. (Alaska)	<4–120	23	1012

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

Table 96 Samarium (Sm) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Bulgaria	5.05–8.39	6.32	558
	Czech Republic	—	3.5	938
	Sweden	—	5.9	1085
	Germany[b]	—	0.86	1085
Andosols	Japan	4.11–5.12	—	1192
Loess	Poland[c]	—	3.61	1027
Fluvisols	Bulgaria	—	3.37	558
Chernozems	Bulgaria	4.17–6.75	5.18	558
	Czech Republic	—	5.9	937
Peat bog	Sweden	—	0.2	1085
	U.S. (Hawaii)	3.71–7.46	5.68	932
	Germany	—	0.25	1085
Forest soils	Bulgaria	2.27—10.19	6.22	558
Various soils	Brazil	13; 26[d]	—	1065
	Bulgaria	2.32–7.68	5.54	558
	Canada[c]	—	12	972
	Czech Republic	—	6.11	937
	Japan	1.89–5.47	—	1192
	Sweden	—	6.2	1084
	U.S.	3.30–11.9	7.05	409
	U.S. (Hawaii)	8.37–22.6	14.38	932

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

[d] Two single analyses of soils near REE ore body.

Table 97 Europium (Eu) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Bulgaria	1.21–1.50	1.34	558
	Czech Republic	—	0.55	938
	Sweden	—	1.5	1085
	Germany[b]	—	0.17	1085
Andosols	Japan	1.30–1.54	—	1192
Loess	Poland[c]	—	0.62	1027
	Russia[d]	—	1.7	1181
Fluvisols	Bulgaria	—	0.72	558
Chernozems	Bulgaria	1.12–1.22	1.17	558
	Czech Republic	—	0.97	937
Peat bog	Sweden	—	0.032	1085
	U.S. (Hawaii)	0.99–2.97	1.89	932
	Germany	—	0.06	1085
Forest Soils	Bulgaria	0.37–2.05	1.1	558
Various soils	Bulgaria	0.43–2.39	1.36	558
	Canada[c]	2.2–3.7	—	927
	Czech Republic	—	1.01	937
	Japan	0.48–1.46	—	1192
	Sweden	—	1.72	1084
	U.S.	0.69–3.21	1.65	409
	U.S. (Hawaii)	2.24–7.66	4.40	932

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soil.

[d] In whole profile.

Table 98 Terbium (Tb) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Bulgaria	0.89–1.7	1.01	558
	Czech Republic	—	0.47	938
	Sweden	—	1.2	1085
	Germany[b]	—	0.2	1085
Andosols	Japan	0.80–1.13	—	1192
Loess	Poland[c]	—	0.58	1027
	Russia[d]	—	1.4	1181
Fluvisols	Bulgaria	—	0.66	558
Chernozems	Bulgaria	—	0.74	558
	Czech Republic	—	0.88	937
Peat bog	Sweden	—	0.044	1085
	Germany	—	0.051	1085
Forest soils	Bulgaria	0.60–1.61	0.92	558
Various soils	Bulgaria	0.11–1.34	0.79	558
	Canada[c]	1.3–1.8	—	972
	Czech Republic	—	0.81	937
	Japan	0.80–1.13	—	1192
	Sweden	—	1.1	1084
	U.S.	0.49–1.66	0.9	409

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

[d] In whole profile.

Table 99 Ytterbium (Yb) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[b]	Ref.
Podzols and sandy soils	Bulgaria	2.06–2.42	2.28	558
	Czech Republic	—	1.45	938
	Sweden	—	2.8	1085
	Germany[b]	—	0.38	1085
Andosols	Japan	2.03–2.27	—	1192
Loess	Poland[c]	—	2.48	1027
Fluvisols	Bulgaria	—	1.15	558
Chernozems	Bulgaria	—	2.35	558
	Czech Republic	—	3.3	937
Peat bog	Sweden	—	0.072	1085
	U.S. (Hawaii)	0.88–3.68	2.01	932
	Germany	—	0.077	1085
Forest soils	Bulgaria	0.81–4.45	2.52	558
Various soils	Bulgaria	1.79–3.43	2.57	558
	Canada[c]	3.4–4.0	—	972
	Czech Republic	—	2.63	937
	Japan	0.86–1.90	—	1192
	Sweden	—	3.14	1084
	U.S.	1.57–3.66	2.46	409
	U.S. (Hawaii)	3.98–5.05	4.51	932
	U.S. (Alaska)	<1–6	1.4	1012

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

Table 100 Lutetium (Lu) Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean[a]	Ref.
Podzols and sandy soils	Bulgaria	0.43–0.51	0.48	558
	Czech Republic	—	0.40	938
	Sweden	—	0.38	1085
	Germany[b]	—	0.054	1085
Andosols	Japan	0.44–0.46	—	1192
Loess	Poland[c]	—	0.33	1027
Fluvisols	Bulgaria	—	0.24	558
Chernozems	Bulgaria	0.19–0.41	0.31	558
	Czech Republic	—	0.45	937
Peat bog	Sweden	—	0.014	1085
	U.S. (Hawaii)	0.13–0.39	0.29	932
	Germany	—	0.012	1085
Forest soils	Bulgaria	0.10–0.72	0.40	558
Various soils	Bulgaria	0.10–0.67	0.43	558
	Canada[c]	0.47–0.50	—	972
	Czech Republic	—	0.45	937
	Japan	0.27–0.44	—	1192
	Sweden	—	0.49	1084
	U.S.	0.24–0.52	0.37	409
	U.S.(Hawaii)	—	0.66	932

[a] Mean or single value when range is not given.

[b] Dune sands.

[c] Standard soils.

Table 101 Praseodymium (Pr), Gadolinium (Gd), and Dysprosium (Dy) Contents of Surface Soils of Different Countries (ppm DW)

Element	Soils	Country	Content	Ref.
Pr	Sandy loam	Sweden	14	1085
	Dune sand	Germany	1.4	1085
	Mineral soil	Sweden	9.15	1084
	Andosols	Japan	5.46–6.20	1192
	Grey lowland soil	Japan	7.69	1192
	Various soils	Canada[a]	13.4–15.0	972
Gd	Sandy loam	Sweden	5	1085
	Dune sand	Germany	0.7	1085
	Mineral soil	Sweden	5.97	1084
	Andosols	Japan	4.09–4.74	1192
	Grey lowland soil	Japan	4.69	1192
	Various soils	Czech Republic	15	937
	Various soils	Canada[a]	10.3–11.0	972
Dy	Sandy soil	Sweden	5	1085
	Dune sand	Germany	0.8	1085
	Mineral soil	Sweden	5	1084
	Andosols	Japan	3.48–4.18	1192
	Grey lowland soil	Japan	3.6	1192
	Various soils	U.S. (Alaska)	4–12	1012
	Various soils	Canada[a]	8.6–11	972

[a] Standard soils.

Table 102 Holmium (Ho), Erbium (Er), and Thulium (Tm) Contents of Surface Soils of Different Countries (ppm DW)

Element	Soils	Country	Content	Ref.
Ho	Sandy loam	Sweden	1.1	1085
	Dune sand	Germany	0.19	1085
	Mineral soil	Sweden	1.1	1084
	Andosols	Japan	0.82–0.92	1192
	Grey lowland soil	Japan	0.8	1192
	Various soils	Czech Republic	1	973
	Various soils	Canada[a]	1.7–2.0	972
Er	Sandy loam	Sweden	1.7	1085
	Dune sand	Germany	0.26	1085
	Mineral soil	Sweden	1.7	1084
	Andosols	Japan	2.05–2.33	1192
	Grey lowland soil	Japan	2.05	1192
	Various soils	Canada[a]	1.7–4.8	972
Tm	Sandy loam	Sweden	0.48	1085
	Dune sand	Germany	0.38	1085
	Mineral soil	Sweden	0.48	1084
	Andosols	Japan	0.42–0.46	1192
	Grey lowland soil	Japan	0.39	1192
	Various soils	Czech Republic	0.6	937
	Various soils	Canada[a]	0.54–0.80	972

[a] Standard soils.

Table 103 Lanthanide Contents of Municipal Sewage Sludges and Cow Manure of the U.S.[1004](ppm DW)

	Sewage Sludge		
Element	Range	Mean	Cow Manure
La	5.1–33.9 (380)[a]	12.7	23.7
Ce	12.4–94 (272)	41.9	55.0
Pr	1.1–15.8 (119)	4.3	10.7
Nd	0.6–8.6	2.5	2.5
Sm	1.0–14.2	3.5	5.2
Eu	0.7–12.2	3.7	0.7
Gd	1.1–22.7	6.8	1.5
Tb	0.3–4.8	1.4	0.3
Dy	0.6–19.8	4.7	1.0
Ho	0.07–0.67	0.32	0.36
Er	0.20–4.50	1.16	0.70
Tm	0.06–3.31	0.39	0.14
Yb	0.17–1.60	0.60	1.76
Lu	0.04–0.34	0.12	0.60

[a] The highest values not included in means of 16 sewage sludges are in parentheses.

pattern somehow follows the Oddon-Harkins rule, and therefore Markert[1085] concluded that it might be possible to calculate the concentration of an unknown lanthanide element once the relationships of elements to each other are known. For each group of plants, of which lichens and bryophytes accumulate relatively more elements (Table 105), the highest contents are reported for La (maximum values vary from 88 to 15,000 ppb DW) and the lowest contents for Lu (maximum values from 2 to 60 ppb DW). Rühling et al.[1135] reported in mosses of Scandinavian countries the range for La from 0.35 to 1.84 ppm (AW), and for Sm from 0.05 to 0.22 ppm (AW). Liu[1067] found the sum of

Table 104 Lanthanides in Terrestrial Plant Species (ppm AW)

Element	Woody Plant U.S.[710]	Lichens and Mosses, Finland[217]	Horsetail, Finland[215]	*Acer pseudoplanatus,* Leaves (ppb DW)[1556]
La	30–300	13–150	1–30	1878
Ce	—	9–280	1–90	3426
Pr	700	1.2–31	0.5–6	—
Nd	—	8–150	3–50	1797
Sm	200–700	2–40	2–4	459
Eu	—	1–8.7	1–2	92.5
Gd	<100–300	2–28	3–8	—
Tb	—	0.3–3.3	1–2	70.3
Dy	50–300	1.3–26	2–9	—
Ho	150	0.2–4.5	1–2	—
Er	<100–300	0.6–13	2–7	—
Tm	—	0.07–2.2	1	—
Yb	300	0.5–26	1–2	152
Lu	—	0.05–2.2	—	15.8

REE contents of food plants (edible parts) to be in (ppm DW): tomato 0.05, corn 0.2, rice 0.6, wheat 1.0, and sesame 3.6.

Wyttenbach et al.[1556] investigated the distribution of REEs in the leaves of six plant species (forest trees and plants), and in pertinent soils and soil extracts. Concentrations of the individual REEs were not a function either of their total contents or their soluble forms in soils. In most cases, however, concentration ratios between species were a smooth function of the atomic number of the REE. The plant:soil ratio for almost all REEs in needles of Norway spruce (grown in Swiss Midlands) was about 5×10^{-3} but revealed large variations among individual trees. As Wyttenbach et al.[1555] concluded, these effects may be due to a change in the oxidation state (in cases of Ce) or due to differences among individual plants or plant species. Variation in REE concentrations in needles and leaves of trees is significant: pseudoplatanus leaves contain more REEs (by about a factor of 10) than spruce needles. Also, organic complexes of the REEs in soils are believed to control plant uptake. The concentrations of each REE and of Sc increase significantly and linearly with the needle age class. No retranslocation of the accumulated elements in spruce needles was observed.

Lanthanides are known to be toxic to cell metabolism; however, there are not many available data on their inhibitory effects on plants. Weinberg[856] reported that lanthanides (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, and Tb^{3+}) inhibit, specifically and competitively, Ca accumulation by mitochondria of micro-organism cells.

Liu[1067] reviewed reports on the effects of the REE on plant growth and yield. Several experiments with cereals, sugar beets, and other plants resulted in the increase of yield at the rate of 7 to 13%. Xijie et al.[1188] observed good effects of the REE treatments on the yield of flower bulbs of the narcissus. These authors, however, did not specify the elemental composition of the REE used for the experiment and did not discuss a possible mechanism of the observed phenomena. The function of the REE in plant metabolism is not clear. Most of the authors, however, referred to the stimulating impact of these elements on seed germination, root growth, uptake of nutrients, nodulation and N-fixation, and on production of chlorophyll and photosynthesis. It should be emphasized that the REE have not been proved yet to be essential and that their biochemical functions in plants still need more study. Zhu et al.[1575] investigated the impact of La on physiological activities in the seedling stage of wheat. The inhibition of seed germination was observed at the La^{3+} concentration higher than 200 mg L^{-1} in Hoagland solution.

Table 105 Lanthanides in Various Terrestrial Plant Species (ppb DW)

Element	Approximate Detection (%)	Various Land Plants[94]	Lichens and Bryophytes[94]	Cheatgrass[462]	Vegetables[94,462,547]	Rice Straw[1192]	Blueberry Tops[1085]	Pine Needles[1085]
La	100	3–15,000	400–3000	170	0.4–2000	88	130–340	260–300
Ce	100	250–16,000	600–5600	330	2–50	174	210–740	370
Pr	90	60–300	80–620	40	1–2	26	70–140	62–130
Nd	90	300	240–3000	150	10	84	73–130	150–160
Sm	90	100–800	60–800	35	0.2–100	20	24–49	30–32
Eu	80	30–130	20–170	8	0.04–70	10	0.82–5.6	4.9–5.3
Gd	80	2–500	60–560	37	<2	20	11–27	23–25
Tb	70	1–120	6–70	9	0.1–1	7	4.7–14	12–22
Dy	70	50–600	40–360	—	—	16	8.6–21	20–22
Ho	70	30–110	4–70	<20	0.06–0.1	5	2.5–4.2	3.9–5.1
Er	70	80–380	10–190	<500	0.5–2	10	1.5–7.7	6–6.8
Tm	50	4–70	1–26	50	0.2–4	4	1	1.1–1.7
Yb	50	20–600	10–900	20	0.08–20	10	2.5–10	8.2–8.5
Lu	40	30	1–20	3	0.01–60	5	1.2–2.3	1.9–2

X. ACTINIDES

A. Soils

Among the actinide series, only two elements exist as long-lived nuclides and occur naturally and in relatively large quantity on Earth—two isotopes of U (^{238}U and ^{235}U) and one of Th (^{232}Th). Other actinide elements have also been found to occur as a result of natural nuclear reactions of U, but in very negligible traces. These are actinium (Ac), proactinium (Pa), neptunium (Np), and plutonium (Pu). The actinide elements are also called transuranium (elements of atomic number below 94) and transplutonium (elements of atomic number above 94). It is not clear yet whether other radionuclides of the actinide series (especially transplutonium) occur in nature. Their existence in measurable amount is not expected in nature. However, their formation during natural nuclear reactions cannot be excluded. Acid rocks usually contain more Th and U than do mafic rocks, and in sediments these elements are likely to be more concentrated in argillaceous deposits than in sandstones and limestones (Table 106). However, in some kinds of alkaline magmatic rocks, Th and U are also known to be concentrated to as much as X00 ppm. The carrier of Th is mainly monazite mineral, $Ce(PO_4)$, which is very resistant to weathering; thus, Th is concentrated in some weathered deposits. When mobilized, Th^{4+} ions are quickly adsorbed or precipitated as hydrolysates. In reference soils, Th concentration is reported to be relatively high, from 8 to 27 ppm in soils of China, and from 3.8 to 12.4 ppm in soils of the U.S.[1313]

Geochemically, U and Th are coherent. They exist in the +4 and +6 oxidation states in most geologic environments. They may substitute the REE in some minerals and are known to be associated with apatite and sphene. Th^{4+} is readily soluble and also quickly adsorbed or precipitated as hydrolysates. During the weathering, U forms complexes, mainly organic, easily soluble and mobile. Under arid conditions, however, U forms various relatively stable compounds (e.g., oxides, carbonates, phosphates, vanates, and arsenates). The distribution of U and Th in the lithosphere is highly controlled by the oxidation state and by the Eh-pH system. Actinides generally form strong complexes with oxygen ligands, and thus their speciation with inorganic ligands such as OH^-, CO_3^{2-}, and HPO_4^{2-} is likely to occur in both geological and environmental conditions.[917] Actinides also appear to be sorbed preferably by naturally occurring organic substances. The importance of

Table 106 Thorium and Uranium in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock type	Th	U
Magmatic Rocks		
Ultramafic rocks Dunites, peridotites, pyroxenites	0.004–0.005	0.003–0.010
Mafic rocks Basalts, gabbros	1–4	0.3–1.0
Intermediate rocks Diorites, syenites	7–14	1.4–3.0
Acid rocks Granites, gneisses	10–23	2.5–6.0
Acid rocks (volcanic) Rhyolites, trachytes, dacites	15	5
Sedimentary Rocks		
Argillaceous sediments	9.6–12.0	3–4
Shales	12	3.0–4.1
Sandstones	1.7–3.8	0.45–0.59
Limestones, dolomites	1.7–2.9	2.2–2.5

microorganisms in the geochemical cycle of U has been emphasized recently by Wildung and Garland[873] and Trudinger and Swaine.[809] Letunova and Kovalskiy[1061] reviewed a role of microorganisms in U migration in the soil environment. They reported that microorganisms have a great capability to accumulate U in their tissues, and the bioconcentration factor for U was up to 300 times compared with its content in soils.

Harmsen and de Haan[306] reviewed the behavior of Th and U in the soil environment and pointed out that the formation of hydrated cations of UO_2^{2+} and of TH^{4+} are responsible for the solubility of these metals over a broad range of soil pH. Also, several organic acids may increase the solubility of Th and U in soils. The mobility of Th and U in soils may be limited due to both the formation of slightly soluble precipitates (e.g., phosphates, oxides) and adsorption on clays and organic matter.

Sorption is a key process in the U cycle, and thus significant accumulations of U in organic deposits (coal or peat) are often reported.[299,688] The affinity of the clay soil fraction to adsorb Th and U is shown in Figure 40. The addition of hydroapatite, $Ca_3(PO_4)_3OH$, to the U-contaminated sediments or soils immobilizes U due to the fixation in secondary Al/Fe phosphate phases.[1204] Megumi and Mamuro[529] explained that the observed conspicuous enrichment of ^{230}Th in soil particles is the result of a higher solubility and thus a higher leaching of uranyl ions (UO_2^{2+}) than of Th^{4+} ions during soil-forming processes.

Comparatively little information seems to be available with respect to Th and U in soils. Only surface soils of the U.S. have been extensively studied, and the results show relatively small variation in the contents of these elements with soil types. However, Meriwether et al.[1090a] reported that in soils of Louisiana, both radionuclides ^{238}U daughters and ^{232}Th daughters are correlated with soil suborders, suggesting that the process of fractionation leads to their increase in the soils of water environments. The worldwide mean of the Th content of soils ranged from 3.4 to 10.5 ppm, and for U, it ranged from 0.79 to 11 ppm (Table 107). Apparently, large amounts of Th and U are introduced into the biosphere from fossil-fuel power plants and also from P fertilizer works. The enrichment of these two elements in surface soils of industrial areas has not yet been very extensive.[355] Spezzano and Silvestri[1152] have applied a procedure for the radiochemical determination of alpha-emitting nuclides of Th and U in soils. The average abundance of these isotopes in two surface soils (close to the U mills) in Italy was as follows (in Bq kg^{-1}): ^{230}Th 52.9, ^{232}Th 40.1, ^{234}U 53.9, ^{235}U 2.5, and ^{238}U 53.7.

Mean contents of U and Th in surface layers of the land (25 to 40 cm) of Poland are 1.36 and 3.29 ppm, and range for most territory from <1 to 4 ppm and <2 to 4 ppm, respectively. Only in the Sudeten Mountains and Piedmont areas do U levels increase locally up to 13.3 ppm, and Th up to >10 ppm.[1509] Surficial sediments (upper part of the C horizon) of Finland contain up to 8.5 ppm

Table 107 **Thorium and Uranium Contents of Surface Soils of Different Countries (ppm DW)**

	Th		U		
Country	Range	Mean	Range	Mean	Ref.
Bulgaria	3.6–17.8	9.3	—	—	558
Brazil	76; 96[a]	—	—	—	1065
Canada	4.2–14.1	8.0	0.72–2.05	1.22	409
Great Britain	—	10.5	—	2.60	818
Germany	0.4–15.0	8.0	0.42–11.02	—	235, 688
India	—	—	—	11.00	276
Italy	—	—	1.5–8	3.17	946
Poland	1.4–7.2	3.4	0.10–2.33	0.79	355
U.S.	2.2–21.0	7.6	0.30–10.70	3.70	462, 706
U.S. (Alaska)	<1.6–76	6.1	<0.22–45	2.3	1012
Russia	—	13.4	—	3.8	1181

[a] Two single analyses of soils near REE ore body.

U, and up to 27 ppm Th. The most common concentrations (90% of samples) were from about 1 to 5.5 ppm for U, and from 5 to 20 ppm for Th.[1368] Surface horizons of forest soils in Japan contain Th within the range from 2.56 to 12.4 pm and U from 0.024 to 1.15 ppm. Other soils of various types in Japan have a larger abundance of these elements. The lowest concentrations are in sand dunes and peat soils (Th 2.56 and U 0.59 ppm) and the highest in red soils and gray lowland soils (Th 12.4 and U 2.94 ppm).[1564]

Both U and Th are slightly available to all kinds of plants, including mushrooms. Yoshida and Muramatsu[1564] gave the following ranges for these elements in forest plants: for Th, 0.003 to 0.036 ppm, and U, 0.001 to 0.012 ppm.

There is considerable contemporary interest in studies on the behavior of other elements of the actinides, which are isotopes released from the nuclear fuel power industry. This group includes various isotopes of plutonium (Pu), americium (Am), curium (Cm), and neptunium (Np), of which the long-lived and highly radiotoxic ^{239}Pu and ^{241}Am are of greatest concern. Most of the aerosols produced and discharged from nuclear facilities, as well as in nuclear bomb fallout, are composed of PuO_2, but some of the Pu may come from the evaporation of $Pu(NO_3)_4$.

The behavior of these radionuclides, and of ^{239}Pu in particular, was extensively reviewed by Wildung and Garland,[873] Vyas and Mistry,[832] and Silver.[1149] Regardless of the forms of Pu and Am entering the soil, their solubilities are controlled by various soil factors, and thus they occur mainly as complexes of fulvic and humic acids and in forms adsorbed by clay mineral particles. Unlike the tightly bound PuO_2^{2+}, $Pu(NO_3)_4$ belongs to the soluble compounds and easily hydrates and hydrolysates in the soil solution, forming soluble hydroxides. Thus, the soluble, and therefore plant-available, fraction of Pu, and apparently of other transuranic elements, appears to be largely present as particulates of hydrated oxides and as organometallic complexes. Bartlett[933] reported that Pu compounds, when converted to the mobile anion form analogous to chromate, became more available and toxic from oxidation by soil Mn oxides. Jakubick[350] studied in detail the behavior of ^{239}Pu and ^{240}Pu in meadow soil around Heidelberg, Germany, where the isotopes have been concentrated from 290 to 450 μCi km^{-2} in the 10-cm-deep upper layer, whereas the activity of these isotopes ranges from 1.6 to 5.8 μCi km^{-2} at a depth below 25 cm. Little et al.[1066] investigated a buffer zone near Denver, Colorado, which was contaminated with Pu between 1959 and 1964. They found that the top 21 cm of soil contained above 99% of the total Pu inventory, which averaged about 53 μCi m^{-2} in the study area. Concentrations of Pu in vegetation were relatively low, but were several orders of magnitude larger than for experimentally grown plants.

Allard et al.[917] studied the adsorption of ^{241}Am in the presence of humic materials and found that this radionuclide is associated to solids of organic origin or to inorganics which are coated with an organic layer. ^{241}Am also makes humate complexes easily. At high pH and high humic content, the adsorption of this radionuclide is reduced, increasing its mobility in the environment.

To protect soils against contamination with radionuclides (U, Th, Np, Pu), they are stored in the form of glass fusion. Aqueous leaching of nuclear glass under geological disposal conditions mobilizes the elements that were precipitated (up to 98% of realized amounts) at the surface of glass. The presence of amorphous silica and phosphates stimulated these processes.[1412]

B. Plants

The assessment of the transfer of Th, U, and transuranic radionuclides from contaminated soils to plants is important in environmental research. However, little information is available on this subject.

The soluble fractions of these elements in soils seem to be readily absorbed by plants, and this is clearly supported by the studies conducted in the U geochemical province where plants accumulated up to 100 times more U than did plants from other areas.[423] Tiffin[789] reported that a U protein complex was found in leaves of *Coprosma australis* (Rubiaceae family), while mineral precipitates (autunite, $Ca[UO_2|PO_4]_2 \cdot 10\ H_2O$) were found in the tips of plant roots.[1042a] Wildung and Garland[873] stated that plants possess the ability to effectively accumulate soluble Pu and to transport the Pu from roots to shoots. However, in the area polluted with Pu, much of the Pu associated with vegetation was attached to the plant surface.[980] Little et al.[1066] concluded that soil erosion is the most significant factor in Pu transport from the soil to the plants and other environmental compartments. Dienstbach et al.[980] found that the proportion of the Pu isotopes (239/240) in soils and in linden leaves showed a relative decrease of ^{240}Pu in the vegetation.

Shacklette et al.[710] found the highest U concentration in trees on mineralized ground to be 2.2 ppm (AW), and Goswani et al.[276] reported the U range from 0.5 to 4.4 ppm (AW) (average, 1.8) in xerophytic and mesophytic vegetation. Sagebrush grown near a P fertilizer works accumulated up to 8 ppm U (AW).[278] Bowen[94] gave the range in U concentrations in terrestrial plants as 5 to 60 ppb (DW), whereas Laul et al.[462] reported U concentrations in corn and potatoes to be 0.8 ppb (DW). Rühling et al.[1135] found in mosses (mainly *Hylocomium splendens*) from the Scandinavian countries that U concentrations ranged from 30 to 120 ppb (DW), the lowest for Denmark and the highest for Finland. A somewhat higher and wider range in the Th content of land plants was reported by Bowen[94] to be <8 to 1300 ppb (DW), while Laul et al.[462] found Th to range from <5 to 20 ppb (DW) in vegetables. Moss samples from the Scandinavian countries contain Th from 90 to 180 ppb (DW) within a similar regional pattern as reported for U.[1135] Recent data for moss collected in Norway (Table 4) give the range for Th from 4 to 5100 ppb (mean 70) and for U, from 2.8 to 1300 ppb (mean 50).[1223]

CHAPTER 9

Elements of Group IV

I. INTRODUCTION

The geochemical properties and terrestrial abundance of the elements in Group IV diverge widely. Their common characteristics are the weak solubility of their hydroxides and oxides in water, an affinity to bond with oxygen, and they often have the coordination number four.

Group IVa (new group 14) contains Si, Ge, Sn, and Pb. Si, in combination with oxygen, is the basic nonmetallic component of all rocks (Table 108) and is considered as a trace element only in respect to its biochemical role. The next elements in this group, Ge, Sn, and Pb, are trace metals, and show chalcophilic properties in the terrestrial environment.

Of the elements of Group IVb (new group 4) Ti is definitely an oxyphile, is associated with silicate minerals, and is considered a trace element only because of its low concentration in plant tissues. The next two metals, Zr and Hf, are widely distributed in both the litho- and biosphere, and are often included in the group of rare earth elements.

II. SILICON

A. Soils

Si is the most abundant and, relatively, the most stable electropositive element in the Earth's crust; however, under specific conditions it can be dissolved and transported, but it moves mainly in its colloidal phase. All silicate minerals are built of a fundamental structural unit, SiO_4, the so-called tetrahedron.

Quartz, SiO_2, is the most resistant mineral in soils and is also known to occur in a noncrystalline form, opal, which is believed to have had a biological origin. In soils, amorphous silicates apparently contribute to anion adsorption processes, and it has been suggested that silicate and phosphate ions compete for sites on mineral soil particles.[530] Tiller[793] has shown that the presence of monosilicic acid in solution increases the sorption of heavy metal cations, such as Co, Ni, and Zn, by clays.

In general, Si is released rapidly from minerals into the soil solution where it occurs at near-equilibrium concentrations. Carlisle et al.[121] reported that soluble Si (mainly as H_4SiO_4) in the soil solution ranges from 1 to about 200 mg L^{-1}. The concentration of Si in soil solutions and drainage waters is highly dependent on several soil and climatic factors. The pH level has an especially marked effect on Si concentrations in solutions, although the mobility of Si in soils cannot be predicted accurately from the pH alone. Usually, Si is more mobile in alkaline soils, but as Carlisle et al.[121] have described, increasing the pH to about 9 decreases the Si concentration in solutions. A pH beyond approximately 9.5 results in a sharply increased Si content of the solution.

Table 108 Silicon, Germanium, Tin, Lead, Titanium, Zirconium, and Hafnium in Major Rock Types (values commonly found, based on various sources)

Rock Type	Si (%)	Ge (ppm)	Sn (ppm)	Pb (ppm)	Ti (%)	Zr (ppm)	Hf (ppm)
Magmatic Rocks							
Ultramafic rocks Dunites, peridotites, pyroxenites	19.0–20.5	0.7–1.5	0.35–0.50	0.1–1.0	0.03–0.30	20–40	0.1–0.6
Mafic rocks Basalts, gabbros	23–24	0.8–1.6	0.9–1.5	3–8	0.90–1.38	80–200	1.0–4.8
Intermediate rocks Diorites, syenites	26.0–29.1	1.0–1.5	1.3–1.5	12–15	0.35–0.80	250–500	2–10
Acid rocks Granites, gneisses	31.4–34.2	1.0–1.4	1.5–3.6	15–24	0.12–0.34	140–240	2–5
Acid rocks (volcanic) Rhyolites, trachytes, dacites	30.8–33.6	1	2–3	10–20	0.27	150–300	4.5
Sedimentary Rocks							
Argillaceous sediments	24.5–27.5	1.0–2.4	6–10	20–40	0.38–0.46	160–200	2.8–6.0
Shales	24.0–27.5	1.3–2.0	6	18–25	0.44–0.46	150–200	2.8–4.0
Sandstones	31.6–36.8	0.8–1.2	0.5	5–10	0.15–0.35	180–220	3.0–3.9
Limestones, dolomites	2.4–4.0	0.3	0.5	3–10	0.03–0.04	20	0.3

Several interferences between Si and other ions such as P, Al, Ca, and Fe may occur in soil and modify the behavior of Si. For example, in acid soils, silicate and phosphate ions form insoluble precipitates which may fix several other cations (e.g., Fe and Al oxides that have a marked capacity to sorb dissolved Si as H_4SiO_4). Appreciable amounts of organic matter in flooded soil induce a higher Si mobility, apparently due to the reduction of Fe hydrous oxides, which release adsorbed monosilicic acid.

B. Plants

Si is a common constituent of plants, and its amounts may vary by two orders of magnitude. Metson et al.[536] reported the mean Si content to range from 0.3 to 1.2% (DW) in grass, whereas this range is 0.04 to 0.13% in clover and 0.1 to 0.2% in alfalfa. Some species of plants may accumulate a much higher amount of Si (e.g., diatoms, sedges, nettles, and horsetails). Rice plants are known as accumulators of Si and can contain up to 10% (DW) in hulls and about 15% (AW) in leaves.[121, 395]Alyoshin et al.[920] found that the Si content of chloroplasts of rice grains is extremely elevated, up to 4% (DW).

Si is absorbed from the soil solution as monosilicic acid or silica, and its absorption is usually proportional to its concentration in the solution and to water flow. However, Tinker[798] reported that while Si uptake by most grasses appears to be passive, in rice it is rather an active process. There is also evidence that plants can restrict the uptake of Si, as do some covers which either exclude H_4SiO_4 at the external surface or bind it within the root tissue, and thus can reduce the concentration of Si in the xylem sap to about 6% of that in the external solution.[121] Although Si-organic complexes have not yet been isolated, plant Si has been shown to exist in at least two forms, one of which is believed to be a hydrogen-bonded Si-organic complex.[121] Körös[1055] reported that a special silicon complex (thujaplicine complex) was isolated from *Thuja plicata* and that most of the Si taken up either as monomeric silicic acid or as organic complex was deposited in plant tissues as opaline silica.

Si (possibly as amorphous silica) impregnates the walls of epidermal and vascular tissues.[387] Thus, Si strengthens plant tissues, reduces water loss, and retards fungal infection. Where large amounts of Si are accumulated, intercellular deposits can be formed as plant opal. Residues of such plants contribute to the formation of amorphous silica in soils.

Wallace[840] reported that soluble Si stimulated plant growth. This stimulation seems to be related to the observed effects of Si on increased P and Mo uptake by plants, as well as on Mn transport within plant tissues.[326]

Antagonistic effects of Si on the uptake of B, Mn, and Fe have also been observed (Figure 30). Si seems to inhibit deleterious effects of As and Ge on mitochondria activities in rice grains,[919] as well as reduce the internal phytotoxicity of Al.[241] The ameliorative effect of an increase in readily available H_4SiO_4 on reducing the toxicity of Al and also Mn is apparently related to cation/anion balance at the root surface, which leads to the immobilization of these elements. Alyoshin et al.[919,920] observed a beneficial impact of Si on metabolic processes in chloroplasts and on phosphorylation processes in rice grains. It has been suggested that Si enhances phosphorylation of sugars, which improves the energy supply for metabolism and enhances sugar synthesis that is reflected in more growth.[3] Miyake and Takahashi[546] reported that Si deficiency affected the reproductive growth of tomato plants grown in culture solution. The biochemical role of Si has not yet been clarified.

III. GERMANIUM

A. Soils

Common amounts of Ge in the major rock types range from 0.3 to 2.4 ppm (Table 108). The distribution of Ge resembles that of Si, and thus the lowest Ge contents are in calcareous sediments and mafic magmatic rocks. Ge mainly exhibits siderophile properties, but is also associated with

Table 109 Germanium and Tin Content of Surface Soils of the U.S. (ppm DW)[706]

	Ge		Sn	
Soil	**Range**	**Mean**	**Range**	**Mean**
Sandy soil and lithosols on sandstones	0.6–2.1	1.1	<0.1–7.7	1.1
Light loamy soils	0.6–1.6	1.2	<0.1–2.2	0.9
Loess and soils on silt deposits	0.9–1.6	1.3	0.3–1.8	1.1
Clay and clay loamy soils	0.7–2.0	1.5	0.3–3.1	1.2
Alluvial soils	0.6–2.1	1.3	0.3–4.2	1.7
Soils over granites and gneisses	1.0–1.4	1.3	0.9–1.5	1.2
Soils over volcanic rocks	1.1–1.8	1.4	0.8–1.7	1.2
Soils over limestones and calcareous rocks	0.6–1.3	1.0	<0.1–1.8	1.1
Soils on glacial till and drift	0.9–1.7	1.2	0.1–1.1	0.6
Light desert soils	0.8–1.6	1.2	0.7–1.9	1.2
Silty prairie soils	0.7–1.4	1.1	0.4–1.9	0.9
Chernozems and dark prairie soils	0.8–1.6	1.3	0.2–5.0	1.4
Organic light soils	<0.1–1.1	0.8	0.1–7.9	1.2
Forest soils	0.7–1.8	1.4	0.2–2.8	1.1
Various soils	1.5–1.8	1.6	—	—

sulfide ores of some metals, where it is likely to occur as germanite, $GeS_2 \cdot 7CuS \cdot FeS$, or similar mineral.

During weathering, Ge is partly mobilized, mainly in an easily mobile form, $Ge(OH)_2$, and is transported to aquatic basins, but then is readily fixed, apparently in the form of $Ge(OH)_4$, to clay minerals, Fe oxides, and organic matter. Its high concentrations in coals have often been reported. Coals often contain considerable Ge. Fly-ash, containing up to 250 ppm Ge, is known to be a commercial source of this metal. Also a main source of Ge in the environment is the emission from coal burning, which is calculated globally at about 700 t per year.

Ge may occur as the divalent cation, but its complex anions are also known, such as $HGeO_2^-$, $HGeO_3^-$, and GeO_3^{2-}. The abundance of Ge in surface soils of the U.S. is fairly uniform and averages 1.1 ppm (Table 109). There is very little information about Ge in soils of other countries. Govindaraju[1313] reported Ge contents in reference soils from China to range from 1.2 to 3.2 ppm (mean, 1.6 ppm).

B. Plants

Although Ge is reported to occur in plants, it is not known to have any physiological functions. Schroeder and Balassa[695] gave the range of Ge concentrations in grains as 0.09 to 0.7 ppm (FW) and in vegetables as 0.02 to 1.07 ppm (FW). Duke[197] found Ge in food plants of a Central American region to range from <0.01 to <0.1 ppm (DW). Connor and Shacklette[145] reported the Ge content of plant ash, if detected, to average 20 ppm, but the element was rarely detected. Ge was found in only 1 of 123 samples of Spanish moss (*Tillandsia usneoides*, Bromeliaceae family) at a concentration of 15 ppm (AW) and this sample was from an area subject to air pollution from industrial operations.[708] Ge contents of willow leaves grown in the Sudeten Mountains and of Turkish hazel grown in Wroclaw (Poland) varied from 12 to 108 ppm, and from 14 to 100 ppm, respectively. The increased concentrations of Ge indicate polluted sites and periods of higher industrial emissions.[1335,1477]

Plants seem to absorb Ge at a relatively high rate, possibly in the form of GeO_2.[395] Rice plants may accumulate Ge readily and concentrate this element to a level as high as 1% (AW) in the tops, although Ge is highly toxic to plants and to rice plants in particular.[516]

It is assumed, although little is actually known, that interaction between Ge and Si exists and that those plants which need Si for growth are most sensitive to Ge. Even at low concentrations, Ge has been shown to inhibit germination and plant growth.[679,919]

IV. TIN

A. Soils

The abundance of Sn in common rocks shows an increased concentration in argillaceous sediments (6 to 10 ppm) and lower amounts in ultramafic and calcareous rocks (0.35 to 0.5 ppm) (Table 108). Sn tends to form only a few independent minerals, of which cassiterite is the most important Sn ore, and is strongly resistant to weathering. Sn is known to occur as Sn^{2+} and Sn^{4+}, in nature is markedly siderophilic, but also forms several complex anions of oxide and hydroxides. Because Sn does not readily associate with other elements, there are not many Sn minerals (cassiterite, SnO_2; stannite, Cu_2SnFeS_4; montesite, $PbSn_4S_5$).

The mobility of Sn during weathering is highly pH dependent. Especially Sn^{2+}, a strong reducing agent, can be present only in acid and reducing environments. Soluble Sn follows the behavior of Fe and Al and remains in the weathered residue along with hydroxides of these metals. The ability of Sn to form complexes with organic substances, both soluble and insoluble, has been reported; therefore, Sn is generally enriched in bioliths.

The occurrence of Sn in soil has not received much study; only Shacklette and Boerngen[706] have presented comprehensive data on Sn in soils (Table 109). Although Sn in soils is largely derived from Sn in the bedrock, all soil surface horizons contain fairly similar amounts of this element, averaging 1.1 ppm. Presant[629] gave the range in Sn concentrations in soils as 1.1 to 4.6 ppm, and Kick et al.[390] gave the range as 1 to 4 ppm. Ure and Bacon [818] found 4.5 ppm Sn in the standard soil samples. Chapman[131] cited the common range of Sn in soils as 1 to 11 ppm, and Gordon (see Griffitts and Milne[286]) reported Sn concentrations in peats to range from 50 to 300 ppm (AW). Govindaraju[1313] reported Sn contents in reference soils from China to range from 2.5 to 17.7 ppm (mean, 1.6 ppm), and in soils of the U.S. to range from 1.7 to 4.0 ppm (mean, 2.4 ppm). In some polluted sites, however, up to 800 ppm of Sn has been reported.[1357]

There is evidence that inorganic Sn is methylated in the aquatic environment to various methyl forms.[970] Organometallic forms of Sn and their ease in bioaccumulation is currently receiving much attention because of the growing Sn distribution in the environment and its relation to health risk. The allowable concentration of Sn in soils is established at 50 ppm.

B. Plants

There is no evidence that Sn is either essential or beneficial to plants, although plants may easily take up Sn, if present in the nutrient solution, but most of the absorbed Sn remains in roots.[662] Under natural soil conditions, however, Sn apparently is less available; therefore, measurable amounts of Sn are not found in all plant species.

Gough et al.[279] reported the common range of Sn to be 20 to 30 ppm (AW). Zook et al.[906] found 5.6 to 7.9 ppm (DW) Sn in wheat grains, and Duke[197] gave the range in Sn concentrations in food plants of a Central American forest region as <0.04 to <0.1 ppm (DW), and Connor and Shacklette[145] reported Sn to average 15 ppm in plant ash, but it was not detectable in all samples. Chapman[131] reported that Sn ranges in grass from 0.2 to 1.9 ppm (DW) and that in corn grains it averages 2.9 ppm.

Plants grown in mineralized areas accumulated Sn to levels as high as 80 ppm (AW),[686] and even to 300 ppm (AW).[613] Sedges and mosses were found to be the best Sn accumulators.[286]

The Sn in plants grown in contaminated soils may be highly enriched. Pešek and Kolsky[608] found Sn concentration to be about 1000 ppm (DW) in sugar beets that were grown in the vicinity of a chemical factory, and Peterson et al.[610] reported Sn concentrations of about 2000 ppm (DW) in vegetation in the proximity of a Sn smelter. Sn is very toxic to both higher plants and fungi.

V. LEAD

A. Soils

The terrestrial abundance of Pb indicates a tendency for Pb to concentrate in the acid series of magmatic rocks and argillaceous sediments in which the common Pb concentrations range from 10 to 40 ppm, while in ultramafic rocks and calcareous sediments its range is from 0.1 to 10 ppm (Table 108). The average abundance of Pb in the Earth's crust is estimated at about 15 ppm. In the terrestrial environment, two kinds of Pb are known: primary and secondary. Primary Pb is of geogenic origin and was incorporated into minerals at the time of their formation, and secondary Pb is of a radiogenic origin from the decay of U and Th. The ratio of Pb of various origins is used for dating the host materials.

Pb has highly chalcophilic properties and thus its primary form in the natural state is galena (PbS). Pb occurs mainly as Pb^{2+}, although its oxidation state, +4, is also known, and it forms several other minerals which are quite insoluble in natural waters.

During weathering, Pb sulfides slowly oxidize and have the ability to form carbonates and also to be incorporated in clay minerals, in Fe and Mn oxides, and in organic matter. The geochemical characteristics of Pb^{2+} somewhat resemble the divalent alkaline-earth group of metals; thus, Pb has the ability to replace K, Ba, Sr, and even Ca, both in minerals and in sorption sites.

The natural Pb content of soil is inherited from parent rocks. However, due to widespread Pb pollution, most soils are likely to be enriched in this metal, especially in the top horizon. There is much data available in the literature on soil Pb, but sometimes it is difficult to separate the data for background Pb levels in soils from those of anthropogenically influenced amounts in surface soils.

Values presented in Table 110 for the natural Pb occurrence in top horizons of different soils from various countries show that amounts range from 3 to 189 ppm, while mean values for soil types range from 10 to 67 ppm and average 32 ppm. High Pb levels (above 100 ppm) have been reported mainly for Denmark, Japan, Great Britain, and Ireland and most probably reflect the impact of pollution. Davies[165] stated that an upper limit for the Pb content of a normal soil could be established as 70 ppm.

Gough et al.[1012] found a relatively low Pb content of soils in Alaska. Although Pb in these soils ranges from 4 to 349 ppm (DW), about 90% of the samples contained only up to 20 ppm, with a geometric mean of 12. Low concentrations of Pb in soils from this remote region suggest that baseline values of this metal in most world soils should not be much higher than 20 ppm. This corresponds closely to the lithogenic concentrations of Pb which do not exceed the above value, with the exception of argillaceous sediments and shales (Table 108). Also, grand mean values for Pb in different soil units vary within the range of 22 to 28 ppm (DW). Only histosols are enriched in Pb, which averages 44 ppm (Table 9). Therefore, the mean Pb concentration for surface soils on the world scale could be estimated as 25 ppm.

Recently estimated Pb geometric means for soils of Poland indicate a growing Pb level with increasing content of clay granulometric fraction; for example, in sandy soils, 12.6 ppm; medium loamy soils, 16.4 ppm; and heavy loamy soils, 20.9 ppm (Table 20). The geometric mean Pb content of surface soils from major agricultural production areas of the U.S. is 10.6 ppm, within the range from <1 to 135 ppm.[1329]

1. Reactions with Soil Components

The natural Pb content of soils is strongly related to the composition of the bedrock, and Pb is reported to be the least mobile among the other heavy metals. The relatively low Pb concentrations in natural soil solutions (Table 16) support this statement. Although the Pb species can vary considerably from one soil type to another, it may be concluded from the results given by Norrish,[570] Riffaldi et al.,[653] Tidball,[787] and Schnitzer and Kerndorff[690] that Pb is associated mainly with clay

Table 110 Lead Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	—	57	196
	Romania	5–41	19	1127
	Canada	2.3–47.5	10.4	243
	Madagascar	—	37	557a
	Poland	8.5–23.5	16	378
	U.S.	<10–70	17	706
	Former S.U.	17.5–22.2	20	1031
Loess and silty soils	Poland	14–32	26	378, 665
	U.S.	10–30	19	706
Loamy and clay soils	Canada	1.5–50.1	16.6	243, 629
	Chad	20–45	—	39
	Madagascar	—	48	557a
	Poland	12.5–52	25	378
	Romania	14–33	21	1127
	U.S.	10–70	22	706
	Former S.U.	—	40	631
Soils on glacial till	Denmark	11.3–17.3	14.7	801, 802
	Poland	7–18	10	974
	U.S.	10–30	17	218, 219
Fluvisols	Austria	16–22	19	6
	Great Britain	24–96	63	166
	Madagascar	19–47	—	557a
	Poland	12.5–48.5	39	378
Paddy soils	Japan	6–189	29	395
Gleysols	Chad	20–50	—	39
	Poland	19.5–48.5	30	378
	Former S.U.	—	67	631
	Great Britain	17–63	40	874
Rendzinas	Ireland	25–45	—	236
	China	17–280	57	1124
	Madagascar	—	20	557a
	Poland	17–46	28.5	378, 685
	U.S.	10–50	22	706
Kastanozems and brown soils	Austria	13–31	21	6
	Great Britain	20–50	35	874
	Romania	8–20	15	1127
Ferralsols	Chad	10–30	—	39
	Sierra Leone	3–91	47	168
Chernozems	Poland	19–29	25	378
	U.S.	10–70	19	706
	Former S.U.	20.2–29	24	1031
Prairien and meadow soils	Former S.U.	—	61	631
	Germany	11.5–79.5	—	46
Histosols, other organic soils	Canada	1.5–50.0	12.6	243
	Denmark	43–176	50.5	1, 801
	Great Britain	26–142	84	69, 874
	Ireland	120	—	236
	Poland	18–85	—	681
	U.S.	10–50	24	706
Forest soils	China	—	26	225
	U.S.	10–50	20	218, 219
	Former S.U.	10–56	37	9, 631
Various soils	Austria	21–33	29	6
	Canada	—	20[a]	521
	Great Britain	15.5–41	29	69, 100, 818
	Italy	4–81	26	946

(*Continued*)

Table 110 Lead Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
	Japan	5–189	35	395, 403
	Poland	5–286	18	1045
	Germany	15–68	—	46
	U.S.	<10–70	26	706
	Former S.U.	2.4–24.5	7.9	1131

[a] Mean for whole profiles of arable soils.
[b] Kazachstan.

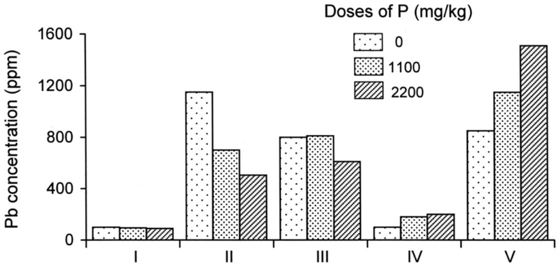

Figure 68 Phosphate (KH_2PO_4) effects on Pb fractionation in the Pb-contaminated soil (Pb—2800 ppm, pH ca. 7.0 after $CaCO_3$ addition). Fractions of Cd (after Tessier et al.[1516]): I, exchangeable; II, carbonate; III, oxide; IV, organic; V, residual. (With permission from the authors[1328].)

minerals, Mn oxides, Fe and Al hydroxides, and organic matter. However, in some soil, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations. Phosphate added to a soil contaminated with Pb slightly decreases its easily soluble fraction, and to a greater extent oxide, and carbonate fractions, while increasing organic, and especially residual fractions (Figure 68). In soils heavily polluted with Pb, the formation of pyromorphite, $Pb_5Cl(PO_4)_3$, is observed.[1263] The concentration of this mineral is mainly close to the roots of grass (*Agrostis capillaris*) and indicates an influence of the rhizosphere on the process of its formation.

The solubility of Pb can be greatly decreased by liming. A high soil pH may precipitate Pb as hydroxide, phosphate, or carbonate, as well as promote the formation of Pb-organic complexes which are rather stable. Increasing acidity may increase the Pb solubility, but this mobilization is usually slower than the accumulation in the organic-rich layer of soils.

Hildebrand and Blume [319] reported that illites show much greater affinity to sorb Pb than other clay minerals, whereas this reaction was not observed by Kabata-Pendias [377] in studies of Pb sorption by clays over a wide range of pH. Farrah and Pickering[228] emphasized that adsorption of Pb is highly dependent on the kinds of ligands involved in the formation of hydroxy complexes of Pb (e.g., $PbOH^+$ and $Pb_4(OH_4)^{4+}$). These authors discussed several possible mechanisms of adsorption of hydroxy species and suggested that Pb sorption on montmorillonite can be interpreted as simply cation exchange processes, while on kaolinite and illite Pb is rather competitively adsorbed. Abd-Elfattah and Wada[2] found a higher selective adsorption of Pb by Fe oxides, halloysite, and imogolite than by humus, kaolinite, and montmorillonite. In other studies, the greatest affinity to sorb Pb was reported for Mn oxides.[377,525]

The characteristic localization of Pb near the soil surface in most soil profiles is primarily related to the surficial accumulation of organic matter. The greatest Pb concentrations are also often found in the organically rich top horizons of uncultivated soils, as was reported by Fleming et al.[236] Therefore, organic matter should be considered as an important sink of Pb in polluted soils.

2. Contamination of Soils

The fate of anthropogenic Pb in soils has recently received much attention because this metal is hazardous to man and animals from two sources—the food chain and soil dust inhalation (or, with children, pica for soil).

The steadily increasing amounts of Pb in surface soils, both arable and uncultivated, have been reported for various terrestrial ecosystems.[331] The impact of land use on the Pb level in topsoils is illustrated by Blum et al. (after Kuttler).[1231] Variable filtration of the atmospheric deposition by the plant canopy affects the Pb input to topsoils, which is three times higher in spruce forest (90 μg Pb L^{-1}) than in pasture soil (30 μg Pb L^{-1}). The accumulation of Pb in surface soil exposed to various pollution sources at some sites has already reached a value as high as about 2% of dry soil material (Table 111). The levels of Pb in soils that are toxic to plants are not easy to evaluate; however, several authors have given quite similar concentrations, ranging from 100 to 500 ppm (Table 6).

Table 111 Lead Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Mean or Range of Content	Country	Ref.
Old mining area	51–21,546	Great Britain	165,166, 808, 659
Nonferric metal mining	170–4563	Great Britain	165,166
	>300	Germany	390
	15–13,000	U.S.	330
	21–3044	Former S.U.	567
Metal processing industry	291–12,123	Canada	363
	137–14,000	Belgium	1142
	1250–18,500	Greece	559
	628–1334	Holland	305
	53–2100	Japan	403, 926
	104	Norway	732
	2480–8000[d]	Poland	871, 507, 1015, 1357
	3170	Romania	1126
	500–6500	U.S.	538
	3074	Germany	1075
	92–2580	Zambia	573
	1612–3640	Russia	854, 1502a
Battery manufactory and reclamation site	881–1058	Chile	1139
	93–3800	Poland	945
	135,000	U.S.	1166
Urban garden and urban vicinity	6–888	Canada	585
	270–15,240	Great Britain	48, 785a, 959
	10–897	Jamaica	1347
	165–12,750	Poland	159, 1015a, 1173
	127–388	Germany	1046, 1051
	218–10,900	U.S.	127, 208, 628
Sludged farmland	175–3916	Great Britain	59, 987
	60–253[a]	Japan	395
	80–254[b]	Holland	314
	>800[c]	Germany	1023
Roadside soil	132–397	Japan	395
	167–2115	Poland	1173
	114–885	Germany	397
	960–7000	U.S	582
Application of waste lime	2400	Poland	1173

[a] Paddy soil.
[b] 6 and 16 t dry matter sludge ha^{-1} $year^{-1}$, for 5 years.
[c] Soils with dredged sediments.
[d] Maximum value for the industrial Silesia region.

Peat bogs are good records of atmospheric Pb deposition due to their great capacity to accumulate and strongly fixate this metal. The anthropogenic Pb deposition extending back at least to Greek and Roman times has been traced in peat cores of several European countries. The Pb concentrations in recent peats are about 100 times higher than the pre-anthropogenic pollution calculated at 0.2 ppm, and dated using ^{210}Pb.[1487]

Studies on Pb compounds in contaminated soils have been reviewed by Hildebrand,[318] Olson and Skogerboe,[582] Harmsen,[305] and Zimdahl and Hassett.[903] The main Pb pollutants emitted from smelters occur in mineral forms (e.g., PbS, PbO, $PbSO_4$, and $PbO \cdot PbSO_4$), while Pb in automobile exhausts is mainly in the form of halide salts (e.g., PbBr, PbBrCl, Pb(OH)Br, and $(PbO)_2PbBr_2$). Exhaust Pb particles are unstable and readily convert into oxides, carbonates, and sulfates. Processes of methylation of some species of Pb are either biological or purely chemical reactions. As Beijer and Jernelöv[935] stated, the conversion of tetraalkyllead compound in soils is most probably not a biological process.

Other important sources of Pb in soils are Pb-containing paints within the home and garden. Thornton[1164] reported that the geometric mean concentration of Pb in 4650 garden soils of Great Britain is 298 ppm (DW). The concentrations of Pb were higher in older homes, which clearly indicates a gradual increase of this metal in garden soils. This phenomenon is closely related to hazardous Pb intake by children as a result of "hand-to-mouth" activity. Pb in soils has received much attention in recent years and some results are summarized as guidelines by Wixson and Davies.[1547] Residential areas, allotment gardens, and industrially impacted soils are especially broadly investigated. The most serious soil Pb issue is associated with a direct transfer of Pb from contaminated soil to children, showing a significant relationship among Pb levels in soils and in children's blood. Lowney et al.[1392a] presented (after Bowers et al.) the equation to calculate adult blood Pb concentration as an effect of the exposure to various sources of this metal, including soil and dust. The former hot Pb issue related to soils pollution along highways is now of smaller concern due to the regulations eliminating Pb from petrol.

Cunningham and Berti[1266] recently reviewed technical and economic issues related to remediation of Pb-contaminated soil. Because Pb is very strongly bound in almost all types of soil, its phytoextraction is rather limited. When Pb is taken up by plants, its translocation to above-ground parts is very poor. The major proportion of Pb is concentrated in root tissues. However, it is promising that dense vegetative cover will stabilize Pb, for a given period, within the rooting zone.

Although Pb is a slightly phytoavailable metal and thus difficult to phytoextract, there are several plants (e.g., *Thlaspi* sp., corn, sunflower) that accumulate larger amounts of Pb, especially in roots. Increasing mobility of Pb using chelates or other technologies (e.g., electroosmosis) can stimulate its phytoavailability.[1338]

Because Pb enters the soil in various and complex compounds, its reactions may differ widely among areas. Indeed, opinion appears to differ as to whether Pb as a pollutant is a mobile or a stable soil component. Tyler[816] reported that Pb is the most stable metal in forest soil, and the time necessary for a 10% decrease of its total concentration by leaching was calculated to be 200 years for polluted soil and 90 years for "control" soil. Kitagishi and Yamane[395] calculated the period in which the amount of Pb in soil will decrease by one half to range from 740 to 5900 years, depending on the kind of soil, the water management, and the organic matter present. Stevenson and Welch[759] observed that Pb moved from the topsoil treated with Pb acetate into the subsoil, even though the soil (silty clay loam) was shown to have a high capacity for binding Pb in nonexchangeable forms. This mobility was attributed to the metal leaching as soluble chelated complexes with organic matter. In general, however, several observations of the Pb balance in various ecosystems show that the input of this metal greatly exceeds its output (Table 17). For example, Hansen and Tjell[304] estimated that an annual increase of Pb in Danish agricultural soils is 3.7% of its total amount in the soil. It must be emphasized that contamination of soils with Pb is mainly irreversible and, therefore a cumulative process in surface soils will continue, even if inputs are low.

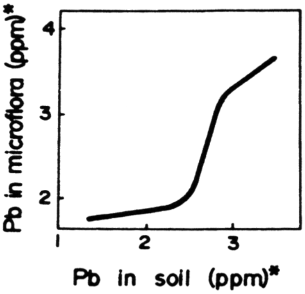

Figure 69 Concentration of Pb in soil microflora as a function of its content in soil.*Values given in powers of ten.[567]

Previously, there was little concern about Pb contamination of soils because of the relative insolubility of adsorbed and precipitated ions of Pb in soils. The strong Pb adsorption in soils may mean that Pb additions to soil are permanent and irreversible. However, the Pb content of the roots is correlated to the Pb content of the soil, which indicates its uptake by plants. Certain soil and plant factors (e.g., low pH, low P content of soil, organic ligands) are known to promote both Pb uptake by roots and Pb translocation into plant tops.

The accumulation of Pb in surface soils is of great ecological significance because this metal is known to greatly affect the biological activity of soils. This topic has been reviewed by Tyler[812,813] Andersson,[19] Doelman and Haanstra,[185] and Hughes et al.,[331] who showed that increased levels of Pb in soil are likely to limit enzymatic activity of microbiota and, as a consequence, markedly increase the accumulation of incompletely decomposed soil organic matter, particularly those materials that do not decompose readily, such as cellulose. A significant accumulation of nitrates in soils enriched in Pb was observed by Woytowicz.[889]

Niyazova and Letunova[567] reported a strong tendency of soil microflora to accumulate Pb at a very high rate that was proportional to the metal content of soils (Figure 69). Consumers such as earthworms also at times concentrate Pb from the soil substrata (Table 28), which greatly contributes to a secondary deposition of Pb in surface soils. Ma et al.[1080] demonstrated a great influence of pH and organic matter content on the worm uptake of Pb, which is significantly stronger in soils with a low pH and low organic matter content than in soils with higher values of these parameters.

Recently, Pb concentrations have gradually increased in soils and may seriously inhibit microbial processes (Table 24). These effects should be expected principally in soils with a low CEC value. However, in the long run, they may also occur in other soils with a higher CEC.

B. Plants

Although Pb occurs naturally in all plants, it has not been shown to play any essential roles in their metabolism. Broyer et al.[108] reviewed this topic and concluded that if Pb is necessary for plants its concentration at the level of 2 to 6 ppb should be sufficient. Pb has recently received much attention as a major chemical pollutant of the environment and as an element toxic to plants.

1. Absorption and Transport

Zimdahl[902] and Hughes et al.[331] extensively reviewed the findings on Pb absorption by roots and concluded that the mode of its uptake is passive and that the rate of uptake is reduced by liming and by low temperature. Pb, although not readily soluble in soil, is absorbed mainly by root hairs and is stored to a considerable degree in cell walls.

Warren[849] and Kovalevskiy[417] described Pb as a very useful element for geochemical prospecting. The Pb content of plants grown in mineralized areas is, in general, highly correlated with the Pb concentration in soil, although this relationship differs among organs of the plant (Figure 70).

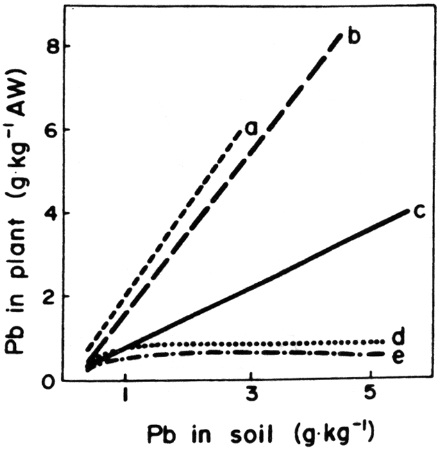

Figure 70 Concentration of Pb in various organs of larch (*Larix dahurica*) as a function of its content in soil overlying an ore deposit. (a) Roots; (b) bark; (c) needles; (d) twigs; (e) wood.[417]

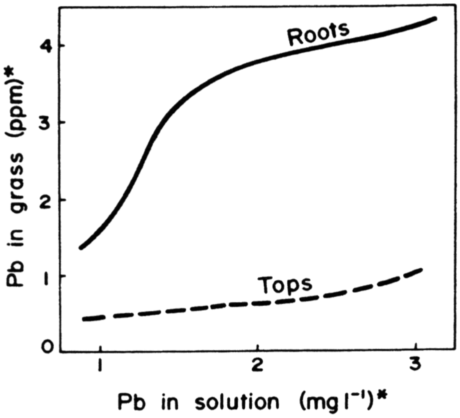

Figure 71 Pb content of a grass (*Bromus uniotoides*) as a function of its concentration in nutrient solution *Values given in powers of ten.[1045]

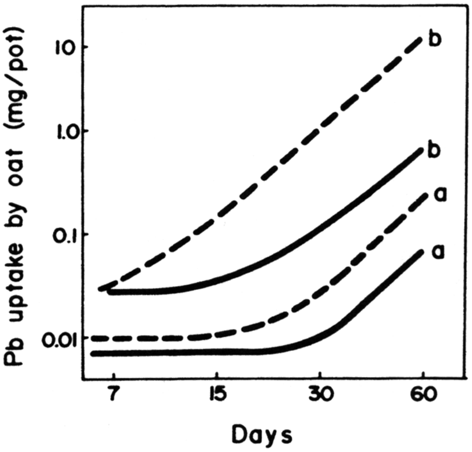

Figure 72 Pb uptake by oats from sand culture as a function of time and of Pb concentration in nutrient solution. (a) 25 mg L^{-1} (b) 200; mg L^{-1}. Solid lines, tops; broken lines, roots.[735]

When Pb is present in soluble forms in nutrient solutions, plant roots are able to take up great amounts of this metal, the rate increasing with increasing concentration in the solutions and with time (Figures 71 and 72). The translocation of Pb from roots to tops is greatly limited, and as Zimdahl[902] described, only 3% of the Pb in the root is translocated to the shoot. The significant accumulation of Pb in roots and low rate of its transport to the other parts of plants are illustrated in Figure 73.

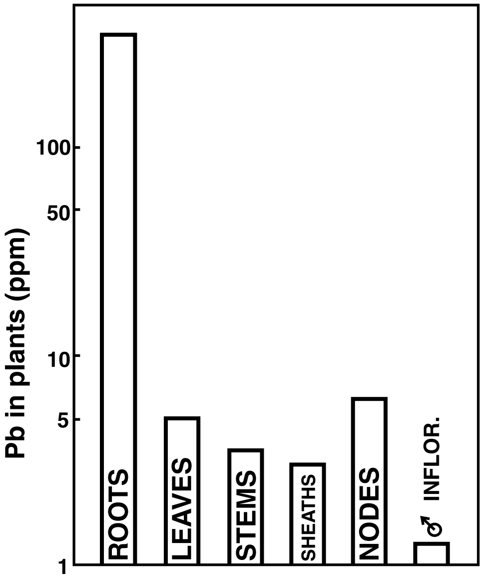

Figure 73 Distribution of Pb in corn plants grown in the soil with 300 ppm Pb.[1045]

The degree to which soil Pb is available to plants is of great environmental concern. Cannon[118] and Zimdahl and Koeppe[904] reviewed this topic and showed that despite several statements in the literature on the slight effect of soil Pb on concentrations of Pb in plant tissues, plants are able to take up Pb from soils to a limited extent. Apparently, most of the Pb in soil is unavailable to plant roots. Wilson and Cline[882] studied the absorption of ^{210}Pb by barley grown using a modified Neubauer technique and showed that only 0.003 to 0.005% of the total Pb in soils may be taken up by plants. This uptake, however, varies significantly over the concentration ranges currently present in soils and with the various forms of Pb that occur in soils.

Zimdahl and Koeppe[904] cited an alternate hypothesis to explain the Pb uptake from soil, in which Pb in not taken up directly from soil by plant roots, but rather is sorbed from dead plant materials accumulated near the soil surface. Nevertheless, there is much evidence that Pb is taken up from soils by roots, at both low and high Pb concentration, and that this process is strongly governed by soil and plant factors.

Airborne Pb, a major source of Pb pollution, is also readily taken up by plants through foliage. Much controversy exists in the literature on the question of how much airborne Pb is fixed to hairy or waxy cuticles of leaves and how much Pb is actually taken into foliar cells. A number of studies have shown that Pb deposited on the leaf surface is absorbed by these cells. Although it has been suggested that most of the Pb pollution can be removed from the leaf surfaces by washing with detergents, there is likely to be a significant translocation of Pb into plant tissues.[340] It has been calculated that up to 95% of the total Pb content of plants may be from aerial deposition on leafy plants.[1270]

The phytoavailability of organolead compounds (mainly alkylated Pb) and their toxic effects on plants have recently received much attention. Röderer[1132] discussed numerous questions concerning effects of continuous exposure to low levels of organic Pb on plants. Diehl et al.[979] found that Pb-tetraalkyls in soils are quickly converted to water-soluble Pb compounds which are easily available to plants. Consequently, the vegetation grown in soils polluted with Pb-tetraalkyls show a relatively large Pb enrichment in both vegetative and generative organs. Zimdahl and Koeppe[904] summarized recent results of translocation and uptake studies and showed that under certain conditions Pb is mobile within the plant. It is generally agreed, however, that Pb from a soil source is not readily translocated to edible portions of plants. These authors stated that the main process responsible for Pb accumulation in root tissue is the deposition of Pb, especially as Pb pyrophosphate, along the cell walls. Malone et al.[506] identified the deposits in cell walls outside the plasma lemma as Pb precipitates and Pb crystals. Similar Pb deposits observed in roots, stems, and leaves suggest that Pb is transported and deposited in a similar manner in all tissues of the plant.

2. Biochemical Roles

Although there is no evidence that Pb is essential for the growth of any plant species, there are many reports on the stimulating effects on plant growth of some Pb salts (mainly $Pb(NO_3)_2$ at low concentrations. Moreover, other reports have described inhibitory effects of low Pb levels on plant metabolism. Due to interactions of Pb with other elements and with many environmental factors, it has not been simple to establish Pb concentrations that are toxic to vital plant processes (Table 36). Several reports describe the toxic effects of Pb on processes such as photosynthesis, mitosis, and water absorption; however, the toxic symptoms in plants are not very specific (Table 40).

Subcellular effects of Pb on plant tissues are related to the inhibition of respiration and photosynthesis due to the disturbance of electron transfer reaction. These reactions have been found to be inhibited by Pb concentrations as low as 1 ppm in corn mitochondria.[902] Photosynthesis processes in sunflower leaves were also reduced by half at Pb concentration of about 1 $\mu M\ g^{-1}$.[1661] Pb is likely to be accumulated in various parts of cells, thus affecting their structures. The most deteriorating is the destruction of the plasma lemma, which in effect disturbs the permeability for water and leads to impaired plant growth.[1551]

Several plant species, ecotypes, and bacterial strains are able to develop Pb-tolerance mechanisms. This tolerance seems to be associated with the properties of membranes. Lane et al.[460] stated that Pb becomes strongly bound to cell walls and that pectic acid is most active in Pb sorption; thus, Pb has a marked influence on the elasticity and plasticity of cell wall, resulting in an increase in tissue wall rigidity.

Sensitive plant species or bacterial strains attract more Pb to their cell walls than do Pb-tolerant plants. A large deposition of Pb on membranes apparently impairs their functions. On the other hand, Pb-tolerant ecotypes may accumulate Pb in inactive forms such as Pb pyro-orthophosphates which have been identified in roots of plants growing under Pb stress.[902] The behavioral differences between Pb-sensitive and Pb-tolerant bacteria strains are manifested mainly by their growth rates, as is demonstrated with bacterial cultures (Figure 74).

Although even a very low Pb concentration may inhibit some vital plant processes, Pb poisoning has seldom been observed in plants growing under field conditions. Zimdahl[902] discussed that

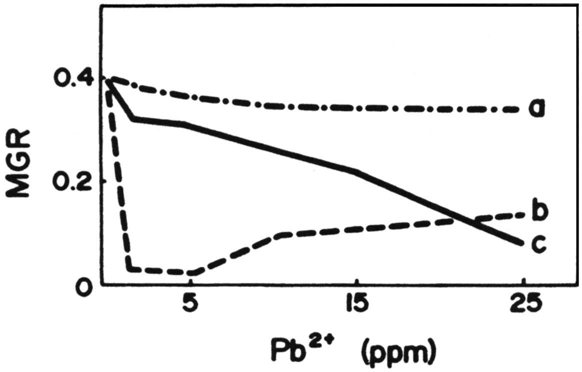

Figure 74 The influence of $PbCl_2$ in culture solution on the maximal specific growth rate (MGR) of (a) Pb-tolerant bacteria strain; (b, c) Pb-sensitive bacteria strains.[184]

problem and suggested two possible explanations: (1) the relatively low Pb concentration in soil and (2) a low Pb availability even under contaminated soil conditions.

Findings have indicated a high toxicity of organolead compounds to a variety of plants. Toxic effects are related mainly to disturbance of fundamental biological processes such as photosynthesis, growth, mitosis, etc. As Röderer[1132] reported, the toxicity of organic Pb not only exceeds by far the toxicity of the inorganic forms, but the effects caused by both types of agents also differ in quality. This difference of action is presumably due to differing physical and chemical properties of the organic and inorganic Pb compounds.

3. Interactions with Other Elements

The interference of Pb with trace elements has been reported only for Zn and Cd (Figure 30). The stimulating effect of Pb on Cd uptake by plant roots may be a secondary effect of the disturbance of the transmembrane transport of ions. The Zn-Pb antagonism adversely affects the translocation of each element from roots to tops.

The interference of Pb with Ca is of metabolic importance since Pb can mimic the physiological behavior of Ca and thus can inhibit some enzymes. The beneficial effect of liming on reducing Pb absorption by roots is governed by soil type. In soils where Pb-organic complexes are formed, Ca^{2+} cations do not significantly limit the availability of Pb.

A favorable P regime is known to reduce the effects of Pb toxicity. This interference is due to the ability of Pb to form insoluble phosphates in plant tissues, as well as in soils. S is known to inhibit the transport of Pb from roots to shoots. Jones et al.[370] concluded that S-deficiency increases markedly the Pb movement into the tops.

4. Concentrations in Plants

Pb is a major chemical pollutant of the environment; therefore, its concentration in vegetation in several countries has increased in recent decades owing to man's activities. This fact has been clearly demonstrated by Rühling and Tyler,[668] who have reported a severalfold increase of Pb concentration in the moss *Hypnum cupressiforme* during the last century (1860 to 1970). For this reason, it is important, as Cannon[118] stated, that information on the Pb content of plants be documented as to both date of collection and location of the samples. There is an urgent need to collect and preserve samples and data from unpolluted areas throughout the world.

The great variation of Pb contents of plants is influenced by several environmental factors, such as the presence of geochemical anomalies, pollution, seasonal variation, and genotype ability to accumulate Pb. Nevertheless, natural Pb in plants grown in uncontaminated and unmineralized areas appears to be quite constant, ranging from 0.1 to 10 ppm (DW) and averaging 2 ppm (DW).[13,118]

Sillanpää and Jansson[1491] summarized results of the worldwide experiment carried out in 30 countries with young wheat ($N = 1723$) and young corn plants ($N = 1892$) and showed that plant-Pb is a function of soil-Pb extracted with AAAc-EDTA solution. Among six soil factors, only soil pH reveals a slight effect on Pb availability. The frequency distribution of Pb contents of both plants indicated the most common (ca. 15%) concentrations ranging from 0.2 to <1 ppm. The highest, >1 ppm, content of Pb was observed in plants from Belgium, Hungary, Italy, Malta, and Mexico. European studies carried out under FAO programs have also indicated a regional variation in Pb contents of young wheat plants (Figure 25). The atmospheric deposition of Pb is apparently a significant source of this metal in above-earth plant parts, as indicated by Dalenberg and van Driel,[1270] by means of ^{210}Pb.

Increased levels of Pb in both grain and straw of barley grown in soil heavily polluted with Pb, despite a high soil pH (7.2–7.8) and increased content of carbonates, were noted. This indicated that these soil parameters do not always inhibit the Pb uptake by plants (Figure 75). Apparently, this phenomenon is related to disturbed function of biological barriers affected by chemical stress to plants.

Table 112 Mean Lead Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis (547, 1187)	DW Basis (131, 188, 705, 852)	AW Basis (705, 852)
Sweet corn	Grains	0.022	0.88, 3, <0.3	34, 94
Bean	Pods	0.08	2, <1.5	37
Beet (red)	Roots	—	2, 0.7	28
Carrot	Roots	0.009, 0.012	3, <1.5, 0.5	38
Lettuce	Leaves	0.001	0.7, 2, 3.3, 3.6	5, 13
Cabbage	Leaves	0.016	1.7, 2.3	17
Potato	Tubers	—	3, 0.5	90
Onion	Bulbs	0.005	2, 1.3, 1.1	35
Cucumber	Fruits, unpeeled	0.024	—	—
Tomato	Fruits	0.002	3, 1, 1.2	44
Apple	Fruits	0.001	0.05, 0.2	2.7
Orange	Fruits	0.002	—	—

Note: References are given in parentheses.

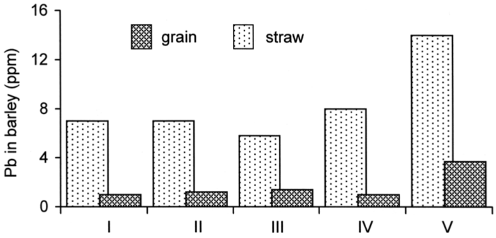

Figure 75 Impact of Pb added, as Zn and Pb smelter flue-dust, to the soil on the concentration of Pb in spring barley grain and straw. Pb levels in soils (ppm) I, 20 (blank); II, 120; III, 320; IV, 1620; V, 6020.[1357]

The Pb contents of edible portions of plants grown in uncontaminated areas, as reported by various authors for the decade 1970 to 1980, range from 0.001 to 0.08 ppm (FW), from 0.05 to 3.0 ppm (DW), and from 2.7 to 94 ppm (AW) (Table 112). Although mean Pb contents calculated for cereal grains of various countries seem to vary considerably (from 0.01 to 2.28 ppm DW), the grand mean, when calculated with the exclusion of two extreme values, is 0.47 and is quite close to the commonly reported concentrations. (Table 113).

There is still great attention oriented toward the Pb levels in plant foodstuffs, especially bread and potatoes as a significant source of this metal in human diets,[1247] though recent data reveal a trend toward a global decrease in Pb emission, mainly because of Pb-free petrol, but probably also due to more precise analytical methods.

The provisional proposed levels for Pb in foods given by the Codex Committee of Food Additives and Contamination[1250] are: for cereals, 0.2 ppm, and for potatoes, 0.1 ppm (FW), while the average concentrations are given as 0.05 and 0.01 ppm (FW), respectively. The average contents of wheat grain and potatoes in Germany (period 1989 to 1993) were 0.02 and 0.06, respectively.[1247] In Poland, average contents of Pb in these food plants sampled during the period 1992 to 1996 were 0.23 and 0.33 ppm (DW).[1514] Crop plants sampled in Poland during the period 1995 to 1998 contained an average amount of 0.06 and 0.07 ppm (FW) in both cereals and in peeled potato tubers.[1416] Similar concentrations of Pb, 0.07 ppm (FW), were reported in wheat flour in Poland.[1402] The Pb mean level in potato tubers (peeled) in the U.S. is 0.009 ppm, and in wheat grain is 0.037 ppm (FW).[1549]

A higher concentration of Pb is commonly observed in cereal grains as compared with potato tubers, which resulted from an easy uptake of Pb from aerial sources.[1357]

The background levels of Pb in forage plants average 2.1 ppm (DW) for grasses and 2.5 ppm (DW) for clovers, when two extreme values (0.36 ppm Pb in grass in Finland, and 8.0 ppm Pb in clover in Sweden) are excluded from the calculation (Table 114). The commonly observed increase in Pb amounts in forage plants during the fall and winter seasons is not yet completely understood.

Table 113 Lead Content of Cereal Grains from Different Countries (ppm)

Country	Cereal	Range	Mean	Ref.
Austria	Rye	—	0.64	323
	Wheat	—	0.59	323
Great Britain	Barley	<1.25–1.50	—	783
Canada	Barley	0.1–0.2	—	195
Egypt	Wheat	0.10–0.92	0.51	213
Finland	Barley	0.29–0.56	0.40[a]	829
	Oats	0.33–1.08	—	829
	Wheat	0.13–0.28	0.18[a]	829
Japan	Brown rice	—	0.19	395
	Buckwheat (flour)	—	0.36[b]	395
Poland	Wheat	0.2–0.8	0.32	267
	Oats	0.05–2.0	0.34	1045
	Rye	0.06–1.3	0.34	1045
	Mixed cereals	0.01–36	0.23	1514
Sweden	Wheat	0.4–0.7	0.57	21
U.S.	Wheat	0.42–1.0	0.64	906
	Rice	<0.002–0.07	0.007[b]	1187
Russia	Oats	—	0.01[c]	735
	Wheat	0.4–0.6	0.5	338

[a] After $PbNo_3$ addition to soil.
[b] FW basis.
[c] After addition of 25 to 100 mg Pb per liter in sand culture.

Table 114 Mean Levels and Ranges of Lead in Grasses and Legumes at Immature Growth from Different Countries (ppm DW)

	Grasses		Clovers		
Country	Range	Mean	Range	Mean	Ref.
Canada	<1.2–3.6	1.8	—	—	237
Great Britain	1–9	2.1	1–3	1.3	369a, 874
Germany	2.4–7.8	3.3	3.3–4.7	4.2	576, 577
Finland	0.19–0.88	0.36	—	—	590
Poland	0.01–35	0.89	1.2–18.8	3.6	1045, 1514
Sweden	5–6	—	—	8.0	668
U.S	<0.8–5.6	1.6	<2–15	2.0a	118, 710
Former S.U.	0.3–10.8	4.6	—	—	1131

[a] Alfalfa, calculated from AW basis.

Of great environmental significance is the ability of plants of absorb Pb from two sources, soil and air, even although Pb is believed to be the metal of least bioavailability and the most highly accumulated metal in root tissues. Several plant species and genotypes are adapted to grow in high Pb concentrations in the growth media; this is reflected by anomalous amounts of this metal in the plants (Table 115). The highest bioaccumulation of Pb generally is reported for leafy vegetables (mainly lettuce) grown in surroundings of nonferrous metal smelters where plants are exposed to Pb sources of both soil and air. In these locations, highly contaminated lettuce may contain as much as 0.15% Pb (DW).[658]

A relatively minor effect on the Pb concentrations in plants has been reported for contamination of soil due to agricultural activities. However, the utilization of Pb-enriched sludges has not been practiced for a long period of time; therefore, it is too early to assess the general environmental impact of built-up Pb levels in soils due to repeated sludge application. Elevated Pb contents of vegetables grown in urban and industrial areas present a health risk to humans.

Table 115 Excessive Levels of Lead in Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean or Range in Content	Country	Ref.
Mining, or mineralized area	Grass, tops	63–232	Great Britain	165, 658, 659
	Maple, stems	135[a]	U.S.	330
	Birch, twigs	277–570	Russia	417
Metal-processing industry	Blueberry, tops	150	Canada	715
	Blueberry, tops	32–294	Poland	1050
	Lettuce, leaves	596–1506[b]	Canada	658, 659
	Potato, tubers	350–425[a]	Canada	848
	Grass, shoots	229–2714	Canada	410
	Chinese cabbage	45	Japan	403
	Lettuce, leaves	45–69	Poland	224
	Carrot, roots	27–57	Poland	224
	Sugar beet, leaves	33–165	Poland	1161
	Blueberry, leaves	141–874	U.S.	357
	Spinach, leaves	322	Zambia	573
	Mushrooms	$<$0.5–300	Finland	1069
Battery manufacturer	Tree foliage	34–459	Canada	480
	Grass, shoots	907–955	Chile	1139
Urban garden and urban vicinity	Spinach, leaves	66	Zambia	573
	Potato, tubers	100–200[a]	Canada	848
Roadside	Corn, leaves	56	Poland	157
	Corn, leaves	16–24[b]	U.S.	594
	Grass, shoots	111–186	Germany	397
	Grass, young shoots	67–950	Sweden	669

[a] AW basis.

[b] Washed and unwashed, respectively.

VI. TITANIUM

A. Soils

Ti is a common constituent of rocks and commonly ranges in concentration from 0.03 to 1.4% (Table 108). In minerals, Ti occurs predominantly in the tetravalent oxidation state, mainly as a major component of oxides, titanates, or silicates. The dioxide of Ti occurs in nature in different modifications—rutile, anatase, and brookite, TiO_2 of various crystallographic coordinations. Relatively common are silicate minerals of composition similar to titanite $CaTiO(SiO_4)$, and also other minerals like ilmenite, $FeTiO_2$, and perovskite, $CaTiO_3$.

Minerals of Ti are very resistant to weathering; therefore, they occur practically undecomposed in soils. When Ti-bearing silicates are dissolved, the element is soon transformed into Ti oxide-aquate, which is transformed to anatase or rutile. Bain[41a] reported that Ti in podzol developed on glacial drift is almost entirely in the form of cryptocrystalline anatase. Hutton,[334] however, stated that Ti can enter into the structure of some layered silicates. Hiller et al.[1025] described Fe-Mn concretions of surface marsh soils containing up to 39% of Ti. Apparently, under reducing conditions, Fe^{2+} ions are adsorbed on surfaces of Ti minerals and, followed by the oxidation to Fe^{3+}, may lead to the formation of pseudorutile.

Although Ti minerals are known to be the most stable minerals in the soil environment, no mineral is completely insoluble, and the Ti level reported in soil solutions is 0.03 mg L^{-1}.[334] The solubility of Ti in soils is, however, very limited and this effects an increase in the absolute amounts

Table 116 Titanium Content of Surface Soils of Different Countries (%DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Ireland	0.10–0.17	—	236
	Madagascar	—	0.60	557a
	New Zealand[a]	0.37–1.70	—	861
	Poland	0.02–0.24	0.17	382
	U.S.	0.02–1.00	0.28	706
	Russia	0.09–0.11	0.10	493
Loess and silty soils	New Zealand[a]	0.57–1.00	—	861
	Poland	0.11–0.67	0.32	382
	U.S.	0.05–1.00	0.41	706
	Russia	—	0.20	493
Loamy and clay soils	Madagascar	—	0.50	557a
	New Zealand[a]	0.54–2.40	—	861
	Poland	0.09–0.51	0.35	382
	U.S.	0.10–1.00	0.36	706
	Russia	—	0.14	493
Fluvisols	India	—	0.21	455
	Madagascar	—	0.60	557a
	Russia	—	0.11	493
Rendzinas	Australia	—	0.49	334
	India[b]	0.17–0.22	—	455
	Ireland	0.2–0.3	—	236
	Madagascar	—	0.94	557a
	Poland	0.04–0.8	0.47	382
	U.S.	0.07–1.00	0.26	706
Ferralsols	Madagascar	0.05–2.10	—	557a
	India	0.30–0.32	—	455
Solonchaks	Madagascar	0.50–1.00	—	557a
Chernozems	Russia	0.40–0.48	0.45	4
	U.S.	0.07–0.70	0.26	706
Histosols	India	0.60–0.67	0.64	455
	Poland	0.008–0.39	0.15	382
	U.S.	0.03–0.50	0.14	706
	Russia	—	0.011	493
Forest soils	Russia	—	0.57	4
	U.S.	0.15–0.50	0.36	706
Various soils	Great Britain	0.05–0.60	0.56	34, 818
	Madagascar	0.065–1.00	—	557a
	New Caledonia	0.20–0.50	—	39
	U.S.	0.05–1.00	0.30	706

[a] Soils derived from basalts and andesites.

[b] Desert calcareous soils.

of Ti in the top horizon of soils after the loss of some clay-size layered silicates due to weathering. The total Ti (also Zr) contents of soil have been used in several studies of soil genesis and of the continuity of soil profiles.

The Ti content of surface soils generally ranges from 0.1 to 0.9% (mean, 0.35%) except for organic soils in the former Soviet Union (Table 116). Greater Ti contents are normally associated with highly weathered soils, tropical soils, and those derived from Ti-rich parent rocks. Light organic soils contain the smallest amounts of Ti. The Ti mean content calculated for worldwide soils is 0.33% and, although it is lower for podzols and histosols, does not differ much with the soil units (Table 9). Soil exposed to effluents or emissions from certain industries (Ti alloys, Ti paint production) may become contaminated by Ti; however, this element does not create any environmental problems.

Table 117 Mean Titanium Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis (574)	DW Basis (197, 267, 705)	AW Basis (145, 705)
Wheat	Grain	—	0.9	—
Corn	Grain	—	2.0	<5–20
Asparagus	Stem	—	—	180
Snap bean	Pods	—	3.2	45
Bean	Pods	<0.2	—	—
Lettuce	Leaves	<0.3	—	—
Cabbage	Leaves	<0.7	—	—
Carrot	Roots	<0.5	—	<5
Potato	Tubers	—	—	18
Onion	Bulbs	—	1.6	37
Cucumber	Fruit	<0.5	—	19
Apple	Fruit	<0.004	0.18	10
Orange	Fruit	<0.1	0.15	4
Food plants	Edible parts	—	0.2–80	—

Note: References are given in parentheses.

B. Plants

No clear evidence of a biochemical role of Ti has appeared, although Chapman[131] and Shkolnik[718] described its possible catalytic function in N fixation by symbiotic microorganisms and in photooxidation of N compounds by higher plants, as well as in some processes of photosynthesis. Pais et al.[597] observed an increase of chlorophyll in tomato plants grown in culture solution after spraying with a Ti-chelate solution. Pais and Jones[1448] also reviewed the biological importance of Ti and reported that Ti-chelates (mainly ascorbates) have a beneficial impact on carbohydrate biosynthesis and possibly on photosynthesis and other metabolic processes resulting in the increased production of biomass. As Simon et al.[1495] reported, Ti addition, as titanium ascorbate, to the water culture stimulates the activity of fructose-1, 6-bisphosphatase and nitrate reductase enzymes, and inhibits the action of phosphorofructokinase in tomato and soybean plants. Ti addition is also reported to stimulate the growth of rhizobium bacteria strains.[1494] Although little attention has been given to Ti absorption by plants, this element is considered to be relatively unavailable to plants and not readily mobile in them. Ti is still far from being accepted as an essential element to plants,[1184] but there are some reports of its beneficial effects on yield of several crops.[1113a]

Levels of Ti in plants vary rather considerably within the range of 0.15 to 80 ppm (DW) (Table 117). Some weeds, especially horsetail and nettle, are known to accumulate much more Ti, and diatoms are reported to contain Ti concentrations ranging from 15 to 1500 ppm (DW).[855] Only one report, Wallace et al.,[841] described Ti toxicity symptoms, and this report cites the chlorotic and necrotic spots that were observed on leaves of bush bean that contained Ti at a concentration of about 200 ppm (DW).

VII. ZIRCONIUM

A. Soils

The crustal abundance of Zr generally varies from 20 to 500 ppm, being lowest in ultramafic rocks and calcareous sediments (Table 108). The predominant stable valency of Zr is +4, and the prevailing reaction is bonding with oxygen. Zr reveals oxyphilic and lithophilic tendencies; its widely distributed minerals (e.g., zircon, $ZrSiO_4$, baddeleyite, ZrO_2) are highly resistant to weathering; therefore, Zr is considered to be only slightly mobile in soils. However, organic acids seem to be the transporting agents for the migration of Zr in soils. Smith and Carson[741] reported that small dissolutions of Zr have been noted in both acidic podzolic soils and in alkaline laterites.

Like, Ti, Zr has been used as an index element in soil studies. Hutton[334] extensively reviewed this topic and concluded that reliable results for soil genesis are obtained when Ti to Zr ratios are considered.

The Zr content of soils generally is inherited from parent rocks; therefore, no significant variation in the Zr content is observed among the soil types. However, lower amounts of Zr are in soils on glacial drift (70 to 200; mean, 140 ppm) and higher amounts are in residual soils derived from Zr-rich rocks (70 to 200; mean, 305 ppm). The average Zr content calculated for various soils of the U.S. is 224 ppm, while Hutton[334] gave the average of about 350 ppm Zr for Australian soils. Wells[861] found Zr in soils derived from basalts and andesites to range from 330 to 850 ppm, whereas Lukashev and Pietukhova[493] gave the range in Zr for sandy soils as 90 to 160 ppm and for peat soil as little as 32 ppm. Waganov and Nizharadze[1181] reported the mean Zr content of deep loess deposit in European Russia to be 470 ppm, and Protasova and Kopayeva[1123] found Zr in Russian chernozems to range from 200 to 550 ppm. Govindaraju[1313] reported that Zr contents in reference soils from China range from 219 to 500 ppm (mean, 281 ppm), and in soils from the U.S. from 184 to 760 ppm (mean, 279 ppm). Chattopadhyay and Jervis[132] reported the range of Zr in garden soils to be 200 to 278 ppm. Smith and Carson[741] reviewed the current and potential uses of Zr in industry and concluded that the only potentially harmful effect on the soil environment would be from production-waste streams containing soluble Zr salts.

B. Plants

Although most soils contain significant amounts of Zr, its availability to plants, presumably in anionic form, $Zr(OH)_n^{4-n}$, is greatly limited. The Zr content seems to be higher in roots, especially in nodules and roots of legumes, than in tops, which apparently indicates a low mobility of this metal in plants.[283]

Smith and Carson[741] reviewed the history of studies of stable Zr and ^{95}Zr in plants and showed that concentration factors for Zr derived from soil are low in plants, while those derived from rainwater are much higher for both soil-rooted plants and epiphytes. This explains the relatively high content of Zr in Norwegian moss (*Hylocomium splendens*), ranging from 0.06 to 12 ppm (mean, 0.35 ppm).[1223] Aquatic plants are also likely to rapidly take up soluble species of Zr.

There are not many data available on the Zr status of plants. The Zr levels in food plants vary from 0.005 to 2.6 ppm (DW) and do not show any trend in their distribution within plant tissues (Table 118). Some herbage, especially legumes, as well as shrubs and mosses are likely to concentrate

Table 118 Zirconium Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis (574, 741)	DW Basis (197, 705, 741)	AW Basis (705, 741)
Cereal	Grains	0.08–10	0.02–1	8–1033
Corn	Grains	—	—	<20
Bean	Pods	<0.13	2.6	—
Lettuce	Leaves	0.41–0.62	0.56	4
Cabbage	Leaves	<0.4	—	<20
Carrot	Roots	<0.32	—	<20
Potato	Tubers	—	0.5	12
Onion	Bulbs	0.45–0.84	—	<20
Tomato	Fruits	0–1.79	—	<20
Apple	Fruits	0.31	—	<20
Orange	Fruits	0.05	—	<20
Grape	Raisins	—	1.5	—
Peanuts	Seed	—	2.3	—
Food plants	Edible parts	—	0.005–0.2	—

Note: References are given in parentheses.

more Zr than are other plants, and thus the highest Zr level reported for leaves and stems of deciduous trees is as much as 500 ppm (AW). However, as Shacklette et al.[710] reported, Zr was detected only in about 30% of the plant species analyzed. Bowen[94] gave the range in Zr concentrations in lichens and bryophytes as 10 to 20 ppm (DW). It should be noted that due to the low reliability of analytical results, the data presented may not be adequate for a realistic estimate of the typical Zr concentration in plants.

Although there is not much agreement among the reported values for Zr in plants, there is, apparently, no bioaccumulation of this metal in food plants. However, the ready uptake of atmospheric ^{95}Zr by terrestrial plants due to deposition of fallout particulates is reported to contribute a great proportion of this radionuclide in the Japanese diet (Yamagata and Iwashima, cited in Smith and Carson[741]).

Although toxic effects of Zr on plants, especially on root growth, are commonly reported, its stimulating effect on the growth of yeasts and on metabolism of other microorganisms has also been observed.[741] Davis et al.[171] reported Zr to be the least toxic element, among the heavy metals, to barley seedlings. Pais and Jones[1448] described that Zr treatment enhances protein synthesis and changes the amino acid composition of the proteins of some microfungi, but also reduces the phytoavailability of phosphates to phytoplanktons.

VIII. HAFNIUM

Crystalochemical properties of Hf are similar to those of Zr; however, its terrestrial abundance is much lower. The common concentration of Hf in rocks ranges from 0.1 to 10 ppm (Table 108).

The Hf content of soils is reported to range from 1.8 to 18.7 ppm in Bulgarian soils,[558] from 1.8 to 10 ppm in Canadian soils,[409] and to average 5 pm in standard soils of Great Britain.[818] The Hf content of deep loess in European Russia averages 20.8 ppm.[1181] Market and Lieth[1086] found Hf in peat bogs in Germany and Sweden to range within the orders of magnitude from 0.0X to 0.X ppm. Reference soils from China contain Hf from 7 to 14 ppm (mean, 7.9 ppm), and in soils of the U.S., from 2.5 to 17 ppm (mean, 7.3 ppm).[1313]

As reported by Furr et al.,[250] Hf is taken up by plants grown on soil amended with sewage sludges which contain, on the average, about 3 ppm Hf. The common range of Hf in plants was given as 0.01 to 0.4 ppm (DW).[381] Lieth and Markert[1063] reported Hf content of blueberry tops to be below 1 ppm (DW), and Oakes et al.[574] reported Hf in food plants to range from 0.6 to 1.1 ppb (FW), but it was not always detectable.

CHAPTER 10

Elements of Group V

I. INTRODUCTION

Geochemical characteristics of the trace elements of Group V are widely diverging. The variation in the electrical charge and in the valence states are especially common features of these elements. The metalloids As and Sb and the metal Bi of Group Va (new group 15) are highly chalcophilic. While As follows P in biogeochemical behavior, Sb rather resembles Bi.

Of the Group Vb (new group 5) elements, V is the least basic and may form both cationic and anionic compounds. Two other elements, Nb and Ta, are rare metals and resemble each other in biogeochemical properties. All metals of this group reveal an affinity for oxygen bonds.

II. ARSENIC

A. Soils

Arsenic is distributed rather uniformly in major types of rocks and its common concentrations in most rocks range from 0.5 to 2.5 ppm (Table 119). Only in argillaceous sediments is As, on the average, concentrated as high as 13 ppm. As is a ubiquitous element in the upper lithosphere.

As has a great affinity to form or to occur in many minerals, and of over 200 As-containing minerals, approximately 60% are arsenates. Arsenite compounds are not common in hypergenic environments. This element is highly associated with deposits of many metals and therefore is known as a good indicator in geochemical prospecting surveys. It is also frequently found combined with S, Se, and Te. Numerous oxide minerals of As are a result of the oxidation of sulfide deposits. These are arsenates and arsenites in which As is combined with some metal (e.g., Fe, Pb, and Cu). The most common As mineral, however, is a sulfide—arsenopyrite (FeAsS).

Although As minerals and compounds are readily soluble, As migration is greatly limited due to the strong sorption by clays, hydroxides, and organic matter. The As enrichment in argillaceous sediments as well as in surface soils, as compared to concentrations in igneous rocks, apparently reflects also some external As sources, such as volcanic exhalations and pollution. Soil As is present mainly in the heavy mineral fraction of soil (up to X00 ppm), but the contribution to total As is very small, commonly about 1%. A much higher proportion of total As (27 to 90%) in soil is associated with the clay granulometric fraction <0.001 mm.[1427]

The oxidation states of As are −3, 0, +3, and +5, of which As^0 and As^{3+} are characteristic of reducing environments. The complex anions AsO_2^-, AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_3^-$ are the most common mobile forms of As, being sorbed at the pH range from 7 to 9. The behavior of arsenate (AsO_4^{3-}) resembles that of phosphates and vanadates. Crecelius et al.[971] studied the

Table 119 Arsenic, Antimony, Bismuth, Vanadium, Niobium, and Tantalum in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock Type	As	Sb	Bi	V	Nb	Ta
Magmatic Rocks						
Ultramafic rocks Dunites, peridotites, pyroxenites	0.5–1.0	0.1	0.001–0.02	40–100	1–15	0.02–1.0
Mafic rocks Basalts, gabbros	0.6–2.0	0.2–1.0	0.01–0.15	200–250	10–20	0.5–1.0
Intermediate rocks Diorites, syenites	1.0–2.5	0.X	0.01–0.10	30–100	20–35	0.7–2.1
Acid rocks Granites, gneisses	1.0–2.6	0.2	0.01–0.12	40–90	15–25	2.0–4.0
Acid rocks (volcanic) Rhyolites, trachytes, dacites	1.5–2.5	0.2	0.01–0.12	70	20–60	3
Sedimentary Rocks						
Argillaceous sediments	13	1.2–2.0	0.05–0.40	80–130	15–20	0.8–1.5
Shales	5–13	0.8–1.5	0.05–0.50	100–130	15–20	1–2
Sandstones	1.0–1.2	0.05	0.10–0.20	10–60	0.05	0.05
Limestones, dolomites	1.0–2.4	0.3	0.10–0.20	10–45	0.05	0.05

behavior of As and found that under most environmental conditions As^{5+} is present as the $H_2AsO_4^-$ species, while As^{3+} as the $H_3AsO_3^0$ species is only dominant in low pH and low Eh environments.

The reactions of As in soils are highly governed by its oxidized state. Under the ranges of Eh and pH in soils, the As +5 and +3 oxidation states predominate. However, arsenate ions are known to be readily fixed by such soil components as clays, phosphatic gels, humus, and calcium, and the most active in As retention are hydrated Fe and Al oxides. Hydroxy-Al on the external surfaces of micaceous minerals is reported to be especially significant in the retention of As.[329] The strong association of As with Fe (mainly goethite) in soils for both natural and added As has been reported by Norrish.[570]

El-Bassam et al.[204] reported that strongly adsorbed As in soil is unlikely to be desorbed again and that generally the retention of As by soil progressed with the years. However, As combined with Fe and Al oxides may be liberated upon hydrolysis with the reduction of soil potential. Little is known about the As compounds in soil, but their formation is good evidence that arsenate in soils behaves like phosphate, and in acid soils Fe or Al arsenates are likely to be most common.[570,887] Elkhabit et al.[986] stated that the oxides and Eh are the main soil parameters controlling the arsenite sorption rate and that the pH of the system influences the concentration of the As species being absorbed at the surface of the oxides. Also, Dudas[984] observed that As is associated with both crystalline and amorphous forms of Fe oxides and that vein and spot soil samples enriched in Fe contained as much as 450 ppm As.

Several strains of bacteria accelerate the oxidation of arsenites to arsenates and are also involved in methylation and alkylation of As. Under anaerobic conditions, As compounds can be reduced, mainly under microbiological processes, to volatile but also easily oxidized trivalent methylated arsenicals. Easily mobile As is leached down to ground waters, and creates a great health risk when used as a source of drinking water. A disastrous calamity of people suffering from As intoxication due to arsenic contaminated water is well known in West Bengal, India.[1475] Thus, microbiota may highly govern the processes of As migration, precipitation, and volatilization as cited by Boyle and Jonasson,[98] Jernelöv,[359] and Weinberg.[856] Dudas[984] reported that microbiologically mediated losses of As had depleted topsoils in this element. Methylation of As conducted by certain yeasts under oxic conditions, and by methanogenic bacteria under anoxic conditions, plays significant roles in the release of volatile As from the soil to the atmosphere. Thus, the biological cycles of As govern its fluxes among the environmental compartments. The biotransformation of organic arsenical pesticides recently has received much attention because their inorganic derivatives may be quite toxic.

Table 120 Arsenic Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Canada	1.1–28.9	5.8	243
	Great Britain	5.1–6.8	—	819
	Japan	1.2–6.8	4.0	395
	Korea	2.4–6.8	4.6	395
	Thailand	—	2.4	395
	U.S.	<0.1–30	5.1	707
Loamy and clay soils	Canada	1.3–16.7	4.8	243, 629
	Thailand	7.2–18.4	12.8	395
	U.S.	1.7–27	7.7	707
Fluvisols	Bulgaria	3.4	—	612
	Great Britain	20–30	25	786
Soils on mafic rocks	Great Britain	5.0–8.2	—	819
Chernozems	Bulgaria	8.2–11.2	8.2	612
	U.S.	1.9–23	8.8	707
Histosols	Canada	1.8–66.5	13.6	98, 243
	U.S.	<0.1–48	5	707
Forest soils	Norway	0.6–5.0	2.2	442
	U.S.	<0.1–93	7	707
Various soils	Bulgaria	2–10.4	5.6	612
	Canada	<1–30	5.8	98, 409, 480, 629
	Great Britain	4–95	16.3	786, 818
	Italy	4–197[a]	41	946
	Japan	0.4–70	11	395
	Norway	0.7–8.8	2.5	754
	Taiwan	—	7.9	472
	U.S.	<1–93	7	707
	Former S.U.[b]	5–30	—	656
	Former S.U.[c]	0.07–0.35	0.2	1131

[a] Maximum values include contaminated soils.

[b] Biogeochemical province in Uzbekistan.

[c] Kazakhstan.

The background As levels in topsoils are generally low, although they exceed those in rocks several times. The range in As in soils of the U.S. is broad, from <0.1 to 93 ppm; and similarly in uncontaminated soils of the other countries, the As content ranges from <1 to 95 ppm (Table 120). The grand mean of soil As is calculated to be the lowest 4.4 ppm for podzols and the highest 9.3 ppm for histosols (Table 9). The geometric mean for As in surficial materials of the U.S. is reported to be 5.8 ppm.[707] The range for As in soils of Poland is 0.9–3.4 ppm, with the highest in soils derived from shales.[1357] Over 650 ppm As is in polluted soils of some industrial area as reported also for Poland.[1390] Chernozems of western Siberia have a content of As from 18 to 32 ppm, of which up to 90% is strongly fixed.[1341]

The lowest As levels are found in sandy soils and, in particular, in those derived from granites, whereas higher As concentrations are related most often to alluvial soils and soils rich in organic matter. Acid sulfate soils are also reported to accumulate a high proportion of native As—up to 30 to 50 ppm in lower horizons.[984] Due to common As pollution, the levels of this element are likely to be increased in topsoils; therefore, the As ranges reported as background values are also given for contaminated soils.

The As content of certain contaminated soils has already been built up to as high as 0.2% (Table 121). Significant anthropogenic sources of As are related to industrial activities (metal processing, chemical works based on S and P minerals, coal combustion, and geothermal power plants) and to the use of arsenical sprays, particularly in orchards. Heavily As-polluted garden soils (up to 200 ppm As) are reported to be located in the vicinity of a former As smelter.[1528] Thornton and Farago[1516]

Table 121 Arsenic Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Maximum or Range of Content	Country	Ref.
Mineralized bedrock	727	Great Britain	915
Nonferric metal mining	90–900	Great Britain	144
Metal-processing industry	130[a]	Czech Republic	1083
	33–2000	Canada	480, 777
	2500	Great Britain	959
	38–2470	Japan	336, 767
	69[b]	Hungary	328
	72–340[c]	Norway	447
	150–2000	Poland	1173
	10–380	U.S.	153, 538
Chemical works	10–2000	Hungary	328
Gardens and orchards	892	Great Britain	1190
	38–118	Poland	1173, 1526
Application of arsenical pesticides	10–290	Canada	98, 585
	21–82	Great Britain	959
	38–400	Japan	303
	31–625	U.S.	208, 279, 887
Application of waste lime	570	Poland	1173
Coal combustion	800–1500	Slovak Republic	1221
Leather industry	105–220[d]	Germany	1307

[a] Data calculated from the Figure.[1083]

[b] EDTA soluble.

[c] HNO_3 soluble.

[d] In deeper soil layers.

reviewed soil As distribution in garden soils, and reported As contents up to about 15,000 ppm. However, only a limited fraction of the total amount of As is easily mobile, and over 80% is strongly associated with Fe and Al and is not available for plants.

Chilvers and Peterson[966] calculated that at least 60% of the atmospheric global inputs of As are derived from natural sources, even when a low rate of volatilization of the soil As (0.126% per year) is present. As pollution is reported most frequently for Japanese soils. Kitagishi and Yamane[395] have reviewed several studies on As behavior in contaminated soils and have shown that paddy soils accumulated most often considerable amounts of As and that this fact is due to the high sorption capacity of these soils and also to the As transportation by irrigation water. As compounds from previous use of As pesticides stored in bottom sediments have now become activated by P anions added with fertilizers to rivers. Since As behavior is dependent on the soil oxidation state, this element varies in its vertical distribution. In heavy gley soil, As is accumulated only in the top horizon and is readily leached from the subsurface layer with a high reduction potential. The As pattern in light well-drained soils is almost the opposite (Figure 76). Also in uncontaminated soils, the patterns of As profile distribution may diverge significantly.

The mobility of As in soil was shown to be proportional to the As added and inversely proportional to time and to Fe and Al contents. The toxicity of As depends on the concentration of soluble As; therefore, sodium arsenate and arsenic trioxide, formerly used as herbicides, are the most toxic. However, plant growth response may also be related to total soil As (Figure 77). Phytotoxicity of As is highly dependent on soil properties; and while in heavy soil about 90% growth reduction appears at 1000 ppm As addition, in light soil 100 ppm As is equally toxic.[887] The maximum allowable limit of As in paddy soils is proposed as 15 ppm.[395]

The toxicity of As in soils may be overcome in several ways, depending on As pollution sources and on soil properties. Increasing the oxidation state of flooded (paddy) soils limits As

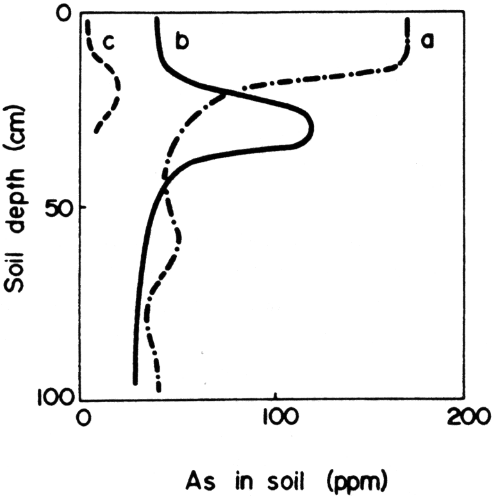

Figure 76 Patterns of vertical distribution of total As in polluted soils from a nonferrous metal mining area in Japan. (a) Heavy gley soil; (b) light gley soil; (c) unpolluted paddy soil.[395]

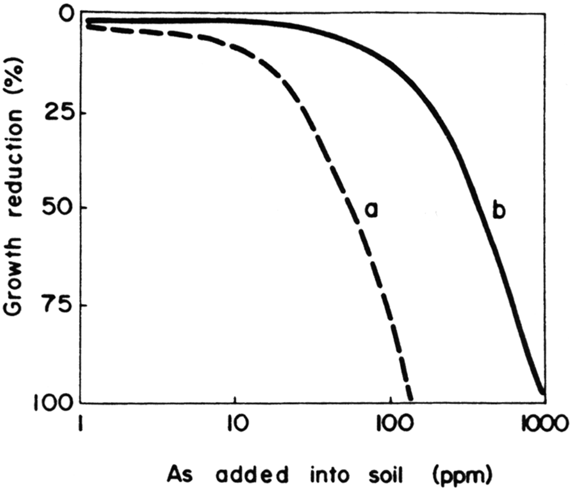

Figure 77 Corn growth response to As added to two soils. (a) Light soil with low organic matter content and with kaolinitic clay predominating; (b) heavy soil with high organic matter content and with vermiculitic clay predominating.[887]

bioavailability.[395] Xie and Huang[1557] reported that without adding any material to As-polluted paddy soils, wetting and drying greatly increased the soil redox potential and therefore lowered solubility, and the phytoavailability of As to rice plants. Application of materials that produce precipitates with As in soil (e.g., ferrous sulfate, calcium carbonate) is reported to be effective when added to soils having less than 10 ppm of soluble As (in 0.05 *N* HCl).[303] Also, fertilizing, mainly the application of phosphate, decreases As bioavailability. However, the literature on phosphate retention of As in soils is confusing, for phosphate could also displace adsorbed or fixed As from sorbing complexes and thereby initially increase the amount of soluble As in soils. As Peryea[1454] found, a popular fertilizer (monoammonium phosphate, MAP) used on soils contaminated with Pb-As pesticide residues can enhance As solubility, and thus increase As phytoavailability. The alleviating effect of S application on As toxicity has also been reported. Kitagishi and Yamane[395] have reviewed this topic and presented several results that require further study.

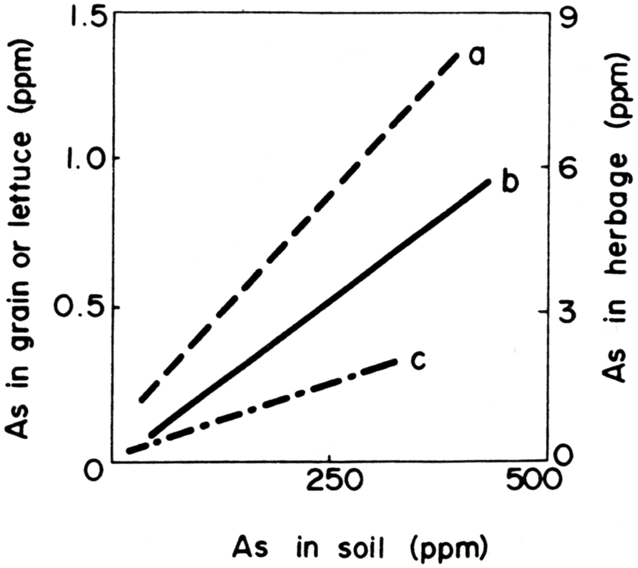

Figure 78 Concentration of As in plants as a function of total soil As. (a) Lettuce; (b) pasture herbage; (c) barley grains.[783]

B. Plants

As is a constituent of most plants, but little is known about its biochemical role. Several reports on the linear relationship between As content of vegetation and concentrations in soil of both total and soluble As suggest that plants take up As passively with the water flow. Some plants, particularly Douglas fir, show a remarkable ability to take up As far more than many of the associated plants. Such plants are useful guides to the recognition of subsurface mineralization with certain metals.[624,851]

Thoresby and Thornton[783] described the ready uptake of As by various plant species (Figure 78). Apparently, As is translocated in plants since its concentration in grain has also been reported. With increasing soil As, however, the highest As concentrations were always recorded in old leaves and in roots, but at a low content of As a higher accumulation in leaves than in roots has also been reported by Tlustos et al.[1519] According to these authors, the uptake of As by radish depends on the As form and follows the order: $As_{org} >> As^{5+} > As^{3+}$.

Concentrations of As in plants grown on uncontaminated soils vary from 0.009 to 1.5 ppm DW, with leafy vegetables being in the upper range, and fruits in the lower range (Table 122). Grasses from a semiarid climatic zone (Kazakhstan, Russia) contain an elevated amount of As, from 1.1 to 5.4 ppm (DW).[1131] Mushrooms are found to be relatively high As accumulators. Siekovec and Irgolic[1490] determined As in 83 species of wild-growing mushrooms. The lowest concentration was in *Ramaria botrytis* (10 ppm) and the highest in *Thelephora terrestris* (38 ppm).

Several plant species are known to tolerate a high level of As in tissues. As toxicity has commonly been noted in plants growing on mine waste, on soils treated with arsenical pesticides, and on soils with As added by sewage sludge treatment. The symptoms of As toxicity are variously described as leaf wilting, violet coloration (increased anthocyanin), root discoloration, and cell plasmolysis. The most common symptom, however, is growth reduction. Kitagishi and Yamane[395] reported that rice grown on apple orchard soil containing 77 ppm As produced almost no yield the first year. The toxic effect of As was partly reduced after 3 years of cultivation without any special treatment, but an application of S greatly limited the phytotoxicity of As.

Wallace et al.[845] have shown that bush bean plants grown in solution culture with 10^{-4} M arsenate accumulated approximately 4, 19, and 42 ppm As, respectively, in leaves, stems, and roots,

Table 122 Arsenic Content of Food and Forage Plants (ppb)[381,395,414,446,462,624,705]

Plant	Tissue Sample	FW Basis	DW Basis
Barley	Grains	—	3–18
Oats	Grains	—	10
Wheat	Grains	—	50, 3–10
Brown rice	Grains	—	110–200
Sweet corn	Grains	25	30–400,30
Snap beans	Pods	0.74–<6.7	7–100
Cabbage	Leaves	1.2–<16.0	20–50
Spinach	Leaves	—	200–1500
Lettuce	Leaves	<5.3	20–250
Carrot	Roots	4.8–<13.0	40–80
Onion	Bulbs	4.5	50–200
Potato	Tubers	—	30–200
Tomato	Fruits	0.46	9–120
Apple	Fruits	<0.21	50–200
Orange	Fruits	1.4–<5.2	11–50
Edible mushroom	Whole	—	280
Clover	Tops	—	20–160
Grass	Tops	—	280–330

Table 123 Excessive Levels of Arsenic in Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean or Range of Content	Country	Ref.
Mining or mineralized area	Douglas fir, stems	140–8200[a]	Canada	851
	Grass, tops	460–6640	Great Britain	624
Metal-processing industry	Grass	0.5–62	Canada	777
	Tree foliage	27–2740[b]	Canada	480
	Rice, leaves	7–18	Japan	395
	Hay	0.3–2.6	Norway	441
Battery manufacturer	Tree foliage	16–387[b]	Canada	480
Sludged or irrigated field	Brown rice	1.2 (max.)	Japan	336
Application of arsenical pesticides	Turnip, roots	1.08	Canada	138
	Potato, tuber peels	1.10	Canada	138
	Carrot, roots	0.26	Canada	138

[a] AW basis.

[b] Washed leaves.

causing considerable damage. Decreased Mn, P, and Ca concentrations in all plant parts, and K in roots, were reported.

Gough et al.[279] reviewed recent findings on As phytotoxicity and reported that the As content of injured leaves of fruit trees ranged from 2.1 to 8.2 ppm DW. In general, the residue tolerance for As in plants is established as 2 ppm DW (Table 36). However, the critical value in rice plants is as high as 100 ppm DW in tops and 1000 ppm DW in roots.[395] Davis et al.[171] gave the critical value of 20 ppm DW for barley seedlings, whereas Macnicol and Beckett[1081] estimated the commonly reported critical upper levels for 10% depression of the yield of various plants to range from 1 to 20 ppm (DW).

Although there are some reports of the stimulating effects of As on the activity of soil microorganisms, As is known as a metabolic inhibitor; therefore, yield reduction of vegetation under a high level of bioavailable As should be expected. Apparently, As is less toxic when the plant is well supplied with P. Se seems to inhibit the As toxicity to mitochondria of the rice cells.[919]

Depending on the location and pollution source, plants may accumulate extremely large amounts of As—above 6000 ppm DW and above 8000 ppm AW (Table 123). Although As poisoning from plants to animals is believed to be very uncommon, unfavorable health effects of such a high As concentration in vegetables and in forage plants cannot be precluded.

Recent findings reported by McSheehy and Szpunar[1411a] indicate that some sea plants are likely to concentrate a great proportion of As from water. Predominant As species in sea plants, the so-called "arsenosugars," are easily converted in the human body to dimethylarsinic acid, which has carcinogenic potential.

III. ANTIMONY

A. Soils

The crustal abundance of Sb is low and, with the exception of argillaceous sediments which contain up to 2 ppm Sb, does not exceed 1 ppm (Table 119). The geochemical characteristics of Sb are closely related to those of As and, in part, to those of Bi. Sb usually occurs with the valence of +3 and occasionally of +5 and shows amphoteric behavior. It has chalcophilic properties and is often associated with ore deposits of sulfide of other metals. Sb may substitute for arsenic in several minerals to form such minerals as pyrargyrite (Ag_2SbS_3) and bourmonite ($PbCuSbS_3$).

The reactions of Sb during weathering are not yet well-known. However, the common occurrence of Sb in waters, its concentrations in coals, and carbonaceous shales, and its association with Fe and Mn hydroxides indicate a relatively high mobility in the environment. Sb is known to occur in soluble forms, some of which are complexed with humates. Sb is easily adsorbed and thus becomes enriched in clay sediments and in hydrous oxides. Isotopic study has shown that ^{125}Sb applied to soil moves readily down the profile.[1042a] In surface soil, Sb ranges from 0.05 to 4.0 ppm (Table 124) and, if the above results are representative, Sb is concentrated in soils as compared to rocks. Jones et al.[1042a] reviewed recent data on Sb in soils of various countries and gave the overall range from 0.3 to 9.5 ppm. The average for soil Sb is given by Wedepohl[855] as 1 ppm, and the grand mean calculated from the data presented in Table 124 is 0.9 ppm. The 90th percentile for total Sb in Finnish soils is 0.6 ppm, at ranges within <0.2 to 0.9 ppm.[1368] Govindaraju[1313] reported recent results for Sb in reference soils from China, to range from 0.5 to 60.0 ppm (mean, 13.6 ppm), and in soils from the U.S. to range from 0.11 to 14.0 ppm (mean, 2.4).

Like As, Sb may be associated with nonferrous ore deposits and is likely to be a pollutant in industrial environments. Thus, the increased level of Sb to about 200 ppm was found in soils near a Cu smelter,[153] and elevated air concentrations of Sb have been reported for different smelter operations and urban areas.[210] Soils from battery reclamation sites are reported to contain up to

Table 124 Antimony Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Canada	0.05–1.33	0.19	244
	Great Britain	0.34–0.44	—	819
Loamy and clay soils	Canada	0.05–2.0	0.76	244, 409, 629
Soils on mafic rocks	Great Britain	0.29–0.62	—	819
Fluvisols	Bulgaria	—	0.82	558
Chernozems	Bulgaria	—	0.99	558
Histosols	Canada	0.08–0.61	0.28	244
Forest soils	Bulgaria	1.25–2.32	1.77	558
Various soils	Nigeria	1–2[a]	—	855
	Canada	0.29–4	1.67	132, 409, 629
	Great Britain	0.56–1.3	0.81	818, 819
	Norway	0.17–2.2	0.61	754
	U.S.	0.25–0.6	—	462

[a] Possible influence of Pb-Zn mineralization.

857 ppm Sb,[1166] whereas forest soils surrounding a metal smelter in the Czech Republic accumulated in A_0 horizon up to 11 ppm Sb.[1083] The trend of variation in the Sb content of surface soil in Norway clearly indicates pollution by long-range transport.[754]

B. Plants

Sb is considered a nonessential metal and is known to be easily taken up by plants if present in soluble forms. Shacklette et al.[710] found the Sb content of trees and shrubs growing in mineralized areas to range from 7 to 50 ppm DW, whereas Bowen[94] reported an Sb mean of 0.06 ppm DW in land plants. Oakes et al.[574] gave the range of Sb concentrations in edible plants as 0.02 to 4.3 ppb FW, with cabbage being in the upper range and apple fruits in the lower range. Laus et al.[462] reported Sb to be <2 ppb DW in corn grains and potato tubers and 29 ppb in grass. Ozoliniya and Kiunke[588] showed that the Sb content of barley and flax roots was, respectively, 122 and 167 ppb DW and exceeded that of leaves having 10 and 27 ppb DW. The same plants grown in peat soil contained several times less Sb in roots, while the concentration in leaves was about the same as that given above. Sb concentrations in mosses from the Scandinavian countries, ranging from 170 to 320 ppb (DW), do not reflect any significant effect of aerial pollution.[1135] Norwegian mosses (Table 4) analyzed in 1995 contained Sb within the range 8.3 to 4300 ppb (average, 150 ppb).[1223] There are no reports of plant toxicity caused by Sb; however, Sb levels may be expected to increase in plants growing in soils contaminated by industrial emissions or sewage sludge applications.

IV. BISMUTH

Bi is considered a rare metal in the Earth's crust (around 0.2 ppm) and is usually found in veins associated with some metals (e.g., Ag, Co, Pb, Zn). Its higher concentrations in argillaceous sediments do not exceed 0.5 ppm (Table 119). However, Bi accumulation in coals and in graphite shales to about 5 ppm has been reported.

Bi reveals chalcophilic properties, but during weathering is readily oxidized, and when it becomes carbonated (e.g., $Bi_2O_2CO_3$) it is very stable. Therefore, the Bi content of most surface soils is directly inherited from parent rocks. There is a dearth of information on the Bi abundance in the upper lithosphere; the little data available give an average figure of 0.2 ppm.

There is a paucity of information on the Bi content of soils. Ure et al.[819] reported the mean Bi content of arable Scottish soils derived from different rocks to be 0.25 ppm (range, 0.13 to 0.42). Chattopadhyay and Jervis[132] reported the range of Bi in garden soils of Canada to be from 1.33 to 1.52 ppm. Bowen[94] gave the approximate mean of soil Bi as 0.2 ppm. Aubert and Pinta[39] reported Bi in ferralitic calcareous soils of Madagascar to be 10 ppm. An increase of Bi in soil horizons rich in Fe oxides and organic matter should be expected. Govindaraju[1313] reported the Bi contents in reference soils of China to range from 0.04 to 1.2 ppm and in reference soils of the U.S. within the range 0.03 to 0.69.

The Bi content of plants has not been studied extensively. Shacklette et al.[710] reported that Bi was found only in about 15% of a number of samples of Rocky Mountain trees and that the Bi range was from 1 to 15 ppm AW. Bowen[94] gave the mean Bi as <0.02 ppm DW in land plants and 0.06 ppm DW in the edible parts of vegetables. Erämetsä et al.[216] found a range of Bi in *Lycopodium* sp. from <1 to 11 ppm DW, with about 60% detectability. Bi is likely to be concentrated at polluted sites due to its high concentration in some coals and sewage sludges. Berg and Steinnes[1223] found Bi in Norwegian mosses collected in 1995 to range from 1 to 800 ppb (average, 33 ppb).

V. VANADIUM

A. Soils

The general abundance pattern of V in common rocks compiled in Table 119 shows that although there is a large variation in the content of rocks, this metal is concentrated mainly in mafic rocks and in shales (within the common range of 100 to 250 ppm). The geochemical characteristics of V are strongly dependent on its oxidation state (+2, +3, +4, and +5) and on the acidity of the media. V is known to form various complexes of cationic and anionic oxides and hydroxy oxides,[256] therefore, V displays various behaviors. It usually does not form its own minerals, but rather replaces other metals (Fe, Ti, and Al) in crystal structures. When cations of Pb, Zn, and Cu are present, the precipitation of vanadates can occur: for example, vanadinite ($Pb_2Cl(VO_4)_3$) and mottramite (Pb (Cu, Zn) (OH) (VO_4)).

During weathering, the mobility of V is dependent on the host minerals, and finally V remains in the residual rock-forming minerals or is adsorbed or incorporated in mineral structures of clays or Fe oxides. A high degree of association of V with Mn and with the K content of soil has also been reported by Norrish.[570] V tends to be associated with organic matter, and therefore its elevated concentration in organic shales and bioliths is common. An especially great range of V in some coals and crude oil has often been observed. V concentration in crude oils is reported to vary from 150 to 900 ppm, being the highest in Venezuelan oil. Wedepohl[855] explained these phenomena, following the assumption of Bertrand, by postulating that in former geologic periods there might have existed some plants with much higher V content than presently found in normal plants. Yen[894] described high concentrations of V in organic sediments as the results of V^{3+} sorption by lipids and cholines, the basic compounds in further formation of porphyrins. A possible diadochous substitution of Mg^{2+} by vanadyl ions VO^{2+} is another explanation for the high amounts of V in some porphyrins.[1120]

The behavior of V in soil has received little attention. Norrish[570] reported that Fe oxides hold a reasonable fraction of the soil V that is more mobile and could supply V to plants. Berrow et al.[71] emphasized that in certain horizons of podzols, the role of the clay minerals as well as organic acids might be more significant than the V fraction adsorbed by Fe oxides. Apparently, the vanadyl cation (VO^{2+}) may be an important form of V in many soils and may result from reduction of the metavanate anion (VO_3^-). Goodman and Cheshire[272] and Bloomfield[81] stated that much of the soil V, mainly the vanadyl cation, is mobilized as complexes with humic acids. Also anionic forms of V (VO_4^{3-}, VO_3^-) are known to be mobile in soils over a wide pH range, in contrast to V^{3+}, which forms insoluble hydroxide when pH is low. Adhesion of $[VO_4]^{3-}$ to clay minerals, especially with Fe cations is responsible for considerable concentrations of V in various concretions and nodules formed in soils.

Surface horizons of some podzols are reported to contain less V as a result of extensive leaching into lower horizons.[71] In general, V is distributed in soil profiles rather uniformly and the variation in V content of soil is inherited from the parent materials. Thus, the highest concentrations of V (150 to 460 ppm) are reported for soils derived from mafic rocks, while the lowest (5 to 22 ppm) were found in peat soils (Table 125). Loamy and silty soils, as well as some ferralitic soils, also contain large amounts of V which exceed that of the parent material.

The average V contents of soils worldwide have been calculated to vary from 18 ppm for histosols to 115 ppm for rendzinas (Table 9). Shacklette and Boerngen[706] gave a geometric mean of 58 ppm for soil samples of the U.S., while Cannon et al.[119] reported the average soil V to be approximately 100 ppm. Govindaraju[1313] reported the V content in reference soils of China to range from 37 to 247 ppm, and in reference soils of the U.S. within the range 36 to 150 ppm. Soils of the lowland of Poland contain HCl-soluble V below 10 ppm, whereas mountain soils contain V within the range 10 to 20 ppm. Areas of metal smelters have increased V levels up to 80 ppm, and in the vicinity of an oil refinery, also above 80 ppm.[1390] The difference in V content, depending on extraction methods, suggests strongly bound forms of V in soils. This is supported by Koljonen[1368] who reported the 90th percentile for V acid soluble in Finnish soils to be 60 ppm, while for the total V in soils, 120

Table 125 Vanadium Content of Surface Soils of Different Countries (PPM DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Great Britain	58–91	—	819
	Madagascar	—	75	557a
	New Zealand[a]	160–220	—	861
	Poland	10–27	—	382
	Russia	10–260	103	180, 493, 1031
Loess and silty soils	New Zealand[a]	—	185	861
	Poland	27–110	—	382
	Russia	—	57	493
Loamy and clay soils	Chad	15–50	—	39
	Madagascar	—	95	557a
	New Zealand[a]	150–330	—	861
	U.S.	20–150	87	706
	Russia	34–210	—	180, 493, 631, 714
Soil on mafic rocks	Great Britain	340–460	—	819
Fluvisols	Madagascar	48–180	103	557a
	Russia	—	18	493
Gleysols	Chad	20–100	—	39
	Russia	—	118	631
Rendzinas	Ireland	38–85	—	236
	China	21–500	220	1124
	U.S.	10–150	72	706
Kastanozems and brown soils	Ireland	25–55	—	236
	Madagascar	—	125	557a
	Former S.U.	—	56	714
Ferralsols	Chad	20–250	—	39
	Madagascar	28–530	137	557a
	Russia	42–360	—	180
Solonchaks and solonetz	Chad	55–260	—	39
	Russia	78–99	88	351
Chernozems	Former S.U.	37–125	85	4, 180, 351, 714, 1031, 1123
	U.S.	30–150	92	706
Meadow soils	Former S.U.	85–380	190	631, 714
Histosols and other organic soils	Denmark	6.3–10	8.1	1
	Sweden	19–22	—	814
	U.S.	<7–150	38	706
	Russia	—	5	493
Forest soils	China	—	92	225
	U.S.	15–200	85	706
	Former S.U.	97–145	—	4, 631, 714, 1476
Various soils	Great Britain	15–200	—	34, 818
	Italy	25–172	76	946
	Madagascar	19–320	75	557a
	U.S.	0.7–98	—	600
	Russia	50–87	69	283
	Czech Republic	117–119	—	1136

[a] Soils derived from basalts and andesites.

ppm. The median V content (by DC-arc emission spectrometry) in Lithuanian soils is given as 26 ppm, with the highest value of 50 ppm for loamy clay soils.[1359]

Although there are not many reports of V pollution of soils, it is likely that industrial processing of certain mineral ores (ore smelters, cement, and phosphate rock plants) and burning of coals and oils will increase the deposition of V residues in soils. Combustion of fuel oils is an especially serious source of V in soil. Tyler[814] reported that forest mor around a densely inhabited area accumulated up to 100 ppm V, and Pawlak[605] found increased V content of soil up to 110 ppm in the vicinity of a crude oil refinery. Belsare[936] determined V contents in soils surrounding a thermal power station at a graphite industry in India within the range of 350 to 840 ppm. Jacks[347] calculated that the V aerial input to soil in the vicinity of Stockholm is approximately 20 mg m^{-2} $year^{-1}$.

B. Plants

The evidence that V is essential for the growth of higher plants is not yet conclusive, while the essentiality of this element for alga species is unquestionable and V is known to stimulate photosynthesis in these organisms. Piispanen and Ländesmäki[1120] found that the amount of blue-green algae increases in relation to the amount of green algae with increasing V concentration, and algal mixture (blue-green) tolerates a higher content of V_2O_5 in the solution (up to L^{-1}) than green algae alone. The enzyme found in some algae (V-Br-peroxidase) is involved in the process of the reduction of hydrogen peroxide due to the alteration from V^{3+} to V^{5+}. In general, the coefficient of V enrichment in algae was relatively high, and therefore these authors concluded that some water plants may be useful in geobotanical exploration for V.

There are evidences that V is a specific catalyst of N_2 fixation and may partially substitute for Mo in this function as carried on by rhizobium bacteria in particular. Dobritskaya[180] reported a high accumulation of V in nodules of several legumes (3 to 12 ppm DW), which suggests the V association with N_2 biofixation. However, no evidence of V deficiency in higher plants was observed, and Welch and Cary claimed that if V is essential for plants, adequate levels in their tissues are less than 2 ppb DW.[860]

Soluble soil V appears to be easily taken up by roots, and some plant species show a great ability to accumulate this metal. Petrunina reviewed this topic and showed that some bryophytes and fungi,[613] especially *Amanita muscaria*, may contain as much as about 180 ppm DW when grown in mineralized areas. Other accumulator plant species are also known.[119]

Welch[859] studied the uptake of V by roots from labeled V solution, and concluded that V is passively absorbed by barley roots. The uptake was a linear function of V concentration and was highly dependent on pH (Figure 79). These results indicate that VO^{2+} species occurring under acid

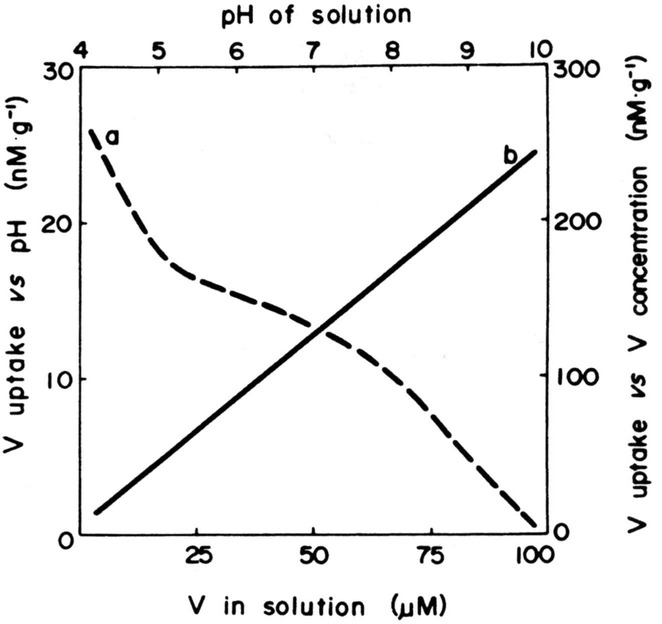

Figure 79 The influence of (a) pH on the rate of V absorption by barley roots from a solution of μM NH_4VO_3; (b) V concentration in the solution on its content in barley roots.[858]

Table 126 Vanadium Content of Food and Forage Plants (ppb)

Plant	Tissue Sample	FW Basis (119, 235, 574, 600)	DW Basis (385, 750, 860)	AW Basis (283, 750, 855)
Wheat	Grains	—	7–10	—
Oats	Grains	—	60	—
Beans	Pods	3.4	—	—
Cabbage	Leaves	8	—	—
Lettuce	Leaves	5.3	280	2800
Carrot	Roots	8.8	—	—
Potato	Tubers	—	6.4	—
Cucumber	Fruits	5.8	56	380
Tomato	Fruits	—	0.5	41
Apple	Fruits	0.01–0.1	8.6	334
Strawberries	Fruits	—	—	660
Kidney bean	Aerial parts	140	760	5600
Clover	Aerial parts	—	2700; 380	27,000
Grass	Shoots	160–230	180–420	—
	Shoots	100–2600	—	—
	Shoots	<1–9800	—	—

Note: References are given in parentheses.

conditions are more rapidly absorbed by roots than are VO_3^- and HVO_4^{2-} species that predominate in neutral and alkaline solutions. However, both cationic and anionic species are capable of being chelated and thus could contribute substantially to V uptake by plants from soils, but no significant relationship between vegetation and soil V has been reported.[600] Morrell et al.[1095] reviewed some recent developments in the biochemistry of V in higher plants, indicating the biotransformation processes of V from vanadate (VO_3^-) to vanadyl (VO^{2+}) during uptake by plants. The reduction of V in plants is of great significance since V^{5+} is recognized as a potent inhibitor of several enzymes which are largely unaffected by the reduced form, V^{4+}. Thus, V in plant tissues exists, at least partly, in reduced tetravalent form.

The mean concentration of V in higher plants has been calculated by Dobritskaya to be 1.0 ppm DW,[180] and the range of V in ash of most vegetables is given by Shacklette et al.[710] to be from <5 to 50 ppm. Several other authors have reported a pronounced difference in V content among most plants (Table 126).

The reported variation in V content of plants may be an effect of both analytical difficulties and pollution. The values given by Shacklette et al.[710] from the Report of the Committee on Biological Effects of Atmospheric Pollutants for V in some food plants follow (ppb FW): lettuce, 1080; apple, 330; potato, 1490; carrot, 990; beet, 880; and pea, 460. These values are much higher than those presented in Table 126 and apparently reflect a pollution source of V. The sporophore of *Amanita muscaria* in unpolluted woodland is reported to contain V up to 345 ppm (DW) although the total V in the soil was relatively low (6.7 ppm DW).[1060]

Bryophytes appear to be most sensitive to aerial sources of V. Bowen[94] gave the mean V content of mosses as 11 ppm DW. Shacklette and Connor (see Cannon et al.[119]) found the range of V in Spanish moss (a flowering plant) to be 50 to 180 ppm AW, being higher in areas affected by emissions from crude oil refining. Gough and Severson[278] found V to be as high as 700 ppm AW in sagebrush near a P fertilizer plant. Pawlak[605] reported the mean V content of clover and grass grown in the vicinity of a crude oil refinery to be 13 and 8 ppm DW, respectively. Folkeson[239] found the range in V concentration in mosses near a peat-fired plant to be 6 to 8 ppm DW and in those near the ash heap to be 14 to 25 ppm DW. Belsare[936] reported that vegetables grown in the vicinity of a thermal power station contained V within the ranges 1.9 to 4.9 ppm (cabbage) and from 0.8 to 1.7 ppm (tomato).

Gough et al.[279] reviewed the topic of V phytotoxicity and stated that there are no reports indicating V toxicity under field conditions. However, under man-induced conditions, V concentrations as high as 0.5 ppm in the nutrient solution, and 140 ppm in the soil solution, may be toxic to plants. Gettier et al.[1010] reported that in greenhouse conditions, V (as vanadyl sulfate) at the concentration 3 ppm in the solution reduced the length of collard roots by 50%. The V toxicity to plants varies with soil types due to the variable phytoavailability. In sandy soil, 80 ppm V can reduce plant growth; whereas in loamy soil, >100 ppm V does not affect plants. Phytotoxicity of V (chlorosis and dwarfing) may appear at about 2 ppm DW V in some plants, as cited by Davis et al.[171] Wallace et al.[841] reported that bush beans absorbed from culture solution as much as 13, 8, and 880 ppm V (DW) in leaf, stem, and root, respectively, and that this resulted in smaller growth but not chlorosis.

VI. NIOBIUM

Data on the abundance of Nb in various rocks are listed in Table 119. The amounts of Nb increase on the average in intermediate and acid magmatic rocks (15 to 60 ppm) and in argillaceous sediments (15 to 20 ppm). Its abundance in the Earth's crust is estimated at 24 ppm.

Nb has strong geochemical relations to Ta, and its association with Fe, Ti, and Zr has been recognized (e.g., mineral niobite, $(Fe, Mn) (Ta, Nb)_2O_6$). Concentrations of Nb in bauxites, bottom clays of oceans, and Mn nodules have also been reported.[855] Ionic substitution of Nb for Zr in the mineral zircon is of special geochemical importance since zircon is widely distributed in igneous rocks and is an important carrier of Nb.

The +5 valence state of Nb is the most stable in the Earth's crust. Most of the Nb compounds are slightly soluble in both acid and alkaline media. However, the presence of organic complexing agents mobilizes Nb. The behavior of Nb during weathering is highly dependent on host minerals; therefore, Nb may be released (e.g., from biotite, amphibolite) or may remain within resistant minerals (e.g., sphene, zircon). The accumulation of Nb in certain residual sediments has often been reported.

There are not many reports on the Nb status of soils. The geometric means of 12 ppm Nb has been calculated for surface soil samples of the U.S., and the distribution of Nb does not show any significant variation between soil types.[707] Gough et al.[1012] found Nb in various soils of Alaska to range from <4 to 44 ppm, with a geometric mean of 8 ppm. Ure and Bacon[818] reported a mean Nb content of 24 ppm for standard soil samples, while Ure et al.[819] gave the range in Nb concentrations in arable soils derived from different rocks as 31 to 300 ppm, with the highest value for soil on trachyte enriched in this metal. Wedepohl[855] stated that Nb averaged 24 ppm in lateritic soils from West Africa. Govindaraju[1313] reported the Nb content in reference soils of China to range from 9.3 to 37.6 ppm, and in reference soils of the U.S. within the range 6.4 to 22.0 ppm. Kadunas et al.[1359] gave the median value of 12.5 ppm for Nb in Lithuanian soils.

Nb is reported to be relatively mobile under humid conditions and therefore may be available to plants. However, Shacklette et al.[710] found that of more than 1000 samples of a variety of plant species from throughout the U.S. only one contained Nb (30 ppm AW). Some mosses and lichens were reported to contain Nb ranging from 0.002 to 0.45 ppm DW and 15 to 20 ppm AW.[94,710,1223] Tiutina et al.[800] found that the common value of Nb in plants is about 1 ppm DW; however, several native plants have a great capacity for extracting Nb from soil that is enriched in this metal. Concentrations of Nb up to about 10 ppm DW, found in selected plant species (mainly *Rubus arcticus* L.) from an Nb mineralized area of the Komi, former Soviet Union, served as an exploration indicator for an Nb deposit.

VII. TANTALUM

Ta closely resembles Nb in geochemical behavior, and exhibits the properties of both a lithophilic and a chalcophilic element. The Ta distribution in rocks follows that of Nb and reaches the highest concentrations in acid magmatic rocks (2 to 4 ppm) and in argillaceous sediments

(1 to 2 ppm) (Table 119). Ta occurs in complex oxides combined with Nb, Ti, Y, lanthanides, and other metals; for example, tantalite, $(Fe,Mn)(Ta,Nb)_2O_6$). Ta is believed to be less mobile than Nb during weathering because of its lower solubility and the slight stability of organic complexes. Thus, the Nb to Ta ratio varies, depending on environmental conditions.

There is a paucity of information on Ta occurrence in soils. Naidenov and Travesi[558] found Ta in various Bulgarian soils to range from 0.42 to 3.87 ppm (mean, 0.65 ppm), and Laul et al.[462] gave the range in Ta contents of U.S. soils as 1.1 to 2.7 ppm. The range of Ta in garden soils of Canada was reported to be from 0.17 to 0.22 ppm.[132] Ta content in reference soils of China is reported to range from 0.8 to 5.3 ppm, and in reference soils of the U.S. to range from 0.7 to 1.2 ppm.[1313] The 90th percentile for Ta in Finnish soils is about 1.5 ppm.[1368] The Ta content of deep loess deposit in the European part of Russia averaged from 1 to 2 ppm.[1181] Oakes et al.[574] found the range of Ta in food plants to be from 0.013 to 0.48 ppb FW, whereas Bowen[94] gave the mean Ta in edible parts of vegetables as <1 ppb DW. Laul et al.[462] reported Ta in vegetation from <1 to <6 ppb DW.

CHAPTER 11

Elements of Group VI

I. INTRODUCTION

The geochemical and biochemical behavior of trace elements of this group is complex and diverse. Se and Te resemble S in geochemical reaction. Po, also belonging to the subgroup VIa (new group 16) is a natural isotope of the U-Ra transformation chain.

Trace elements of the Group VIb (new group 6) Cr, Mo, and W, have strong lithophile tendencies and although they have variable oxidation states, they are preferably hexavalent in their oxygen compounds. The geochemical behavior of Mo and W is very similar, and in biochemistry some substitution by W for Mo has been observed.

II. SELENIUM

A. Soils

Se occurs in nearly all materials of the Earth's crust and is present in magmatic rocks in concentrations rarely exceeding 0.05 ppm. In sedimentary rocks, Se is associated with the clay fraction and thus the smallest quantities of Se are in sandstones and limestones (Table 127). The main geochemical characteristics of selenium are: (1) chalcophilic tendencies, especially in meteorites, where it can be concentrated up to 300 ppm, (2) readily entering the lattice of sulfides, (3) concentration in oxidic sulfuric layer of the Earth, and (4) common occurrence in native sulfur of volcanic origin, but not of sedimentary origin.

Selenium easily forms compounds with metals and occurs in about 50 minerals, the most common being: clockmannite, CuSe; ferroselite, FeSe; clausthalite, PbSe (often associated with galena), naumannite, Ag_2Se (common in Cu ores); and tiemannite, HgSe. Se also forms a large number of organic compounds that are analogous to those of sulfur organic compounds.

Much of the Se occurs in S and sulfide minerals where it may be concentrated up to 200 ppm; however, in S deposits of sedimentary origin, the Se level is usually below 1 ppm. During chemical weathering of rocks, Se is easily oxidized and the state of its oxidation, as well as its solubility, are controlled by the oxidation-reduction regime and by pH of the environment. Also, the biological methylation of Se, yielding the volatile Se compounds, is common and plays a significant role in the geochemical cycle of Se. Selenite ions resulting from oxidation processes are stable and able to migrate until they are adsorbed on mineral or organic particles. In consequence, the Se level is increased in several coals, as well as in clay sediments. Apparently, selenites are the preferable species of Se being adsorbed by clay minerals, particularly by montmorillonite and Fe oxides.[246] Adsorption of SeO_3^{2-} by goethite is highly pH dependent.[93]

Table 127 Selenium, Tellurium, Chromium, Molybdenum, and Tungsten in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock Type	Se	Te	Cr	Mo	W
	Magmatic Rocks				
Ultramafic rocks Dunites, peridotites, pyroxenites	0.02–0.05	0.001	1600–3400	0.2–0.3	0.10–0.77
Mafic rocks Basalts, gabbros	0.01–0.05	0.001	170–200	1.0–1.5	0.36–1.10
Intermediate rocks Diorites, syenites	0.02–0.05	0.001	15–50	0.6–1.0	1.0–1.9
Acid rocks Granites, gneisses	0.01–0.05	0.005	4–25	1–2	1.3–2.4
Acid rocks (volcanic) Rhyolites, trachytes, dacites	0.02–0.05	—	4–16	2	2
	Sedimentary Rocks				
Argillaceous sediments	0.4–0.6	—	80–120	2.0–2.6	1.8–2.0
Shales	0.6	<0.01	60–100	0.7–2.6	1.8–2.0
Sandstones	0.05–0.08	—	20–40	0.2–0.8	1–2
Limestones, dolomites	0.03–0.10	—	5–16	0.16–0.4	0.4–0.6

Table 128 Impact of Soil Conditions on the Formation of Soluble Se Species[1353]

Redox Value (Eh, mV)	pH	Oxidation State of Se	Major Se Species in Soil Solution	
High	7	+6	SeO_4^{2-},	Selenates
>400	<2	+6	SeO_4^-, $H_2SeO_3^-$	
Moderate	>7	+4	SeO_3^{2-}	Selenites
200–400	<7.3	+4	$HSeO_3^-$	
Low	>3.8	+2	HSe^-	Selenides
<200	<3.8	+2	H_2Se^0	

On the basis of the geochemistry of Se, it seems to be possible to predict trends of Se behavior in a particular soil environment. Elrashidi et al.[989] studied equilibrium reactions and constants for 83 Se minerals and solution species that relate to soils and observed that the redox potential (Eh) of soils controls Se speciation in solution (Table 128). They described Se species and Se-metal complexes that are likely to occur in soils under various conditions. In soils of high Ca and Mg concentrations, both $CaSeO_4$ and $MgSeO_4$ contribute to the total Se in solution; whereas in acid and very acid soils, the most important compounds seem to be KHSe, NH_4HSe, and MnSe. A generalized summary of Se species that may occur in soils is presented in Figure 80.

Lakin and Dawidson,[454] Allaway,[13] Paasikallio,[591] Combs and Combs,[969] and Frankenberger and Engberg[1303] have extensively reviewed Se behavior in soil and have emphasized its complex character. It can be generalized that the main factors controlling Se forms and behavior in soils are Eh and pH factors (Table 128). Thus, specific forms of selenium are associated with defined soil parameters:

- Selenates (Se^{6+}) are mobile in inorganic forms in ordinary alkaline soils, and are not absorbed on hydrous sesquioxides (especially $Fe_2O_3 \cdot nH_2O$)
- Selenites (Se^{4+}) are slightly mobile in ordinary neutral or acid soils of humid temperate regions, and are easily absorbed on hydrous sesquioxides and organic matter
- Selenides (Se^{2-}) are rather immobile in acid soils due to the formation of stable mineral and organic compounds

Se can be included in various organic compounds, especially those containing S, and also sorbed on organic particles. The transformation of Se forms in all soil conditions is based mainly on the

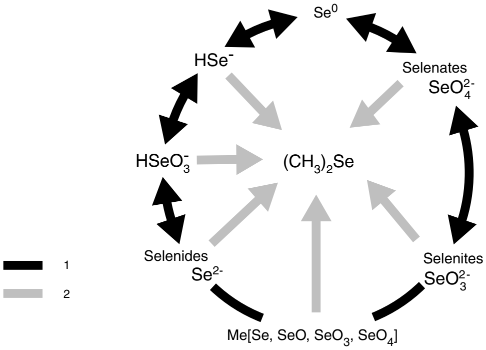

Figure 80 Ionic species and transformation of Se compounds in soils. (1) reduction-oxidation; (2) methylation.

following processes: (1) selenates to selenites—slow process, and (2) selenites to selenides, to elemental Se, and to organic compounds—very slow process.

According to the geochemical classification of the elements after Goldschmidt (*vide* Kabata-Pendias and Pendias[1357]), Se reveals chalcophilic and siderophilic properties. These variable properties define its complex behavior in various geochemical processes.

Selenium present in soils originates from different sources:

- Lithogenic—parent materials are highly variable in Se content
- Pedogenic—increased content in A and B horizons of soils due to the fixation by organic matter, hydroxides (mainly Fe and Mn), and clay minerals (mainly montmorillonite)
- Atmospheric—deposition with rainfall, especially close to the ocean and sea, Se is present in the atmosphere due to volcanic exhalation, industrial emission, methylation, and volatilization from sea and soil surfaces
- Phytogenic—volatilization from plants and soil microorganisms, and burning of seleniferous vegetation.
- Anthropogenic:
  - *Agricultural:* Se applied to soils, foliar sprays, seed treatments, and phosphatic fertilizers
  - *Industrial:* fly-ash, smelting of some ores, wastes of some ores, some sewage sludge

However, several complex anions of Se as well as organic compounds and chelates greatly modify the behavior of Se in each particular soil (Table 129). This has been nicely illustrated by various trends in Se distribution along soil profiles (Figure 81).

It has been estimated that absorbed forms of Se in soil ranges from 15 to 40% of its total contents and that Se-organic ranges from 4 to 22% of the total contents.[1353] Vuori et al.[1534] carried out a long-term experiment with similar doses of Se salt applied to different soils and found that its availability to plants varies significantly, depending on soil parameters. Application of farmyard manure is reported to be a good means of increasing the levels of Se content in Se-deficient soil.[1229] Addition of Se (as sodium selenate) to fertilizers in Finland from 1983 to 1992 resulted in increasing Se in river waters (up to 180 μg L^{-1}), and especially in bottom sediments (up to 3.94 ppm).[1537,1538]

Elevated concentrations of Se, resulting from irrigation practices, in soils in California (San Joaquin Valley, an area underlain with seleniferous parent material) is now of real environmental concern.[1303] A number of projects are presently under way for remediation and prevention strategies. Phytorestoration seems to be a promising method.[1367,1450]

The Se content of soils has received much attention in certain countries, mainly those where the role of Se in man and animal health has been widely recognized. Surface soil on a worldwide

Table 129 **Soil Factors Affecting the Mobility of Selenium**[1353]

Soil Factor	Se Form	Mobility
pH:		
High (alkaline)	Selenates	High
Medium (neutral)	Selenites	Moderate
Low (acid)	Selenides	Low
Eh:		
High (high oxidation)	Selenites	High
Low (low oxidation)	Selenides	Low
Hydroxides (Fe, Mn):		
High content	Absorbed all forms of Se	Low
Low content		High
Organic matter[a]:		
Undecayed	Absorbed	Low
Decayed (e.g., peat)	Complexed	High
Enhanced biomethylation	Volatilized	High
Clays[b]:		
High content	Absorbed	Low
Low content	Not fixed	High
Interactions:		
Sulfur	Antagonistic effects	Rather low
Phosphate		
Nitrogen		

[a] Variable impact of organic matter depends on its kind.

[b] Absorption by clay minerals decreases with increasing pH values and, at pH 8, is almost negligible.

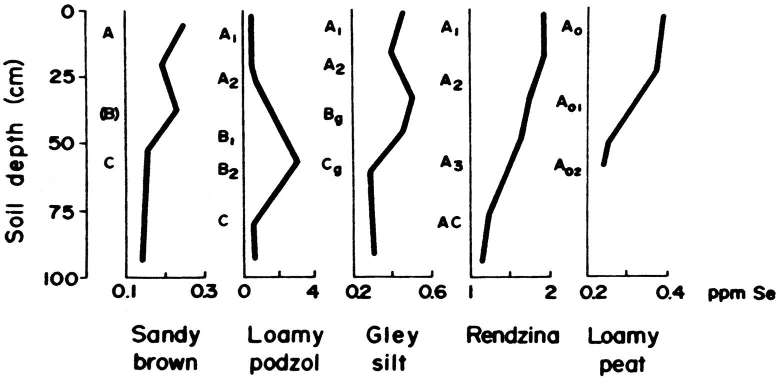

Figure 81 Distribution of Se in some profiles of soils in New Zealand. (Letters indicate genetic soil horizons)[862]

scale contains an average of 0.33 ppm Se. But the Se mean differs for the soil units from 0.25 ppm in podzols to 0.37 ppm in histosols and rendzinas (Tables 9 and 130). Forest soils contain especially elevated amounts of Se; for example in those soils of Poland, the average Se is at the 0.7-ppm level.[1238] Elevated concentrations of Se are observed in some ferralsols, organic soils, and other soils derived from Se-rich parent materials (Table 131). Also, in salt-affected soil, the total as well as the water-soluble Se is likely to be elevated.[729] There is great concern about enriched water-soluble Se levels in soils because increased bioavailability of Se is a direct health risk to livestock. Certain diseases of people ("Keshan"—cardiomyopathy, and "Kashin-Beck"—tubular bone changes) are recognized to be associated with Se-deficient soils. The water-soluble Se content of soils is reported to range from 0.2 to 2 ppb (DW) in the endemic areas in China; whereas in neighboring nonendemic areas, easily soluble Se varies from 1 to 11 ppb.[1189]

The solubility of Se in most soils is rather low; therefore, many agricultural areas produce crop plants and forage with a low Se content. However, in naturally Se-enriched soils, in poorly drained

Table 130 Selenium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Great Britain	0.15–0.24	—	819
	Canada	0.10–1.32	0.27	244,294
	Poland	0.06–0.38	0.14	618a
	U.S.	0.005–3.5	0.5	454
	Former S.U.	0.05–0.32	0.18	358
Loess and silty soils	Poland	0.17–0.34	0.23	618a
	U.S.	0.02–0.7	0.26	454
Loamy and clay soils	Canada	0.13–1.67	0.43	244,294
	U.S.	0.1–1.9	0.5	707
	Poland	0.18–0.60	0.30	618a
Cambisols	Germany	0.18–0.53	0.30	1179
Soils on mafic rocks	Great Britain	0.02–0.36	0.20	819
Soils over granitoids	Yugoslavia	0.16–0.35	0.23	1348
Soils over volcanic rocks	Yugoslavia	0.12–0.13	0.19	1348
Fluvisols	Egypt	0.15–0.85	0.45[a]	212
	Poland	0.12–0.34	0.22	618a
Rendzinas	Germany	0.33–0.54	0.40	1179
	Poland	0.24–0.64	0.44	618a
	India	0.32–0.66	—	1144
	U.S.	0.1–1.4	0.19	454
Ferralsols	India	—	0.55	729
	U.S.	0.2–2.5	1.05	364
Chernozems	Poland	0.14–0.24	0.17	618a
	Former S.U.	0.32–0.37	0.34	358
	U.S.	<0.1–1.2	0.4	707
Histosols and other organic soils	Canada	0.10–0.75	0.34	244
	Finland	0.08–0.18	0.13[a]	408
	U.S.	<0.1–1.5	0.3	707
	Former S.U.	—	0.34	358
Various soils	Canada	0.41–2.09	0.94	468
	Canada	0.03–2.00	0.30[a]	521
	Germany	0.09–0.45	0.27	1179
	Great Britain	—	0.21	818
	Finland	0.005–1.24	—	734
	Iceland	0.02–0.07	0.05	408
	Ireland	—	1.27	454
	India	0.14–0.68	0.39[a]	729
	New Zealand	—	0.6	862
	Norway	0.15–2.32	0.78	442,754
	Sweden	0.17–0.98	0.39	473
	U.S.	<0.1–4.0	0.31	707

[a] Data for whole soil profile.

Table 131 Selenium Content of Surface or Subsurface Soils from Areas Having Se-Toxicity Symptoms in Livestock (ppm DW)

Country	Soil	Range	Mean	Ref.
Great Britain	Peat	92–230	138	880
Ireland	Peat	3–360	54	234
U.S. (South Dakota)	Mineral	6–28	17	454
Former S.U. (Armenia)	Mineral	0.8–2.2	1.3	358

or calcareous soils, in soils of aridic zones, and also in soils heavily amended with sewage sludges or fly-ashes, Se may be accumulated by plants in concentrations high enough to be toxic to grazing livestock. Phosphates and sulfates reduce Se adsorption, especially on Fe oxides, and are effective in releasing and mobilizing up to 90% of the soil-adsorbed selenites and selenates.[948]

The water-soluble fraction of soil Se is considered to be the fraction that is available to plants. Van Dorst and Peterson[190] reported the close positive correlation between the Se content of plants and the selenate ion concentration in the soil solution. However, other Se fractions may also be soluble in soils, and thus Elsokkary[212] concluded that, on average, about 45% of the total soil Se could be available to plants and that plant-available fractions could be extracted with K_2SO_4 or NH_4OH solutions. Soltanpour and Workman[745] found a good correlation between Se uptake by alfalfa and the Se, that was soluble in DTPA with ammonium acid carbonate. The amount of water-soluble Se in soils varies considerably and does not correlate with the total soil Se. The total Se level is, therefore, a poor predictor of the phytoavailability of the element.

The behavior of Se in highly calcareous soil is of special concern because when soils are low in sesquioxides, the Se becomes easily water soluble. Bar-Yosef and Meek[934] observed that the adsorption of Se by clay minerals decreased with elevating pH values and became negligible above pH 8. Singh[729] stated that the best effects in correcting Se toxicity to plants in such soils are obtained by the application of S, P, and even N onto the soils.

The biological methylation of Se occurs in plants and microorganisms as well as in the soil and aquatic environments. Inorganic Se undergoes methylation to gaseous compounds (dimethylselenides). Thus, methylated derivatives of Se are often volatile from soils. On the other hand, a considerable input of Se to the soils takes place through precipitation. Kubota et al.[436a] calculated that the amounts of Se in rainwater that fall on land surfaces reflect also other sources of Se such as volcanic exhalations and industrial emissions, in particular, the combustion of coals.

B. Plants

Although Se in plants has been investigated in many studies, its physiological role is not fully known; and as Combs and Combs[969] reviewed, various investigations have failed to confirm the premise that Se may have essentiality in plant nutrition. There are some opinions stating that Se may be involved in certain metabolic processes, especially in plants that are Se accumulators.[555] Several compounds of Se, mainly with cysteine and methionine, were found in such plants (e.g., *Astragalus* species), but their metabolic functions have not been conclusively established. The Se-accumulator plants synthesize Se-methyl-cysteine, whereas nonaccumulator species produce Se-methyl-methionine. The physiological significance of this difference is not yet understood.[1303] A great proportion of the Se species in mushrooms is reported to be associated with low-molecular-weight components.[1119] The great interest in plant Se is due to the importance of this element in nutrition, particularly for domestic animals, since Se can act both as a micronutrient and a toxin. Furthermore, the margin of safety of Se concentrations is rather narrow.

When present in soluble forms, Se is readily absorbed by plants, although differences between plant species are commonly observed (Figure 82). The availability of soil Se is also controlled by several soil factors, among which pH is believed to be the most pronounced (Figure 83).

The uptake of Se by plants is also a temperature-dependent process; on a soil low in Se, plants absorb a much higher amount when the temperature is >20°C than during cooler seasons with a temperature of <15°C.[474] Rainfall may also highly influence the Se concentration of herbage. As Reuter[649] reported, low Se in plants frequently occurred in high-rainfall areas. However, Haygarth[1324] calculated that the absorption of Se by plants from atmospheric deposits contributes from 33 to 82% of its total amount in a plant.

There is a positive linear correlation between Se in plant tissues and Se content of soils, and Sippola[734] stated that total soil Se gives a better measure of plant response than does its soluble fractions—which contrasts with other opinions.[969] The complex impact of variable factors on Se uptake by plants can significantly alter the relation of Se in plants and soils. As presented in Figure 84, grass can take up more Se from mineral soil with 0.07 ppm Se than from peat soil with 0.71 ppm Se. A significant variation in Se content of wild plants is observed regardless of its concentrations in

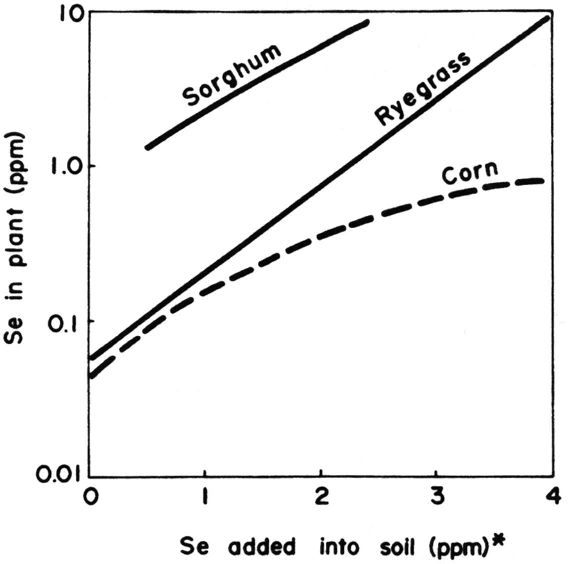

Figure 82 Influence of Se added as Na_2SeO_3 into the soil on Se content of plants. *Se level in soil in the experiment with sorghum is given in ten-times lower concentration (e.g., at the range of 0.05 to 0.25 ppm).[551,729]

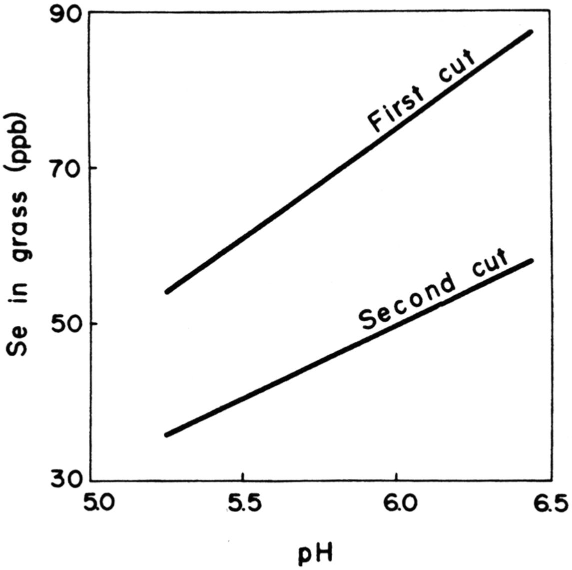

Figure 83 Se content of ryegrass as a function of the soil pH.[551]

soils. Miladović et al.[1419] found considerably higher contents of Se in hairy milk-vetch (155–177 ppb) than in comfrey (62–118 ppb), which varied within the stages of plant growth. Se taken up by plants (ryegrass and lettuce) from Se-amended soil is incorporated mainly (up to 75%) in insoluble proteins. The activity of glutathione peroxide increases in plants with increasing Se doses, while superoxide dismutase activity and the concentration of vitamin E decrease.[1323]

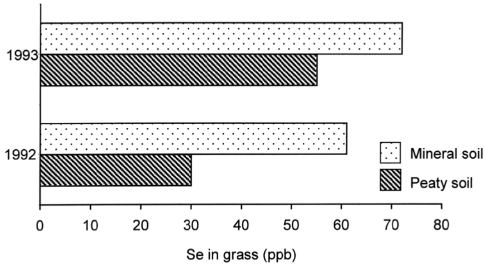

Figure 84 Se content in grass (average of 10 grass species) grown in two soils: (a) mineral, pH 6.5, OM 1.2%, Se 0.07 ppm, and (b) peat, pH 5.5, OM 75%, Se 0.71 ppm. (With permission from the authors[1237].)

The volatilization rate of Se by plants differs for species within the highest for tragacanth (70 μg Se per m^2 leaf area per day) and the lowest for fescue (2 μg Se per m^2 leaf area per day).[1282] The role of rhizobium bacteria is also significant in Se uptake by plants; for example, the inoculated plants have a fourfold higher rate of Se volatilization than noninoculated plants, which is probably due to the microbially induced increase in Se uptake.[1515] In some specific root-soil surface interactions, root exudates reveal a greater ability to oxidize SeO_3 to SeO_4, which stimulates the availability of Se for plant uptake.[1230]

Zayed and Terry[1571] have studied Se compound transformation in plants, along with its possible pathways for Se volatization. This differs for Se accumulator plants and for Se nonaccumulator plants. The final product of the Se compound transformation is dimethyl selenide, easily volatilized from both roots and above-earth plant parts. This process, however, depends on several plant factors, as well as on the kind of Se compounds supplied to plants.[1569] As Lin et al.[1389] stated, biomethylation of Se converts inorganic soluble Se into organic volatile Se, which is released into the atmosphere. This process completely removes Se from the water-soil-plant system, and has a significant implication in removing excess Se from the Se-contaminated water-soil system. The first environmental problem of Se phytoextraction was in California (San Joaquin Valley), where drainage Se-enriched water threatens health, plant food, and fodder. Several plants were investigated for Se accumulation, mainly *Brassica, Astragalus,* and *Graminaceae* sp.[1407] Plant-based phytoextraction of Se is based on the removal of its mobile fraction from soil, which is selenate. Four plant species are identified as highly tolerant of salinity and boron in growing media. Among these plants, *Astragalus* sp. seems uniquely capable of accumulating Se to high concentrations in the presence of high soil sulfide levels. Parker and Page[1450] reviewed management strategies for the phytoremediation of Se-contaminated soils and concluded that any large-scale project to utilize these plants for Se dissipation will require further research. In general, soil Se uptake by plants depends on climatic condition, water regime of soil, oxidation-reduction, pH, and sesquioxide content of the soil. Combs and Combs[969] reviewed studies demonstrating the importance of the available Se content of local soils as the primary determinant of the Se content of food and feedstuffs of plant origin (Table 132).

The distribution of Se within plants differs, depending on several nutritional factors, but its concentration in growing points, in seeds, and also in roots was most often observed. Arvy et al.,[37] however, studied Se distribution between various organs of corn and did not find any significant differences.

In plants, Se partly resembles S in its biochemical properties and is able to replace S in amino acids as well as in several biological processes. About eight Se-organic compounds have been identified in plants.[254] Amino acids, especially cysteine, are likely to bind Se, which may have several metabolic implications. Volatile Se compounds (i.e., dimethyl diselenide) isolated from plants, and from Se-accumulating species in particular, are known to be responsible for Se release from plants and also for the unpleasant odor of plants (such as *Astragalus*).[222] As Zayed et al.[1569]

Table 132 **Selenium Contents of Food Plants from Areas of Different Se Levels in Soils[969] (ppb FW)**

Food Plant	Se Contents of Soils in China			Se Contents of Soils in the U.S.		
	Low	Moderate	High	Low	Moderate	High
Corn, grains	160	50	6900	—	4	12
Oat meals	—	—	—	440	110	280
Sweet corn	0.5–3	75–85	2800	7	4	12
Wheat, whole grains	6	40	1100	630	320	2400–21,300
Cabbage	—	2–38	2900	—	23	11
Potatoes, fresh	2	6	400	—	6	16

Table 133 **Mean Selenium Content of Mushrooms from Some European Countries[951,1119] (ppm DW)**

Mushroom	Finland	Norway	Poland[a]	Switzerland[a]
Boletus edulis	17	—	16, 16	14, 13
Macrolepiota procera	4.8	—	4.9	2.4, 0.7
Agaricus campestris	2.7	2.9	5.9	5.7, 3.6
Leccinum testaceoscabrum	0.6	1.3	1.1, 6.9	1.2
Lactorius deliciosus	0.9	—	2.0	1.2, 0.6
Cantharellus cibarius	0.07	0.17	0.23, 6.29	0.05, 0.17
Sarcodon imbricatus	—	0.18	3.06, 0.63	1.87, 1.66

[a] Two values given for mushrooms of different forest ecosystems.

reported, the uptake of Se by plants and its volatilization are highly governed by Se chemical species applied to plants and by variable plant ability to accumulate and immobilize Se in their tissues.

The ability of a plant to accumulate and tolerate Se is apparently related to different Se metabolisms. Opinions vary, however, as to whether Se is incorporated in proteins or in non-protein amino acids.[531,1569]

Toxicity of Se to plants growing under natural conditions has not been reported, but symptoms of Se toxicity to crop plants have been described (Table 40). In culture solutions, toxic effects of Se on onion roots were observed by Fiskesjö[232] at as low as 1 mg L^{-1} concentration. Also, a decrease in yield of several crops was effected by the application of about 2 ppm Se onto the soil.[729]

Increased Se levels in plants suppresses concentrations of N, P, and S as well as of several amino acids. Also, the absorption of heavy metals, mainly Mn, Zn, Cu, Fe, and Cd, is inhibited by increasing Se. This relationship is dependent on the ratio between the elements, and thus some stimulating effects of high Se concentrations on uptake of heavy metals may also be expected.

The application of P, S, and N is known to help in detoxifying Se, which may be a result either of depressing the Se uptake by roots or of establishing a beneficial ratio of Se to these elements, even when the Se content of plants is elevated. There is also a report that the addition of lime, S, B, and Mo to the soil under field conditions did not affect the Se concentration is plant tissues.[294] In practice, the application of S is an important remedial treatment on Se-toxic soils.[729] However, as Johnson[364] reported, S fertilizers are effective in preventing Se toxicity only to plants growing on low Se soils.

Ehlig et al.[202] reported that differences among plant species in Se accumulation from soils low in Se were small, with the exception of seleniferous indicator plants such as *Astragalus* sp. or other legumes which concentrate Se to extremely high levels (up to about 1000 ppm DW). Se seems to be easily absorbed from the atmospheric deposition since its content in mosses from the Scandinavian countries varies from 500 to 2900 ppb (DW).[1135,1223] Generally, high accumulations of Se in rootless mushrooms have also indicated its ready absorption from atmospheric sources (Table 133). The available systematic data concerning Se content of forage plants show that, for most countries, Se ranges in grasses from 2 to 174 ppb (DW, mean 33), for clover and alfalfa ranges from 5 to 880 ppb (DW, mean 99), and for other forage plants ranges from 4 to 870 ppb (DW, mean 67).

Table 134 Selenium in Forage Plants from Different Countries (ppb DW)

Country	Grasses		Clovers or Alfalfa		Hay or Fodder Plants		Ref.
	Range	Mean	Range	Mean	Range	Mean	
Canada	5–23	13	5–31	15	—	—	294
Denmark	—	32	—	35	—	44	265
Germany	30–210	110	50–130	90	—	—	578
Finland	1–54	11	—	—	2–48	14	221,371,734
France	19–134	47	36–39	38	29–35	31	37,551
	—	—	—	—	40–150	130	487
India	200–450	352	440–870	672	200–870	—	729,1141
Japan	5–174	43	6–287	33	—	—	395,765
Norway	—	—	—	—	4–28	13	371
Sweden	11–64	30	18–40	—	4–46	10[a]	473
	—	—	—	—	13–34	23	371
U.S.	10–40	32	30–880	320	28–360	98	14,265

[a] Cereal plants.

Table 135 Selenium Content of Cereal Grains from Different Countries (ppb DW)

Country	Cereal	Range	Mean	Ref.
Australia	Wheat	1–117	23	867
Canada	Barley	9–38	21	294
	Oats	4–43	28	294
Czech Republic	Wheat	11–49	25	1168
Denmark	Barley	2–110	18	265
	Oats	3–54	16	265
	Rye	6–72	16	265
	Wheat	4–87	21	265
Egypt	Wheat	140–430	340	213
Finland	Barley	<10–50	—	411
	Wheat	100–170	—	411
	All grains[a]	2–85	7	371
France	Barley	27–42	33	37
	Oats	20–44	35	37
	Wheat	30–53	36	37
Germany	Oats	70–140	110	578
	Rye	160–250	210	578
	Wheat	190–200	200	578
Japan	Oats[a]	8–17	—	765
	Rye[a]	—	22	765
Norway	Barley	—	8	247
	Oats	—	10	247
	Wheat	1–169	33	446
	All grains[a]	2–29	—	247
Sweden	All grains[a]	4–46	13	371
U.S.	Barley	200–1800	450	200
	Oats	150–1000	480	200
	Wheat	280–690	490	492
	Corn[a]	10–2030	87	371
Yugoslavia	Wheat	5.6–23.1[b]	—	1081a

[a] Animal fodder.

[b] Range of mean values.

The greatest amounts of Se were reported for India, Japan and Germany (Table 134). The Se levels in cereal grains vary greatly within the range of mean values from 7 to 490 ppb (DW) (Table 135), and presumably the controlling factor is its content in soils, which is clearly illustrated by the data presented in Table 132.

Table 136 Selenium Content of Food Plants from Different Countries (ppb)

Country	Plant	Tissue Sample	FW Basis	DW Basis	Ref.
U.S.	Sweet corn	Grains	—	11	705
	Cabbage	Leaves	8	150	574,705
	Lettuce	Leaves	1.6	57	574,705
	Carrot	Roots	5.3	64	705
	Onion	Bulbs	—	42	705
	Potato	Tubers	—	11	705
	Tomato	Fruits	—	36	705
	Apple	Fruits	1.1	2.6	574,705
	Orange	Fruits	3	7.7	574,705
China	Tea	Leaves		52–160 110[a]	1032
Czech Republic	Potato	Tubers	—	83	1168
	Apple	Fruits	—	8	1168
India	Tea	Leaves	—	21–420 180[a]	1032
Japan	Tea	Leaves	—	22–980 380[a]	1032
Yugoslavia	Garlic	Bulbs	3.2–62[b]	—	1081a

[a] Average content as given by the authors.

[b] Range of mean values.

The mean Se contents of all food plants do not exceed 100 ppb (DW) (Table 136).

The levels of Se in crops that are adequate and safe for animals are believed to be about 100 ppb (DW), although the requirements for Se vary widely with the form of the Se ingested and with other dietary factors. Disorders in livestock may be expected when Se concentrations in forage plants are within, or below, the order of 10 ppb (DW). Other threshold values, such as a lower toxic level of 3000 ppb Se and a minimum requirement of 100 ppb Se, are also proposed for grasslands.[395] Low Se contents of plants are known to be associated with "Keshan" disease in China. Xu and Jiang[1189] gave an Se range of 21 to 32 ppb (DW) in grass and soybean seeds for the endemic areas, and a range of 31 to 83 ppb for nonendemic areas. Se concentrations in crop and grassland plants vary significantly for both plant species and/or genotypes, as well as for soil and climatic conditions. A good illustration of the variability among plant species has been presented by Burau et al. *(vide* Wu[1552]), who calculated in 1988 the ranked geometric mean values of Se in edible tissues of crops sampled from the west side of the San Joaquin Valley, California. The range of Se was from <25 ppb in corn grain to 475 ppb in broccoli. The content of Se in plants, however, is highly controlled by soil; for example, garlic grown in alkaline Se-rich soil contains up to 600 ppb Se (FW), whereas garlic grown on acid soils poor in Se contain only 14 ppb Se (FW).[1395] The Se content of most food plants varies within the range from <1 ppb (FW) (cabbage) to 110 ppb (wheat flour).[969] Elevated levels of Se have always been observed in mushrooms (Table 133).

In general, the trend in variation of Se concentrations in plants indicates higher Se levels in plants from aridic zones than in those from humidic zones. It may be summed up that Se in plants is positively correlated with pH, salinity, and $CaCO_3$ in soils. High levels of Se in plants may also occur near seacoasts where the return of Se to land surfaces may be higher than in other regions because of sea spray.

The dietary Se intake by inhabitants of different countries has been broadly investigated in recent years. An increase of Se intake has been observed in some countries, especially in Finland, where Se applied to agricultural soils since 1983 has resulted in an increase of daily uptake by adult persons from 25 to 124 μg Se day^{-1}.[1296] Calculated daily intake of Se by inhabitants of other European countries in the period 1990 to 1995 was as follows (in μg day^{-1}): Czech Republic, 14 to 26; Turkey, 30; Germany, 33; Sweden, 38; Poland, 40; The Netherlands, 67; and Switzerland, 70.[1247,1296,1382] Some plants are known as especially good sources of dietary Se, for example, Brazil nuts, which naturally contain very high concentrations of Se. The average content of Se in nuts is

36 ppm (FW) when grown on Se-rich soils derived from Cretaceous limestones in the Amazon area, while nuts from other areas have average Se concentrations of 3.1 ppm (FW).[1253]

Pollution with Se is observed in industrial areas where Se is released into the atmosphere due to some metal-processing operations and by the combustion of coal. Some legumes (e.g., sweet-clover) grown on coal ashes are known to contain as much as 200 ppm (DW) Se.[296] Grass grown in the vicinity of a P fertilizer plant contained up to 1.2 ppm (DW) Se,[278] the edible mushroom *Agaricus bitorquis* from an urban area accumulated 11.2 ppm (DW) Se,[636] and tree leaves from a nearby Cu refinery contained from 141 to 550 ppm (DW) Se.[113] Fly-ash derived from refuse incineration is reported to be a significant source of Se, which is relatively easily available to plants grown on soils amended with this ash.[1180] On the other hand, there was little or no measurable uptake of Se by barley grown on soil with increased Se content up to 1.2 ppm, after sludge application.[1073a]

The phytoremediation of Se-enriched soils, especially in the western U.S. where drainage water contains Se as a natural contaminant or from urban and industrial (e.g., oil refineries) sources, has been the subject of recent studies.[1322,1389,1515] Transgenic plants (e.g., Indian mustard) may develop a mechanism of immobilization of Se in their tissues and serve in the phytoremediation of Se-contaminated soils. Also plant species (e.g., *Astragalus* and *Brassica*), which have the ability to absorb, accumulate, and finely volatilize Se, have been studied as a remedy to remove Se from contaminated sites.[1215] The action of the remediation of Se-enriched soils is of special importance because Se is one of the most biomagnified elements and therefore its increased level in soils creates a health risk to humans and wildlife. In areas with low soil Se, applications of sodium selenite to the soil or as a foliage spray are proposed for correcting Se nutritional deficiencies. In view of the toxic properties of Se salts, however, these practices should be carefully controlled.

III. TELLURIUM

The crustal abundance of Te has not been widely studied and the scarce data show that its content in rocks ranges from 1 to 5 ppb, apparently being elevated in organic shales (Table 127). The geochemical behavior of Te resembles Se in some respects, therefore, its association with S and sulfide minerals (e.g., hessite, Ag_2Te; sylvanite, $AuAgTe_4$; and tetradymite, Bi_2Te_2S), mainly in areas of Au, As, Sb, Ba, Hg, and Bi mineralization, has been observed.

Te shows variable valencies of +2 to +6 and, like Se, forms di- and trivalent oxides. During weathering, Te is oxidized to slightly mobile tellurites, and most commonly is sorbed by Fe hydroxides. The accumulation of Te in coals (0.02 to 2 ppm) indicates Te sorption also by organic matter. Asami et al.[1207] found elevated concentration of Te in soils in the vicinity of nonferrous metal smelters. Geometric mean values for Te in soils of different smelters range from 0.1 to 0.5 ppm, but the maximum value was reported to be 6.55 ppm.

Little data on Te occurrence in soils is available. Govindaraju[1313] reported that Te content in reference soils of China ranges from 0.03 to 4.0 ppm, and in reference soils of the U.S. is within the range 0.02 to 0.69 ppm. The given range of Te content in soils may suggest some biomagnification in upper soil horizons when compared with its range found in various rocks.

The biological cycling of Te is known to resemble that of Se, and the microbial metabolism of Te also seems to be similar to that of Se. Weinberg[856] stated that bacteria capable of methylating As and Se can also methylate Te, whereas the reduction of tellurite to Te can readily occur under the influence of a variety of microorganisms.

Apparently, Te occurs in plant tissues at concentrations lower than those of Se. Bowen[94] cited high Te accumulations, from 2 to 25 ppm (DW), in a few plants from Te-rich soils. Schroeder et al.[697] also reported a relatively high concentration of Te in soils (0.5 to 37 ppm) and in plants (0.7 to 6 ppm DW). Oakes et al.[574] gave the range in Te content of vegetables as <0.013 to 0.35 ppm (FW), being the lowest in apple fruits. Some high values given for the Te content of soils and plants may be errors and these values require further study. Mean Te content of Norwegian mosses is very low—0.0052 ppm.[1223] The garlicky odor of some plants is caused by vapors of dimethyl telluride. Concentrations of Te in onion and garlic are reported to be as high as about 300 ppm (DW).[697]

IV. POLONIUM

Po occurs in the geosphere and biosphere as natural radioisotopes, including ^{210}Po and several other short-lived radionuclides, all associated with the radioactive decay within uranium chains U-Ra-Pb.

The natural abundance of ^{210}Po in soil is reported to range from 8 to 220 Bq kg^{-1} and in land plants to range from 8 to 12 Bq kg^{-1} (DW).[94] Elevated contents of this radionuclide in some vegetables and tobacco plants can be derived from either the soil or the air and apparently reflect pollution with radionuclides.[549,710]

V. CHROMIUM

A. Soils

The terrestrial abundance of Cr indicates that it is associated mainly with ultramafic and mafic rocks in which Cr can be as concentrated as 0.X% (Table 127). The Cr content of acid igneous and sedimentary rocks is much lower and commonly ranges from 5 to 120 ppm, being the highest in argillaceous sediments.

Cr shows highly variable oxidation states (from +2 to +6) and it is also known to form complex anionic and cationic ions (e.g., $Cr(OH)^{2+}$, CrO_4^{2-}, CrO_3^{3-}). Naturally occurring Cr compounds have principal valences of +3 (chromic) and +6 (chromate). Highly oxidized forms of Cr are much less stable than Cr^{3+}.

Most of the Cr^{3+} is present in the mineral chromite ($FeCr_2O_4$) or in other spinel structures, substituting for Fe or Al. In general, Cr^{3+} closely resembles Fe^{3+} and Al^{3+} in ionic size and in geochemical properties. Chromite, the common Cr mineral, is resistant to weathering and therefore accounts for most of the Cr in residual material. However, under progressive oxidation, Cr forms the chromate ion (CrO_4^{2-}), which is readily mobile and also is easily sorbed by clays and hydrous oxides.

The behavior of soil Cr has been extensively studied by Bartlett and Kimble,[51] Bartlett and James,[50] Cary et al., [122] Bloomfield and Pruden,[82] and Grove and Ellis,[289] and recently by James et al.[1343] and Bartlett.[1218] A broad review of Cr balance in the environment is presented by Mukherjee.[1432] It has been shown that most of the soil Cr occurs as Cr^{3+} and is within the mineral structures or forms of mixed Cr^{3+} and Fe^{3+} oxides. Since Cr^{3+} is slightly mobile only in very acid media, and at pH 5.5 is almost completely precipitated, its compounds are considered to be very stable in soils. On the other hand, Cr^{6+} (CrO_4^{2-} and $HCrO_4^{2-}$) is very unstable in soils and is easily mobilized in both acid and alkaline soils (Figure 85).

El-Bassam et al.[205] emphasized that Cr behavior is governed by both soil pH and redox potential. Under the same redox potential of 500 mV, Cr^{3+} predominated at pH 5, $Cr(OH)_3$ was formed between pH 5 and 7, and CrO_4^{2-} occurred at pH >7. Griffin et al.[284] found that adsorption of Cr by clays is also highly pH dependent, and while Cr^{6+} adsorption decreased as pH increased, the adsorption of Cr^{3+} increased as pH increased. The behavior of Cr in soils may be modified by organic complexes of Cr; however, the dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} to Cr^{3+} (Figure 86). Wittbrodt and Palmer[1545] investigated the reduction of Cr^{6+} by soil humic acids, and described the difference between the rate coefficients for the humic acid and fulvic acid even from the same soil. The rate of the reduction depends on several soil parameters,

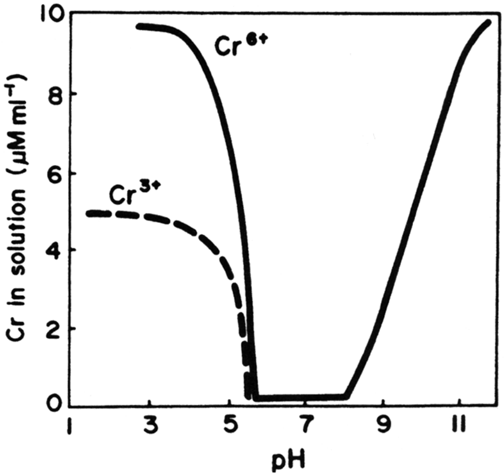

Figure 85 Solubility of trivalent and hexavalent Cr as a function of pH.[51]

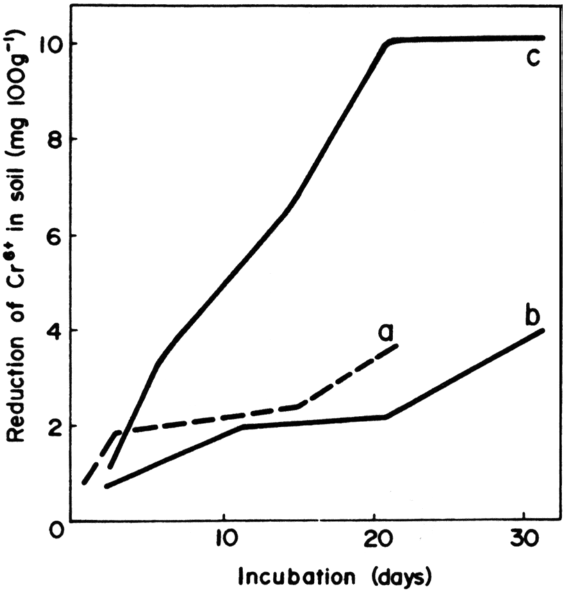

Figure 86 Reduction of Cr^{6+} by soil (pH 6.7) during the incubation. (a) Aerobic; (b) anaerobic; (c) anaerobic with added dry alfalfa material.[82]

and increases especially with soil acidity. The process can be adequately described by an empirical rate equation presented by these authors. Organic substances added as sewage sludge to the soil (loamy sand, pH 6.1) caused a significant increase of two Cr species—associated with hydrous oxides and bound to organic matter (Figure 87).

The ready conversion of soluble Cr^{6+} to insoluble Cr^{3+} under normal soil conditions is of great importance because it is responsible for the low Cr availability to plants. Although the reduction of Cr^{6+} and Cr^{4+} is commonly reported, the oxidation of Cr^{3+} in soils has also been observed, apparently as an effect of the oxidizing ability of Mn compounds.[50] Bartlett[1219] broadly described the mechanisms of Cr^{3+}/Cr^{6+} redox transformations in soil. As he has summarized, if thermodynamics ruled the behavior of Cr it would be oxidized, in most environmental conditions, to

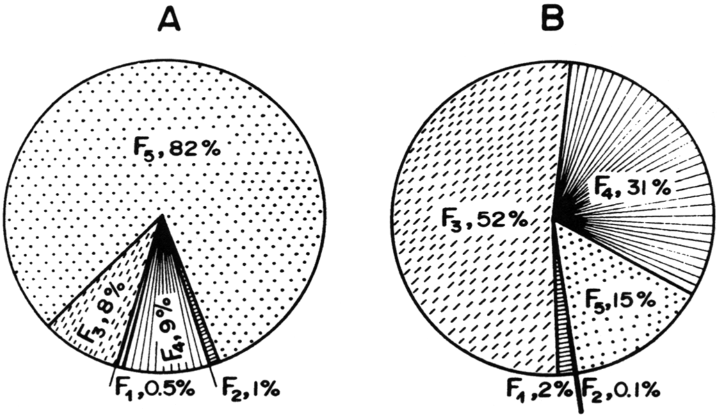

Figure 87 Variation in Cr species in soils under sludge application. (A) unsludged soil, (B) sludged soil. Cr species: (F_1) easily soluble; (F_2) exchangeable; (F_3) associated with hydrous oxides; (F_4) bound to organic matter; and (F_5) residual.[985]

the hexavalent state and thus would be easily available to all organisms. Fortunately, reduction and adsorption processes in field soils rule the behavior of Cr and its transfer in the soil-plant system. James et al.[1343] described the Cr^{3+}/Cr^{6+} balance as a seesaw with Mn and organic matter, where the soil pH acts as a controllable master variable that helps to set the oxidizing reactivity of Mn oxides *vs*. the reducing properties of organic matter or other compounds.

The soil Cr is inherited from parent rocks and therefore its higher concentration is in soil derived from mafic and volcanic rocks (Table 137). Soils on serpentines in particular are known to contain as much as 0.2 to 0.4% Cr. Sandy soils and histosols are usually poorest in Cr, and contain an average of 47 and 12 ppm, respectively (Table 9). The soil Cr reveals a significant positive relationship with contents of fine granulometric fraction.[1357] The grand mean Cr content is calculated to be 54 ppm for worldwide surface soils. In Finnish soils, the 90th percentile for Cr soluble (leached) in acids (HNO_3, HCl) is given as 50 ppm, while the 90th percentile of Cr-total content (fusion H_2F_2) is 150 ppm.[1368]

The immobility of soil Cr may be responsible for an inadequate Cr supply to plants. Cr is of nutritional importance because it is a required element in human and animal nutrition. However, as Cary et al.[122] stated, the Cr added to soil appeared to be very inefficient in terms of its recovery by food crops, although it caused an increase of this element in various plants.

Readily soluble Cr^{6+} in soils is toxic to plants and animals. Therefore, the variability in the oxidation states of Cr in soils is of great environmental concern. Pacha et al.[1111] reported harmful effects also of Cr^{3+} compounds on the biochemical activity of soils. The sensitivity of soil enzymes differs, the highest being for dehydrogenase (Figure 88).

The Cr content of surface soil is known to increase due to pollution from various sources, of which the main ones are several industrial wastes (e.g., electroplating sludges, Cr pigment and tannery wastes, leather manufacturing wastes) and municipal sewage sludges. The Cr added to soils is usually accumulated at the thin top layer. El-Bassam et al.[205] found that after 80 years of irrigation with sewage sludge containing 112 ppm Cr, the metal concentration in soil increased from 43 to 113 ppm. Other authors also reported a high Cr accumulation for surface horizons of sludged farmland, where the highest Cr levels ranged from 214 to 727 ppm [59,176,314,1173] Especially contaminated surface soils were found in a proximity of Cr smelter heaps where the metal concentration exceeds 10,000 ppm.[1173] Surface soil from the reclaimed land (1-m-deep layer above the Cr slag deposit) in Japan contains up to 4560 ppm Cr^{6+} (DW) due to the movement of this cation with capillary water and despite earlier reduction of Cr^{6+} to Cr^{3+} with $FeSO_4$ in the surface layer of the slag.[926] Izasáki et al.[1035] reported the movement of Cr pollutants to deeper layers of the sandy soil, where it was detected in groundwater at a depth of 2 to 3 m.

Table 137 Chromium Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Austria	1.4–3.5	—	6
	Canada	2.6–34	—	243
	Great Britain	5–360	42	944
	Madagascar	—	110	557a
	New Zealand	47–530[a]	—	861
	Poland	30–91	51	665
	Romania	12–86	42	1127
	U.S.	3–200	40	706
	Belarus	18–25	21	493
Loess and silty soils	Bulgaria	77–128	—	255
	Chad	180–300	—	39
	New Zealand	31–160[a]	—	861
	Poland	21–38	29	268
	U.S.	10–100	55	706
	Belarus	—	84	493
Loamy and clay soils	Austria	23–24	—	6
	Bulgaria	107–122	115	558
	Canada	4–46	19	243
	Chad	100–200	—	39
	New Zealand	70–1100[a]	—	861
	Poland	35–81	58	665
	Romania	19–73	40	1127
	U.S.	20–100	55	706
	Former S.U.	—	51	493, 631, 714
Soils on glacial till	Denmark	—	12	801
	Poland	10–46	25	974
	U.S.	30–150	80	706
Fluvisols	Austria	13–30	16	6
	Bulgaria	—	91	558
	Madagascar	—	190	557a
	Former S.U.	—	55	4, 493
Gleysols	Austria	—	19	6
	Poland	27–100	57	665
	Former S.U.	—	85	631
Rendzinas	Austria	—	38	6
	China	22–500	150	1124
	Ireland	35–50	—	236
	Madagascar	—	95	557a
	U.S.	5–150	50	706
Kastanozems and brown soils	Austria	11–31	19	6
	Romania	15–67	40	1127
	Former S.U.	—	72	714
Ferralsols	Burma	69–331	—	575
	Chad	100–280	—	39
	Madagascar	130–540	—	557a
Solonchaks and solonetz	Burma	81–110	82	575
	Chad	25–80	—	39
	Madagascar	—	215	557a
	Former S.U.	78–99	88	351
Chernozems	Bulgaria	116–173	153	558
	U.S.	15–150	55	706
	Former S.U.	71–195	121	4, 351, 714
Meadow soils	Former S.U.	30–110	—	631, 714
Histosols and other organic soils	Canada	4–39	15	243
	U.S.	1–100	20	706
	Denmark	1.8–10	7	1, 801
	Belarus	—	8	493
Forest soils	Bulgaria	152–1384	—	558
	U.S.	15–150	55	706
	Former S.U.	—	54	631, 714

(*Continued*)

Table 137 Chromium Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Various soils	Bulgaria	71–1085	221	558
	Great Britain	—	69	818
	Canada	11.6–189	50	409, 540
	Canada	10–100	43[b]	521
	Chad	4–80	—	39
	Denmark	—	15	801
	Italy	20–307	95	946
	Japan	3.5–810	50	395
	Poland	4–68	20	183, 1045
	Germany	9–57	28	325, 390
	U.S.	7–1500	50	706

[a] Soils derived from basalts and andesites.

[b] Data for whole soil profiles.

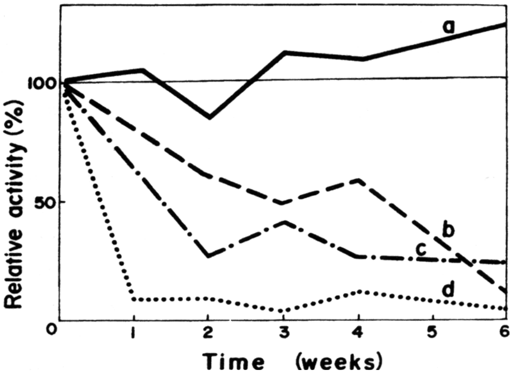

Figure 88 Enzymatic activity of beech forest soil as affected by Cr^{3+}(2000 ppm Cr as $CrCl_3$). Activity: (a) amylolitic; (b) alkaline phosphatase; (c) acid phosphatase; and (d) dehydrogenase.[1111] (Modified from Pacha et al.[1111])

Chaney et al.[130] extensively discussed the Cr hazard in biological waste management and stated that the food chain is well-protected from an excess of Cr by the “soil-plant barrier.” This statement, however, is not fully supported by the findings of Diez and Rosopulo,[176] who reported the ready availability of Cr from soils amended with sewage sludge. Solubility and toxicity characteristics of Cr^{3+} and Cr^{6+} in soil present a challenge for the establishment of MAC value by regulatory agencies. The rule proposed (“Hazardous Waste Identification Rule”) establishes the cumulative land application limit at 3000 kg Cr ha^{-1}, based on data showing no effects on plants (LOAEC) at this maximum level of Cr used in a field study.[1343] However, the Cr valence state and soil conditions for oxidizing Cr^{3+} should be considered.

Liming, P application, and organic matter are known to be effective in reducing chromate toxicity in Cr-polluted soils. If contamination of soil is by Cr^{6+}, acidification and then reducing agents (e.g., S and leaf litter) could be used to speed the Cr^{6+} reduction. After the reduction, liming to further precipitate Cr^{3+} compounds might be advisable.[289]

B. Plants

There is no evidence yet of an essential role of Cr in plant metabolism, although Mertz[534] has reviewed the positive effects on plant growth of Cr applications to soils having a low soluble Cr content. The Cr content in plants is controlled mainly by the soluble Cr content of the soils.

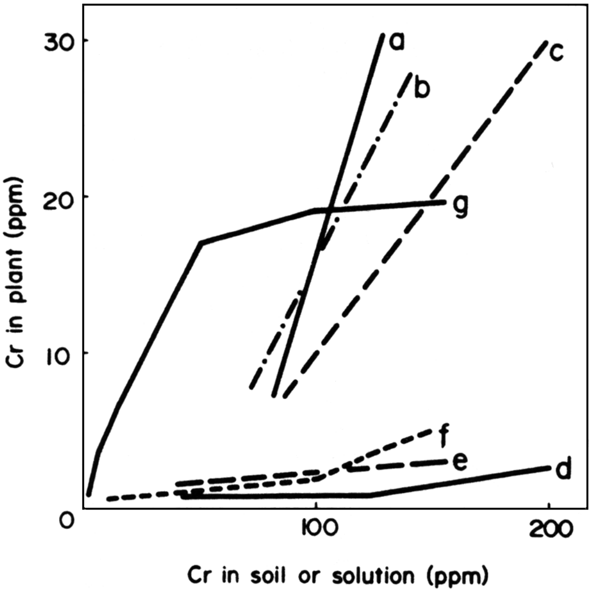

Figure 89 Concentration of Cr in plant tissues as a function of Cr content of soil. (a) Potato stalks; (b) corn leaves; (c) wheat straw; (d) wheat grains; (e) barley grains; (f) tomato tops; (g) tomato roots.[122,176]

Most soils contain significant amounts of Cr, but its availability to plants is highly limited. However, the addition of Cr to soil affects the Cr content of plants, and the rate of Cr uptake by plants is dependent on several soil and plant factors. Usually, a higher Cr content is observed in roots than in leaves or shoots, whereas the lowest concentration is in grains (Figure 89). Several native plants, mainly those from areas of serpentine or chromite deposits, can accumulate as much as 0.3% (DW) or 3.4% (AW) Cr.[535,613] The elevated Cr content of soils in such areas is known to be responsible for the poor growth of forest trees.[855]

A low rate of Cr uptake by plants from the soluble fraction of this metal is related to the mechanism of uptake by roots. Apparently, root tissues are not capable of stimulating the reduction of Cr^{3+} to readily soluble Cr^{2+}, which is the key process in Fe absorption by plants.[122,788] The form most available to plants is Cr^{6+}, which is the most unstable form under normal soil conditions. There are also reports on the easy absorption of CrO_4^{2-} anions by plant cells.[1110] Nevertheless, the mechanisms of absorption and translocation of Cr in plants seem to be similar to those of Fe, which is reflected in a fairly stable Cr/Fe ratio in plant tissues.[122] Tiffin[789] concluded that Cr is transported in plants as anionic complexes which have been identified in the extract of plant tissues and in xylem fluid. The presence of trioxalatochromate in plant leaves has been reported.[798] There is evidence that Cr^{6+} cations can be transformed in plant cells into Cr^{3+} cations, which readily interact with DNA and protein compounds. Pacha and Galimska-Stypa[1110] reported that Cr^{6+} compounds exhibit a strong mutagenic impact on *Bacillus subtilis* cells, while treatment with the Cr^{3+} compounds reveal slight mutagenic activities. Due to a low solubility, Cr^{3+} compounds are apparently not translocated through cell membranes.[1165]

The recent results of the experiments conducted by Zayed et al.[1570] have shown that patterns of accumulation and translocation of the two Cr ions (Cr^{3+} and CrO_4^{2-}) are rather identical. There is a great difference, however, in the accumulation of Cr by shoots and roots of various vegetable crops. The highest concentration of Cr, supplied in two forms (Cr^{3+} and Cr^{6+}), was found in roots of plants of the *Brassicaceae* family, and the lowest in roots of *Allium* sp. The Cr contents of shoots were much more uniform in all vegetable crops. The root to shoot translocation of Cr was quite limited due to the propensity of Cr^{3+} to bind to cell walls of roots. A highly increased accumulation

Table 138 Chromium Content of Food and Forage Plants (ppm)

Country	Plant	Tissue Sample	FW Basis	DW Basis	AW Basis	Ref.
Finland	Grass	Tops	—	0.11–0.35	—	388
Poland	Oats	Grains	—	0.55	—	1045
	Wheat	Grains	—	0.2	—	267
	Rye	Grains	—	0.16	—	1045
	Clover	Tops	—	0.2–4.2	—	1045
	Grass	Tops	—	0.6–3.4	—	27
U.S.	Buckwheat	Seeds	—	0.03	—	122
	Wheat	Grains	—	0.014	—	122,860
	Potato	Tubers	0.018	0.021	0.49	574,705
	Beans	Pods	0.009	0.15	2.3	574,705
	Lettuce	Leaves	0.008	—	<1.5	574,705
	Onion	Bulbs	0.002	0.021	0.5	705
	Carrot	Roots	0.018	—	<1.5	574,705
	Tomato	Fruits	0.004	0.074	0.62	705
	Apple	Fruits	0.008	0.013	0.70	574,705
	Orange	Fruits	0.004	0.029	0.80	705
	Alfalfa	Tops	—	0.10–0.91	—	122,200

of Cr in roots (up to 160 ppm), especially of Indian mustard and fodder radish, was observed in plants growing in Cr-polluted soil (247 ppm Cr) in the vicinity of a former galvanization plant.[1493] The Cr concentration in shoots of those plants did not exceed 10 ppm.

The Cr content of plants has received much attention since the relatively recent discovery that Cr participates in glucose and cholesterol metabolism, and therefore is essential to man and animals.[696] There is not much literature on Cr in plants. Common levels of Cr found in plant material are usually on the order of 0.02 to 0.2 ppm (DW); however, a relatively great variation is observed in the Cr content of food plants (Table 138). Concentrations of Cr in plants vary widely for kinds of tissues and stages of growth, and the trend in Cr variation appears to be irregular, as can be concluded from the data given by Mertz et al.[535] for various trees.

Although stimulating effects of Cr on plants have been observed by several authors, the phytotoxicity of Cr has been often reported, especially in plants on soils developed from ultrabasic rocks. Anderson et al.[23] reported toxicity in oats having a Cr content of 49 ppm (DW) where grown on soil containing 634 ppm Cr. Turner and Rust[810] observed initial symptoms of Cr toxicity with the addition of as little as 0.5 ppm Cr to the nutrient culture, and 60 ppm to the soil culture. These Cr additions resulted in decreased concentrations of almost al major nutrients in tops and of K, P, Fe, and Mg in roots. The antagonistic interaction between Cr and Mn, Cu, and B has also been reported by Turner and Rust,[810] and this can be related to interferences both within the soil medium and in the plant tissues. In some cases, however, synergistic interactions between Cr and Fe are also observed.

The toxicity of Cr depends on its oxidation state, but is also related to readily available forms of chromate. While a Cr_2O_7 addition at the 10^{-5} N concentration level decreased plant growth by about 25%, the same level of $Cr_2(SO_4)_3$ was without any effect on growth, but the Cr additions resulted in 2.2 and 1.3 ppm Cr, respectively, in bush bean leaves.[841] The phytotoxic concentrations of Cr in tops of plants were reported as follows (DW basis): 18 to 24 ppm in tobacco, 4 to 8 ppm in corn, 10 ppm in barley seedlings, and 10 to 100 ppm in rice.[171,279,395] Kloke et al.[1052] estimated that a very low Cr content, 1 to 2 ppm (DW), inhibits the growth of sensitive plant species. The toxic levels of Cr reported by Macnicol and Beckett[1081] are much broader and range from 1 to 10 ppm (DW). At the same dose (750 μg Cr per g soil) of Cr^{6+} and Cr^{3+}, an increased uptake of Cr and reduced oat yield was observed; however, the harmful effect and mobility were significantly greater in the case of Cr^{6+} addition.[1405]

Symptoms of Cr toxicity appear as wilting of tops and root injury; also, chlorosis in young leaves, chlorotic bands on cereals, and brownish-red leaves are typical features. Increased levels of Cr in the nutrient solution (up to 10^4 μM) are reported to disorganize the fine structure of chloroplasts and the chloroplast membranes of *Lemna minor* (duckweed).[53]

Anthropogenic sources of Cr are responsible for the elevated content of this metal in plants. Elevated contents of Cr (up to 600 ppm) in some phosphate fertilizers (Table 23) may be a significant source of this metal in soils. The most hazardous addition of Cr to a soil is related to tannery sludges, which can contain up to 2.8% of this metal.[1269] A special environmental concern, however, is the oxidation stage of Cr in tannery sludges, of which Cr^{6+} can reach 1459 μmol kg^{-1}.[1218] Czarnowska[158] reported mean Cr concentrations in grass near city streets to be as high as 17 ppm (DW). Kitagishi and Yamane[395] gave a range of Cr in lichens collected within urban areas to be 5 to 10 ppm (DW). Folkeson[239] found 5 ppm Cr (DW) in mosses near peat-fired plants and 9 ppm Cr in mosses from the edge of a waste heap of the ash, as contrasted with background concentrations of 1 to 1.5 ppm. Average content of Cr in Norwegian moss is 2.6 ppm.[1223] Gough and Severson[278] found 500 ppm Cr in ash of sagebrush from the vicinity of a P fertilizer factory. Vegetables grown in allotment gardens near the oil refinery in Plock (Poland) have elevated concentrations of Cr; the maximum contents are (in ppm): carrot roots 13, and leaves 148; red beet roots 6, and leaves 154.[1418]

Wastes containing increased Cr concentration are reported by Chaney et al.[130] not to be hazardous to human health; there is evidence of Cr toxicity to livestock grazing grass with an elevated Cr content due to rich Cr sewage sludge amendment.[381]

VI. MOLYBDENUM

A. Soils

The terrestrial abundance of Mo, estimated at about 3 ppm, shows its association with granitic and other acid magmatic rocks. The common range of Mo in these rocks is 1 to 2 ppm, while in organic-rich argillaceous sediments, the Mo content may be above 2 ppm (Table 127). Mo behaves both like a chalcophile and a lithophile element, and its geochemistry in the surface environments is related mainly to anionic species. The primary mineral of Mo^{4+}, molybdenide (MoS_2), is known to contain most of the terrestrial Mo and is associated with Fe and Ti minerals.

During weathering, Mo sulfides are slowly oxidized and yield mainly the MoO_4^{2-} anion which dominates in neutral and moderate alkaline pH ranges, and $HMoO_4^-$ which occurs at lower pH values. However, easily mobile anions are readily coprecipitated by organic matter, $CaCO_3$, and by several cations such as Pb^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and Ca^{2+}. Also, differential adsorption of Mo by Fe, Al, and Mn hydrous oxides contributes to the retention of Mo in surfacial deposits. All these reactions are highly dependent on pH and Eh conditions and therefore the net results of Mo migration during weathering may be poorly predictable.

The Mo content of soils usually resembles that of their parent rocks, and ranges from 0.013 to 17.0 ppm in world soils (Table 139). Kubota[435] gave the range of Mo in U.S. soils as from 0.08 to over 30 ppm and the median concentration as slightly more than 1 ppm. The Mo means for different soil units vary from 1.3 to 2.8 ppm (DW) for podzols and cambisols, respectively (Table 7). Thus, the world mean of 1.8 ppm calculated from these data appears to be reasonable and is supported by the value given by Wedepohl.[855] In general, soils derived from granitic rocks and from some organic-rich shales are likely to contain large amounts of Mo. Koljonen[1368] reported that the total content of Mo (fusion H_2F_2) in Finnish soils, at the 90th percentile, is 1.5 ppm. Govindaraju[1313] presented the results for Mo in reference soils from China to range from 0.3 to 18 ppm, and in soils from the U.S. in the range 1 to 2 ppm. A very high content of Mo, up to 24 ppm, is reported to be in soils of British Columbia (Canada) where commercial production of vegetables takes place.[1453] The median content of Mo in Lithuanian soils is 0.62 ppm and does not show any variability due to different soil texture.[1359]

The behavior of Mo in soils has been extensively studied because it has a rather unique position among other micronutrients in that it is least soluble in acid soils and readily mobilized in alkaline

Table 139 Molybdenum Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	2.6–3.7	—	792
	Canada	0.40–2.46	1.5	244
	New Zealand	1–2[a]	—	861
	Poland	0.2–3.0	—	382
	Yugoslavia	0.17–0.51[b]	—	687
	Russia	0.3–2.9	1.5	274, 914
Loess and silty soils	New Zealand	2.2–3.1[a]	—	861
	China	0.4–1.1	0.7	1068
	Poland	0.6–3.0	—	381
	U.S	0.75–6.40	2.5	434, 435
	Russia	1.8–3.3	2.2	274
Loamy and clay soils	Great Britain	0.7–4.5	2.5	819
	Canada	0.93–4.74	1.7	736, 244
	Mali Republic	0.5–0.75	—	39
	New Zealand	2.1–4.2[a]	—	861
	Poland	0.1–6.0	—	382
	U.S.	1.2–7.2	4.1	434, 435
	U.S.[c]	1.5–17.8	5.8	434, 435
	Russia	0.6–4.0	2	274, 914
Fluvisols	India	0.4–3.1[b]	1.6	645, 730, 455
	Czech Republic	2.8–3.5	3.1	973
	Mali Republic	0.44–0.65	—	39
	Yugoslavia	0.35–0.53[b]	—	687
	Russia	1.8–3.0	2.4	914
Gleysols	Australia	2.5–3.5	—	792
	Dahomey	—	3.0	617
	India	1.1–1.8[b]	—	544, 645
	Ivory Coast	0.18–0.60	—	650
	Yugoslavia	0.52–0.74[b]	—	687
	Russia	0.6–2.0	1.3	914
Rendzinas	India	1.4–1.8	—	455
	China	0.32–7.35	1.9	1124
	Ireland	—	1	236
	Poland	1–3	—	382
	Yugoslavia	0.76–1.03[b]	—	687
	U.S.	0.3–2.0	1.3	434, 435
	Russia	0.6–1.9	1.4	274, 914
Kastanozems and brown soils	Australia	3.5–6.9	—	792
	China	1–4	2.3	1068
	Ireland	<1–1	—	236
	Russia	0.4–2.8	1.3	343, 914
Ferralsols	India	1.3–11.6	—	455, 772
	China	0.5–5.1	3	1068
	Ivory Coast	0.4–10.0	—	650
	Madagascar	2.5–17.0	—	557a
Solonchaks	Former S.U.	0.9–5.7	2.4	12, 914
	Czech Republic	2.6–3.2	3	973
Chernozems	Former S.U.	1.6–4.6	2.6	274, 914
	Kirgiz Republic	0.6–0.8	0.7	1097
Meadow soils	Former S.U.	1.0–3.9	2.0	12, 274, 914
	Czech Republic	1.4–1.7	1.5	973
Histosols and other organic soils	Canada	0.69–3.2	1.9	244
	Russia	0.3–1.9	1.2	914
Forest soils	Bulgaria	0.3–4.6	—	39, 188
	China	—	2.2	225
	Former S.U.	0.2–8.3	3.1	420

(*Continued*)

Table 139 Molybdenum Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Various soils	Great Britain	1–5	1.2	785, 818
	India	0.013–2.5	—	772
	Italy	0.4–2.2	0.9	946
	Japan	0.2–11.3	2.6	395
	U.S.	0.8–3.3	2	434, 435
	Russia	0.8–3.6	2.2	914

[a] Soils derived from basalts and andesites

[b] Data for whole soil profiles.

[c] Soils from areas of the western states of Mo toxicity to grazing animals.

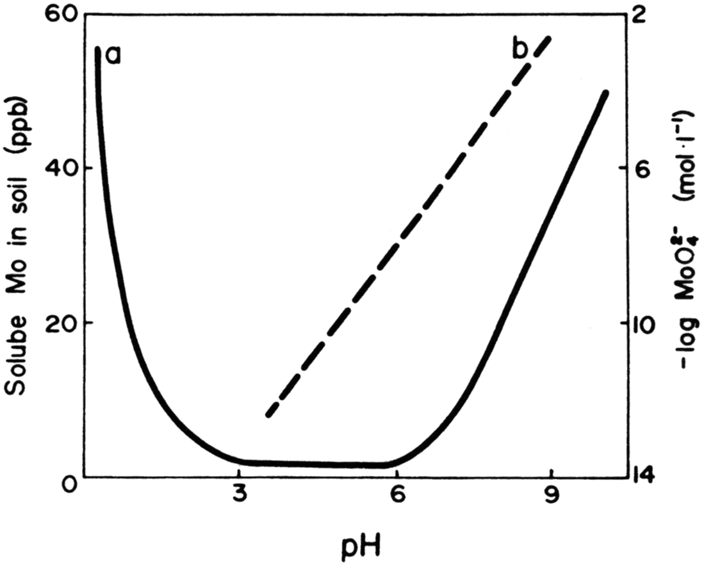

Figure 90 Solubility* of Mo (a) and activity of Mo (b) as a function of soil pH. *Soil containing 1.6 ppm Mo leached with HCl and KOH in the presence of 1 μM $CaCl_2$.[384,475]

soils (Figure 90). Vlek and Lindsay[827] and Lindsay[477] studied the behavior of different Mo minerals and concluded that soil solubility of Mo is very close to that of $PbMoO_4$-soils-Pb systems. This mineral (wulfenite), however, cannot be expected to be the most common Mo compound in soil. It seems most likely that a great proportion of soil Mo is associated with matter and Fe hydrous oxides. This is supported by findings of Čumakov,[973] who studied the Mo speciation in various soils. He found the highest proportion of Mo to be associated with polymeric organic compounds resistant to oxidation processes. Other kinds of organic substances also reveal a higher affinity to Mo than clay minerals (Table 140). Due to the great affinity of Mo to be fixed by organic matter, its concentration in forest litter can reach 50 ppm.

Kraushkopf,[427] Norrish,[570] and Lindsay[477] have reviewed findings on Mo behavior in soils and have concluded that, in the inorganic forms, Mo is associated mainly with Fe oxides, probably as an adsorbed phase. The molybdate adsorbed on freshly precipitated $Fe(OH)_3$ is readily exchangeable; but as the precipitate ages the Mo becomes less soluble and ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 8H_2O$) or other slightly soluble Fe-Mo semicrystalline forms may occur.

Table 140 Molybdenum Species in Soils (mean values for chernozems and fluvigleysols)[973]

Species	Content of Mo Species ppm (DW)	% of Total Mo
H_2O soluble	0.097	3.5
Fixed on clay surface	0.269	9.8
Fixed by organic substances occluding sesquioxides	0.455	16.8
Fixed by organic substances (only)	0.439	16.2
Fixed by polymeric organic compounds resistant to oxidation	0.846	31.3
Fixed by inorganic C-particles	0.150	5.6
Residual	0.458	16.8

The solubility, and thus availability of Mo to plants, is highly governed by soil pH and drainage conditions. Mo from wet alkaline soils is most easily taken up, but the geochemical processes involved in this phenomenon are not completely understood. Apparently, this uptake is related to the high activity of MoO_4^{-2} in an alkaline medium (Figure 90), as well as to an ability to form soluble thiomolybdates under reducing conditions (e.g., MoS_4^{-2}, $MoO_2S_2^{2-}$). Lindsay[477] assumed that plants growing in a reducing environment are capable of transporting O_2 through the stem to the roots, and therefore Mo compounds close to the root surface become more oxidized and thus more soluble. The impact of sewage sludges on the mobility and phytoavailability of Mo has been observed.[1357]

On acid soils ($pH < 5.5$) low in Mo, and especially on those with a high Fe oxide level, Mo is hardly available to plants. The low availability of Mo that occasionally appears in peat soils seems to be affected by strong fixation of Mo^{5+} by humic acid following the earlier reduction of the MoO_4^{-2} as stated by Mengel and Kirby.[531] On the other hand, organic-rich soils can supply adequate amounts of Mo to plants due to a slow release of this element from organic bond forms.

Liming of acid soils is a common practice to increase Mo availability to plants. However, at higher rates of liming, the solubility of Mo may decrease due to its adsorption by $CaCO_3$.[772] The application of Mo salts also increases the available Mo pool in soils, and it is preferable to liming when an increase in soil pH is not desired. Great caution must be taken in Mo fertilization, as this can result in high Mo levels in fodder. This method for assessing the need for Mo application has been extensively described in several textbooks. Ammonium oxalate solution is currently used in many laboratories to extract the available Mo from soil, as well as hot water leaching.[151]

Soils in arid and semiarid regions, especially ferralsols, generally have higher Mo contents. However, in humid and temperate regions, soils over Mo-rich material may also contain hazardous amounts of Mo. These soils, and soils polluted with Mo, need amelioration to depress the Mo availability to plants. The application of S is most effective, whereas increasing the soils P is known to stimulate Mo uptake by plants.

Industrial pollution (mining, smelting, processing of metals, and oil refining) may be responsible for elevated Mo concentrations in soils. Hornick et al.[324] found 35 ppm Mo in the soil surrounding a Mo processing plant in the U.S., and Schalscha et al.[1139] reported Mo accumulation up to 38 ppm (range of 22.2 to 38.2) in surface soils at a similar site in Chile. Some sewage sludges contain elevated amounts of Mo (up to 50 ppm) and may have an impact by both enriching the total Mo content and increasing the solubility of soil Mo.[314,452] Also, fallout or the application of fly-ash from some coal-fired power plants should be considered as potential sources of Mo, since even if only small amounts of Mo are added, its availability is increased by the alkaline reaction of the fly-ashes. Mo is also frequently found in sludges (at average concentration of 40 PM DW),[1116] in forms easily available to plants. Where Mo-enriched sludges are destined for application to land, crops should be monitored to ensure that Mo concentrations are within safe limits, especially for grazing animals.

B. Plants

1. Absorption and Biochemical Functions

Mo is an essential micronutrient, but the physiological requirement for this element is relatively low.

Plants take up Mo mainly as molybdate ions, and its absorption is proportional to its concentration in the soil solution. Although there is no direct evidence, there is a suggestion of the active uptake of Mo.[548] Mo is moderately mobile in plants, but the form of translocated Mo is unknown. Tiffin[788] discussed the possibility of organic complexing, mainly of the Mo-S amino acid complex that was found in the xylem fluid.

Mo, the essential component of nitrogenase and nitrate reductase, is also present in other enzymes (oxidases) that catalyze diverse and unrelated reactions. The basic enzymatic role of Mo is related to its function as redox carrier and is apparently reflected in the valency change between Mo^{6+} and Mo^{5+}.[564] Ivchenko[1034] reviewed findings on Mo functions in the metabolism of plants and emphasized a high concentration of Mo in nucleic acids and its inhibitory and regulatory functions in enzymatic activities of DNA and RNA.

Normally, there is 1 ppm (DW) or less of Mo in leaf tissues, whereas nodulated roots contain several times these concentrations. Most of this Mo apparently is in the nitrate reductase of root and shoot and in the nitrogenase of the nodule bacterioids. Two Mo-containing enzymes in N metabolism are involved in either N_2 fixation or NO_3 reduction. Thus, the requirement of plants for Mo appears to be related to the N supply; plants supplied with NH_4-N have less need for Mo than those utilizing NH_3-N.

Mo is known to be essential to microorganisms, and some bacteria species are able to oxidize molybdenite in soils. Rhizobium bacteria and other N-fixing microorganisms have an especially large requirement for Mo. Some fungi and nitrogen-fixing bacteria tend to concentrate Mo up to 100 ppm.

Since the most important function of Mo in plants is NO_3 reduction, a deficiency of this micronutrient causes symptoms similar to those of N deficiency. Some plants, however, also show more specific Mo deficiency symptoms (e.g., “whiptail” in cauliflower) (Table 38).

A deficient Mo content of plants depends on various factors, in particular, on interactions with other elements. Requirements for Mo are generally met at concentrations within the range of 0.03 to 0.15 ppm (DW) in tissues of most plants; only some leguminious crops require more Mo (Table 36).

Although easily soluble soil Mo is also readily taken up by plants and some plant species are known to accumulate much Mo, its toxicity symptoms in plants under field conditions are very rare, whereas toxicities to animals feeding on forages high in this element are well-known. The only relatively high concentration of Mo that was toxic, 135 ppm (DW), was reported by Davis et al.[171] for young spring barley.

Crop response, particularly of leguminous crops, to Mo application has been widely reported for soil conditions throughout the world, especially for acid and ferralitic soils. While correction of Mo deficiencies may be accomplished by Mo application as soil, foliar, or seed treatments, care must be taken in its use since Mo may be very toxic, even at quite low concentrations, in fodder plants. Therefore, the preferable control of Mo deficiency is liming the soil to a pH of around 6.5.

2. Interactions with Other Elements

Several complex interactions between Mo and other elements are observed within plant tissues and also in the external root media (Figure 30). The most important interactions are those between Cu, Mo, and S, which are differentially governed by diverse factors. The Mo-Cu antagonism in plants is strongly related to N metabolism (Chapter 6, Section V.B.3). Mo-S relations may have antagonistic or stimulative effects on Mo uptake by plants, depending on the rate of application of S-containing fertilizers.[581] However, a wide range of combinations between Cu, Mo, and S in herbage and, further, in animal nutrition, may occur. Gartrell[257] has reviewed this topic and made a few generalizations showing that soil factors that increase the availability of Mo to plants usually have inhibitory effects on the Cu uptake by plants and that the physiological barrier to Mo uptake by plants is much less effective than that to Cu uptake. Nutritional effects of Cu/Mo ratios in pastures on animal health is controlled by the sulfate concentration in plants, and an increased level of SO_4^{2-} may reduce Cu absorption with even small amounts of Mo. It has been established that soils with 5 ppm Mo can be associated with growth retardation and lower reproduction in cattle due to the Mo-Cu nutritional relationship.

Mo-Mn antagonism resulting from soil acidity influences the availability of these elements; therefore, liming can correct both Mo deficiency and Mn toxicity. Mo-Fe interactions are demonstrated as low Mo availability in Fe-rich soils, whereas increased Mo levels may induce Fe deficiency, or accentuated Mn-induced Fe chlorosis. Although mechanisms of the various interactions are not well-understood, the formation of Fe-Mo precipitates within root tissues may be responsible for low Mo translocation.[581]

Mo-W and Mo-V metabolic interactions are not precluded, since a substitution is possible between these elements in biochemical processes. A Mo-P interaction is often demonstrated as an enhancing effect of P on Mo availability in acid soils, apparently due to both a higher solubility of the phosphomolybdate complex, as well as to a higher Mo mobility within plant tissues. However, reported effects of P fertilizers on Mo availability are contradictory, and while the ordinary SO_4-containing superphosphate reduced Mo uptake, concentrated superphosphate increased Mo uptake.[3] Thus, Mo-P interactions are variable and highly governed by diverse soil factors and are also related to plant metabolic processes. Mo-Ca interactions are complex and highly cross-linked with the range of the soil pH.

3. Concentrations in Plants

No simple relationship is apparent between the total Mo content of soils and plants, although some authors have reported a linear relationship for Mo content of herbage and its total concentration in soil. The Mo concentrations in plants closely reflect the soluble Mo pool, for Mo seems to be very readily absorbed by plants when present in soluble forms. The Mo uptake by plants is a function of soil pH (Figure 91). Usually a positive correlation is observed between the relative Mo uptake and the soil pH.[784] This has been clearly demonstrated by Doyle et al.,[193] who found

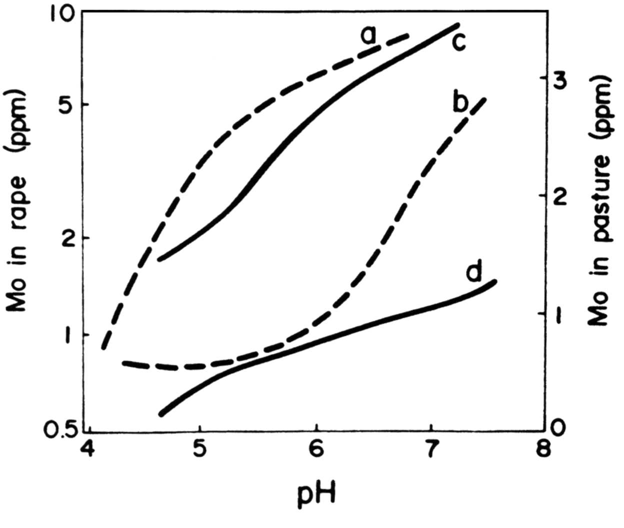

Figure 91 The effect of soil pH on the Mo content of (a) pasture on peat bog soil; (b) pasture on mineral soil; (c) rape, shoots; and (d) rape, roots.[275,384]

Table 141 Molybdenum Content of Grasses and Legumes from Areas Where Mo Toxicity in Grazing Animals Was Not Observed (ppm DW)

	Grasses		Legumes		
Country	Range	Mean	Range	Mean	Ref.
Bulgaria	—	—	0.04–0.32	0.18	220
Canada	0.4–8.0	1.3	—	—	192
Czech Republic	—	0.3	—	—	154
Finland	0.14–0.80	0.38[a]	—	—	221
	0.23–0.91	0.45	0.20–1.3	0.70	591,727
Germany	0.08–1.04	0.33	0.21–5.0	0.80	31,65
Germany	0.42–0.88	0.70	—	—	596
Great Britain	0.5–4.0[b]	—	—	—	784
	0.25–1.47	0.56	—	—	543
Ireland	0.18–0.77	—	0.28–0.52	—	235
Japan	0.04–3.05	0.72	0.01–3.64	0.92	770
Poland	<0.02–1.68	0.33	0.02–3.56	0.50	1045
Sweden	0.2–4.8	1.4	0.3–20.5	2.5	384
U.S.[c]	0.5–2.0	—	<0.7–15.0	1.8	710
U.S.	—	—	0.01–3.46	0.73	435
Russia	—	—	1.31–3.61	2.3	337

[a] Grass heavily fertilized with N.

[b] Pasture herbage.

[c] Calculated from AW basis.

Table 142 Molybdenum Content of Forage Plants from Areas Where Mo Toxicity in Grazing Animals Was Observed (ppm DW)

	Grasses		Legumes		
Country	Range	Mean	Range	Mean	Ref.
Canada	0.6–17.0	4.0	1.0–20.0	5.2	192
	2.4–12.0	5.0[a]	4.8–6.0	5.4[a]	237
Great Britain	0.1–7.2	1.5[b]	—	—	784
Sweden	1–234[b]	—	—	—	384
U.S.	0.7–6.8	3.7	18.9–39.6	26.6	434
Russia	10–50[b]	—	—	—	420

[a] Samples from the periphery of a Mo ore body.

[b] Pasture herbage.

abnormally high Mo values (up to 52 ppm, mean 11 ppm) in native plants grown on neutral or alkaline soils, whereas on Mo-rich acid soils, and Mo-low soils, Mo concentrations in the same varieties of plants averaged respectively, 0.9 and <0.2 ppm.

Some native plants, particularly leguminous species, are known to accumulate as much as about 500 ppm (AW) Mo, or about 350 ppm (DW), without showing toxicity symptoms.[556,618] The Mo content of forages is of special concern; therefore, most available data are on the Mo status in grasses and legumes. Mean Mo levels range from 0.33 to 1.5 ppm (DW) in grasses and from 0.73 to 2.3 ppm in legumes from different countries. In areas where Mo toxicity was observed in grazing animals, the Mo content of grasses ranged from 1.5 to 5.0 ppm (DW) and in legumes from 5.2 to 26.6 ppm (DW) (Tables 141 and 142). In general, greater than 10 ppm (DW) Mo levels in forage present a serious problem to most classes of livestock. In pasture, Mo is known to vary with different stages of plant development and with periods of the growing season. The reported Mo content was high in the spring and autumn seasons.[384] Phillips and Meyer [1117a] observed a decrease in Mo concentrations of alfalfa fields known for high Mo levels, during the period from 1950 to 1985. The decline in Mo average contents from 10.78 to 3.57 ppm is, according to these authors, caused by leaching of soluble salts with irrigation, acidification of soils by N fertilizers, and crop removal.

Table 143 Molybdenum Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis (574, 705, 1187)	DW Basis (337, 589, 705, 910)	AW Basis (705)
Sweet corn	Grains	0.045; 0.22	0.18	6.9
Kidney bean	Seeds	—	0.9–1.6	—
Pea	Seeds	—	1.2–1.75	—
Snap bean	Pods	0.23	2.1	30.0
Carrot	Roots	<0.08; 0.015	0.04	<7.0
Sugar beet	Roots	—	0.45–0.75	—
	Leaves	—	0.39	—
Lettuce	Leaves	0.005	0.074	0.53
Cabbage	Leaves	<0.099	0.85	9.1
Potato	Tubers	0.047	0.25, 0.15	5.9
Onion	Bulbs	0.024; 0.016	0.24, 0.16	5.6
Cucumber	Fruits	<0.087	0.82	8.3
Tomato	Fruits	0.042; 0.024	0.82	6.8
Apple	Fruits	0.0018	0.07	3.9
Orange	Fruits	0.014	0.11	3.1
Tea	Leaves	—	0.2–0.3	—

Note: References are given in parentheses.

Table 144 Molybdenum Content of Cereal Grains from Different Countries (ppm DW)

Country	Plant	Range	Mean	Ref.
Canada	Barley	—	0.29	293
	Oats	—	0.41	293
	Wheat	—	0.18	293
Czech Republic	Barley[a]	0.28–0.41	0.32	563
	Oats	0.59–0.84	0.69	563
	Wheat[b]	0.18–0.42	0.32	563
Finland	Barley	0.19–0.49	0.33	727
	Oats	0.21–0.59	0.40	727
	Rye	0.23–0.57	0.40	727
	Wheat[b]	0.14–0.38	0.26	727
Norway	Barley	0.02–0.59	0.16	446
	Wheat	0.07–1.09	0.29	446
Poland	Wheat[b]	0.20–0.60	0.35	267, 335
Sweden	Barley	0.54–1.00	0.79	384
U.S.	Barley	0.58–2.4	0.92	200
	Oats	0.28–1.9	0.88	200
	Wheat[a]	0.08–1.1	0.49	200
	Wheat[b]	0.40–1.1	0.64	200
	Rice	0.18–3.05	0.66[c]	1187
Russia	Barley	0.69–0.75	0.72	337
	Oats	0.42–0.62	0.50	337
	Rye	0.12–1.31	0.50	337, 501
	Wheat	0.26–1.31	0.64	337

[a] Spring wheat.

[b] Winter wheat.

[c] FW basis.

Plant foodstuffs contain variable amounts of Mo within the range 0.0018 to 1.23 ppm (FW), 0.07 to 1.75 ppm (DW), and 0.53 to 30 ppm (AW), with legume vegetables being in the upper range and fruits being in the lower range (Table 143). The Mo content of cereal grains averages 0.49 ppm (DW) and does not show a great variation under widely ranging field conditions (Table 144). Recent data presented by Brüggemann et al.[1247] for Mo in plant foodstuffs, collected in Germany during the period 1989 to 1994, are as follows (in ppm): rye grain, 0.539; wheat grain, 0.394; potato (unpeeled tubers), 0.210; and dehydrated potato, 0.007. The concentration of Mo in grass is of great concern, since grazing cattle can suffer from Mo toxicity, especially when there is a low content of Cu (ratio Cu:Mo below 4 to 5) and low S supply in forage.

The ready availability of Mo causes a great increase in uptake when plants are grown in contaminated sites. Karlsson[384] found up to 200 ppm DW of Mo in pasture plants from the vicinity of a metallurgical factory. Hornick et al.[324] reported that plants grown on the Mo-polluted soil near a Mo processing plant accumulated this element in concentrations ranging from 124 to 1061 ppm (DW) in lettuce and cabbage, respectively. Furr et al.[250] found that beans and cabbage grown on soil amended with municipal sludge ashes had an increased Mo content up to 18 and 19 ppm (DW) contrasted to the control values of 0.8 and 0.4 ppm, respectively. Thus, elevated Mo concentration in soils resulting from industrial pollution or agricultural practices may be locally responsible for the pronounced abnormal Mo content of plants. For example, grasses grown in the vicinity of a Mo ore-processing plant in Chile contain as much as 6.5 to 36.0 ppm (DW).[1139]

VII. TUNGSTEN

The distribution of W in the Earth's crust shows that its concentration seems to increase with increasing acidity of magmatic rocks and with increasing clay content of sedimentary rocks (Table 127). The common W contents of acid granitoids and of argillaceous sediments range from 1 to 2 ppm, whereas in mafic rocks and sandstones or limestones the W range is 0.5 to 1.1 ppm.

All W minerals are only slightly soluble and hence have low mobility in hypergenic environments. Shcherbina[716] reported that WO_4^{2-} as well as W-complexed compounds may be readily transported in a particular geochemical environment. Presumably, the geochemical behavior of W resembles that of Mo.

There is a scarcity of data concerning the occurrence of W in soils. Ure et al.[819] found a range of W from 0.68 to 2.7 ppm in Scottish soils derived from different parent material, with the highest value for soil over quartz-mica schist and the lowest in the soil over serpentine. Furr et al.[250] reported 1.2 and 2.5 ppm W in two soils of the U.S. These authors gave the W content of two sludge ashes as 43 and 186 ppm. Recent data for W in the reference soils from China gave a broad range from 0.95 to 85.5 ppm, and in soils from the U.S. a range from 0.5 to 5 ppm.[1313] The soils of Finland contain 2.23 ppm W at the 90th percentile range.[1368] Panova[1115] described W species in polluted soils surrounding a W ore-processing plant in the former Soviet Union. The total W contents of soils varied from 100 to 2000 ppm (DW), of which 50% was present in the forms of primary minerals, 30% was H_2O soluble, 15% was bound to Fe oxides, and 5% was associated with organic matter (HA and FA).

Apparently, like Mo, W is easily available to plants under certain conditions; therefore, its concentrations are likely to be elevated in plants growing on soil overlying W ore bodies. Wilson and Cline[882] found that barley grown in soils with added ^{185}W removed a large proportion of that radionuclide and that the lower uptake from acid soil suggested that plants probably take up an anionic form, WO_4^{2-}. Also Bell and Sneed[62] reported a high accumulation of ^{185}W, release from nuclear reactions, in plant roots.

Shacklette et al.[710] reported that Curtain and King found the range in W concentrations in trees and shrubs of the Rocky Mountains in Colorado to be 5 to 100 ppm (DW), with the highest value in juniper stems. Connor and Shacklette[145] found a W range from 30 to 70 ppm in ash of single tree samples. Duke[197] reported the range of W in various food plants to be <0.001 to 0.35 (DW). Bowen[94] gave the overall range of W as 0.0 to 0.15 ppm (DW) in land plants, 0.01 to 0.15 in edible parts of vegetables, and 0.02 to 0.13 ppm in lichens and bryophytes. Mosses of Norway have a broad range of W, from <0.002 to 1.5 ppm.[1223] Furr et al.[249] found W to range from 0.7 to 3.5 ppm (DW) in vegetables growing on soil amended with fly-ash. Panova[1115] studied W distribution in semiarid herb (mother wort) grown in the vicinity of a W industry and observed a linear decrease of W content, from 600 to 50 ppm (AW), with increasing distance from the pollution source.

Gough et al.[279] reviewed the possible toxicity of W to plants, which appears to be moderate. Plants growing in a mineralized zone contained up to 18 times the background W value of 2.7 ppm without showing toxicity symptoms.

There are some suggestions of a possible biological significance of W in plants. Nicholas[564] mentioned that when W is substituted for Mo in the nitrate reductase enzyme, it has no catalytic activity. Apparently, W^{6+} is more stable than Mo^{6+} and does not readily change its valence. Zajic[898] described the antagonistic influence of W on Mo activity in N-fixation, but this effect is differentially governed by the pH of the media. There are some observations that W can be readily taken up by plants under specific soil conditions.[1448]

CHAPTER 12

Elements of Group VII

I. INTRODUCTION

Geochemical and biochemical characteristics of the elements in Group VII are widely diverging. Trace elements of the Subgroup VIIa (new group 17) the halogens (F, Cl, Br, and I), are much less common in the biosphere than Cl which some authors include also as a trace element. The last element of this subgroup, astatine (At), occurs as radioactive isotopes of very short lives. In nature, halogens form simple anions or, except F, combine with oxygen anions and play a significant role in biochemical processes. These anions are highly mobile in the Earth's crust although they are considered to reveal lithophile properties.

Of the Subgroup VIIb (new group 7) Mn is the only element essential to living organisms and is common in natural environments. Technetium (Tc) does not occur in nature because all of its radioactive isotopes are short-lived. However, Tc is potentially hazardous via soil-plant pathways in view of the high probability of its release in significant amounts during a reactor accident. ^{99}Tc is reported to have an extremely high transfer factor from soils to wheat, reflecting the high level of its phytoavailability.[1016] Metallic Tc is a product of fission and reveals chemical features similar to Re. Re is a dispersed element in nature and, like Mn, has variable valency and shows lithophile or chalcophile character.

II. FLUORINE

A. Soils

F is a typical lithophile element under terrestrial conditions, and its larger concentration (850 to 1200 ppm) is found in intermediate and acid siliceous igneous rocks (Table 145). In sediments, F is known to be associated with clay fractions and therefore is likely to occur in larger amounts in argillaceous deposits. A high concentration of F is known to be associated with some phosphate deposits over large areas (e.g., in Africa and the U.S.). Appreciable quantities of fluorite (CaF_2) also occur in some limestones and dolomites as fissure veins and in other forms.

There are not many stable F minerals; the most common are topaz ($Al_2(F,OH)_2SiO_4$), cryolite (Na_3AlF_6), and fluorite (CaF_2). Free F may sometimes occur in rocks in gaseous nebulae. Compounds of F are also important constituents of magmatic gases and volcanic exhalations.

F reveals an affinity to replace hydroxyl groups in minerals, and these reactions have resulted in fluoroapatite ($Ca_{10}(PO_4)_6F_2$), the most common F mineral, and have also been responsible for increased amounts of F in amphiboles, micaceous minerals, etc. A strong association of F with phosphates is also observed in both primary and secondary minerals.

Table 145 Fluorine, Chlorine, Bromine, Iodine, and Manganese in Major Rock Types (ppm) (values commonly found, based on various sources)

Rock Type	F	Cl	Br	I	Mn
		Magmatic Rocks			
Ultramafic rocks Dunites, peridotites, pyroxenites	50–100	40–80	0.2–1.0	0.01–0.50	850–1500
Mafic rocks, Basalts, gabbros	300–500	60–300	0.5–3.0	0.08–0.50	1200–2000
Intermediate rocks Diorites, syenites	500–1200	100–300	1–4	0.3–0.5	500–1200
Acid rocks Granites, gneisses	520–850	130–200	0.3–4.5	0.2–0.5	350–600
Acid rocks (volcanic) Rhyolites, trachytes, dacites	300–700	200–300	0.2–1.0	0.1–0.5	600–1200
		Sedimentary Rocks			
Argillaceous sediments	500–800	160–180	5–10	1.0–2.2	400–800
Shales	500–800	160–200	6–10	2–6	500–850
Sandstones	50–270	10–20	1–5	0.5–1.5	100–500
Limestones, dolomites	50–350	150–300	6	0.5–3.0	200–1000

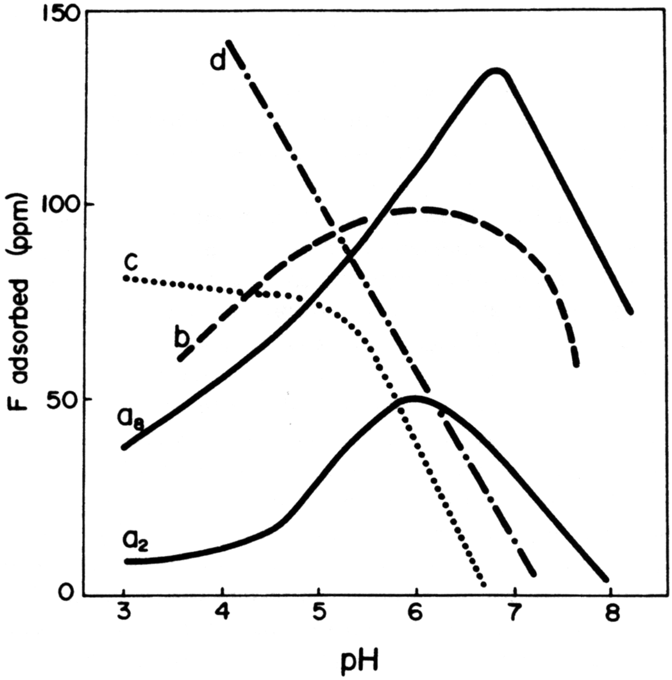

Figure 92 Adsorption of F by soil and clay as a function of pH. (a_2 and a_8) Soil equilibrated against 2 and 8 mg F^- per liter solution, respectively; (b) bentonite; (c) bauxite; (d) kaolinite. All clays equilibrated against 2 mg F^- per liter solution.[583]

During weathering, F combined with siliceous minerals remains in residual materials. Fluoroapatite and fluorite dissolve slowly, while cryolite (Na_3AlF_6) and similar minerals are readily soluble. Mobile F is easily sorbed by clays and phosphorites.

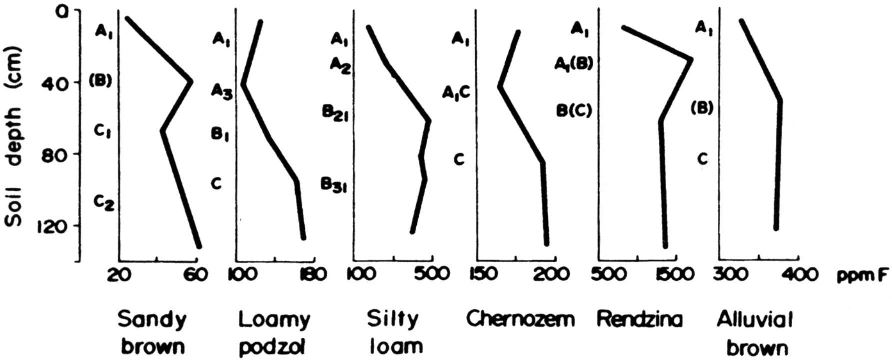

Figure 93 Distribution of F in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

The behavior of F in soils has been studied by Larsen and Widdowson,[461] Perrott et al.,[607] Chhabra et al.,[137] and Omueti and Jones.[584] The results obtained show that the mobility of F in soils is complex and that the predominant factors controlling the level of this ion in the soil solution are the amount of clay minerals, the soil pH, and the concentrations of Ca and P in soils. In general, the greatest adsorption of F by soil mineral components is either at the distinct acid range of pH, or at about pH 6 to 7 (Figure 92). Soil can accumulate relatively high amounts of F, particularly in B horizons, which usually have high levels of amorphous Al-oxides/hydroxides. The maximum sorption of F occurred at pH 4.8 to 5.5.[1205]

Fluoroapatite is considered to be the most common form of F in soils. However, several fluorides (e.g., CaF_2, AlF_3) and aluminosilicates (e.g., $Al_2(SiF_6)_2$) are also reported to occur in soils. F is also known to form complex ions most easily with Al (AlF^{2+}, AlF_2^+, and AlF_4^-; therefore, the mobile F^- in the soil solution might control the activity of Al^{3+} in soils.[477]

As F is known to readily replace hydroxyls of clays, the clay minerals, illites in particular, are believed to be the seat of most of this element in soils. The range of F content of illite and chlorite mineral groups is reported as 0.1 to 2.3% by Thomas et al.[781]

Under natural soil conditions, F is slightly mobile, but it is not accumulated in the surface horizon, especially of acid soils. The high solubility of F in acid soils is attributed to the occurrence of readily soluble fluorides such as NaF, KF, and NH_4F, whereas AlF_3 is known to be of low solubility. Thus, the increasing F content with depth reflects the response to the soil pH; however, the enriched clay content usually contributes more to the F distribution in soil profiles. This relationship with clay content has been reported by Piotrowska and Wiacek[619] and Omueti and Jones.[584]

In calcareous soils, the formation of slightly soluble CaF_2 and F complexes with Fe, Al, and Si are responsible for the low migration of this element. In sodic soils, on the other hand, a high exchangeable Na affects increased solubility of F.

The F concentration in soils is inherited from parent material, whereas its distribution in soil profiles is a function of soil-forming processes, of which the degree of weathering and clay content are the most pronounced. Apparently, F has been lost from the surface horizons of most soils (Figure 93) and this reflects partly a low F affinity for organic matter. Omueti and Jones[584] gave the range in F concentrations in organic matter of surface horizons to be as low as 0.03 to 0.12 ppm.

The average F content of worldwide soils has been calculated to be 329 ppm and to be 360 ppm for U.S. soils (Tables 9 and 146). In general, the lowest F amounts are in sandy soils in a humid climate, whereas higher F concentrations occur in heavy clay soils and in soils derived from mafic rocks. The range for most normal soils seems to be from 150 to 400 ppm, but the overall variation is much broader, and in some heavy soils F levels above 1000 ppm have been found. Much higher

Table 146 Fluorine Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Poland	20–150	83	619
	Sweden	41–198	90	568
	U.S.	<10–1100	205	200, 706
Loess and silty soils	Poland	122–228	175	619
	U.S.	30–600	395	200, 706
Loamy and clay soils	Poland	250–750	418	619
	Sweden	248–657	450	568
	Great Britain	110–700	462	819
	U.S.	<10–800	410	262
Fluvisols	Russia	1175–1360	—	73
Soils on mafic rocks	Great Britain	470–680	566	819
Rendzinas	U.S.	<10–840	360	200, 706
Solonchaks	Russia	444–1024	—	73
Chernozems	Russia	454–1194	—	73
	U.S.	<10–940	350	200, 706
Histosols and other organic soils	Sweden	42–123	73	568
	U.S.	10–300	250	200, 706
	Russia	333–335	—	73
Forest soils	Russia	463–652	560	73
Various soils	Great Britain	113–580	360	1000, 1001
	Germany	80–1100	460	855
	Japan	260–520	370	855
	Russia	30–320	200	855
	U.S.	<10–1050	300	262

Table 147 Fluorine Contamination of Surface Soils (ppm DW)

Site and Pollution Source	Maximum or Range of Content	Country	Ref.
Old mining area	2000	Great Britain	166
Al-processing industry	1350	Czech Republic	500
	1500–3200	Poland	85
Other metal-processing industry	305–345	Poland	512
China clay industry	1200–3560	Great Britain	1001
P fertilizer manufacturer or application	308–2080	Canada	478, 782
	385[a]	Poland	620

[a] After 10 years of P fertilizing, against the background value of 296 ppm F.

levels of F (exceeding 1000 ppm DW) in uncontaminated soils are reported for areas of the F high bedrocks,[1001] most often associated with the provinces of endemic fluorosis.[73]

Naturally occurring F in soils is slightly available to plants. Hall[300] found that in particular tropical soils, organically bound F (monofluorinated compounds) may occur. These compounds are shown to be highly available to plants, and highly toxic to animals. Their origin, however, is not yet clear, but presumably they are synthesized by certain microorganisms.

The F-emitting industrial sources are mostly Al smelters and phosphate fertilizer factories, but also coal combustion, steel works, brick yards, and glass and china works may significantly contribute to the total F pollution. Moreover, artificially high soil F levels can occur through contamination by the application of phosphate fertilizers or sewage sludges, or from pesticides (Table 147). Assuming a high F content of phosphate fertilizers (Table 5), an input of F to arable soils may be of ecological importance.

Fluoride emissions from industrial sources are known to introduce soluble fluorides into the surface layer of soils. Fluorides moving down the soil profile extract those elements which form stable, soluble fluoro-complexes. The F compounds added to soils by pollution are usually readily soluble and thus available to plants. Most of the added F to soil is either effectively fixed by soil components (clays, Ca, and P) or readily removed from light soils by water. More F is usually absorbed by acid soils than by alkaline soils. The sorption of F by acid soils has been attributed to interaction with Al oxyhydroxy species present.[1118] Easily soluble F-bearing fertilizers (e.g., potassium fluoroborate) or sewage sludges may effect a remarkable increase in the bioaccumulation of F from soils.[166,857]

The most important hazard of F contamination in soils concerns changes in soil properties due to the great chemical activity of hydrofluoric acid which is temporarily formed from both solid and gaseous F pollutants. Bolewski et al.[85] reported the decomposition of clays and other silica minerals in soil having heavy F pollution. They also reported the destruction of humic mineral complexes resulting in a significant loss of organic matter in soils. The reduction of enzymatic activity of some soil microorganisms with the addition of NaF has been reported by Russel and Świecicki.[670] Thus, the availability of F in polluted soils is a function of a number of soil characteristics and is not the only cause of limited plant growth on those soils. Continued F deposition will affect its accumulation in the surface soils and may increase the availability to plants and soil biota.

Presently, great attention is given to the possible formation of highly toxic organic F compounds that can be synthesized by both higher plants and microorganisms under various soil conditions.[288] Although a high level of F in soils is not in itself harmful to plants, F-polluted soils should be ameliorated for a proper growth of vegetation. The application of materials which increase the sorption capacity or fixation ability for F ions is known to improve soil properties and to limit F uptake by plants. Recent findings of Grishko[1318] have indicated that soil microorganisms using organic nitrogen forms are more resistant to the harmful effects of F pollution than bacteria using inorganic nitrogen compounds.

B. Plants

1. Absorption and Transport

The availability of F to plants is usually not closely related to the total or soluble F content of a soil. However, under certain soil and plant conditions, the F content of plants seems to reflect its occurrence in soils.[723] Bieliyakova[73] gave the ratio of F in plant ash to F in topsoils as 0.2 and 0.6 for cultivated and natural vegetation, respectively. These values indicate a relatively low F bioavailability. F concentration in orange leaves, however, showed a fairly close relationship with hot-water-soluble F in soil.[1210] The stimulating effect of increased levels of Cr^{6+} in soils on F uptake by plants has been observed, but the mechanism is not yet understood.[1574]

The soluble F fraction in soil is taken up passively by roots and apparently is easily transported in plants. This statement is supported by the observation of a ready F uptake from fields irrigated with F-containing waters. Most often, the availability of F increases with decreasing soil pH.

Vandeputte[1176] found that F absorption from the solution media by alfalfa and wheat is positively correlated with F concentration. He obtained results that indicated a very high accumulation in the grains (up to 3250 ppm DW at 50 ppm F^- in solution). This phenomenon reflected a possible influence of the formation of an F complex that may be more easily taken up by plants than are F ions.

Although it has been shown that plants can take up F quite easily from polluted soils, the bioavailability of soil F is of much less significance than that from airborne compounds. The effects of atmospheric F depositions, both in soils and on plant surfaces, have been extensively studied. The results, as summarized by Groth[288] and Weinstein,[857] have indicated that the deposition of airborne F on soil has little or no effect on the F content of plants, but that this conclusion is not a unanimous one. However, when F is present as both an air pollutant and a soil pollutant, the F uptake by plants from air is much more significant than their uptake from soil. Several factors affect plant accumulation of airborne F, but the most pronounced are atmospheric F concentration and the duration of exposure (Figure 94).

Foliar uptake of gaseous F apparently follows the path of the penetration of other gases into the leaf. Chamel and Garbec[125] reported that F penetration through the cuticle is slight; however, under

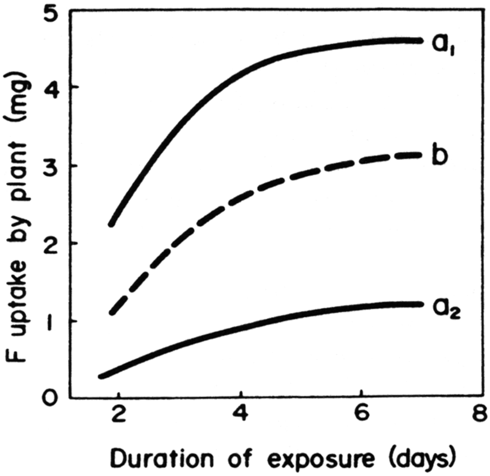

Figure 94 F uptake by plants as a function of the F contamination in air and of exposure time. (a_1 and a_2) Beans (tops) at the F concentration of 11 and 5 μg m^{-3}, respectively; (b) tomato plants at F concentration of 5 μg m^{-3}.[381]

natural conditions, most leaf surfaces have open stomata and also show breaks and punctures that facilitate the F uptake by foliage. Soluble F compounds are also known to be absorbed through the cuticle when deposited on the leaf surface. When F is accumulated in vegetative tissues during exposures to gaseous HF, it is not translocated to the developing grains.[499] Biological factors such as plant species, stage of development, and others are very important determinants of F accumulation.

2. Biochemical Roles

Centuries ago, symptoms of F toxicity to animals were observed after volcanic eruptions. During the last century, the role of plants as a sink for emitted F and in its transfer to animals was recognized. Contemporary investigation on grasses collected immediately after the eruption of Hekla volcano in Iceland in 1970 showed that their F content was 4300 ppm (DW), and that it rapidly decreased during 40 days to a concentration of less than 30 ppm.[598]

At present, F is considered to be the most hazardous and the most phytotoxic trace pollutant among the common air pollutants such as O_2, SO_2, and NO_x. The phytotoxicity of airborne F is influenced by ecological and biological factors and also by the physical and chemical characteristics of the pollutant.

The literature on the biological aspects of plant pollution by F has recently grown at an astonishing rate. Among other excellent monographs, the effects of atmospheric F on plants have been extensively reviewed by Groth,[288] Kluczyǹski,[401] and Weinstein.[857]

There is no evidence of F phytotoxicity when this element is absorbed by roots, whereas airborne F, especially when it occurs as hydrofluoric acid, is highly toxic. The most emphasized effects of F on plant metabolism are related to:

1. Oxygen uptake decrease
2. Respiratory disorder
3. Assimilation decrease
4. Reduction in chlorophyll content
5. Inhibition of starch synthesis
6. Inhibition of pyrophosphatase function
7. Altered metabolism of cell organelles
8. Injured cell membranes
9. Disturbance of DNA and RNA
10. Synthesis of fluoroacetate, a most hazardous F compound

Although Shkolnik[718] and Weinstein[857] have reviewed studies on plant growth stimulated by F, neither a plant requirement for this element nor its essential role in plant metabolism has been established. As Weinstein[857] described, the apparent stimulation of some isoenzymes (e.g., acid phosphatase and dehydrogenase) by HF fumigation may, in fact, be the result of the inhibition of other enzymes.

Interactions between F and other elements are not unanimously agreed upon. There is some evidence that an increased F content is likely to inhibit the absorption of several nutrients, whereas a synergistic effect, mainly to P uptake, has also been observed (Table 43). In general, a sufficient supply of major nutrients increased plant tolerance to F.[47]

Mutual pollution by SO_2 and F is reported to cause more significant damage to pine trees than changes induced separately by these pollutants.[663] The reactions of plants exposed to F pollution, even before any visible symptoms of F toxicity occur, are retarded growth, inhibited reproduction, and yield reduction. However, the most significant effect of increased F concentrations in plants is toxicity to animals. Thus, the F content of forage crops seems to be of greater ecological concern than that of other plants. However, recent findings of increased F levels in food plants, especially of fluoro-organic residues in several vegetables, indicate a possible toxicity to man.[539]

The best-documented plant responses to F are foliar symptoms such as chlorotic and necrotic lesions and deformation of fruits. These symptoms are not specific, and mimicking symptoms induced by other agents as well as the increased susceptibility of F-polluted plants to microbial diseases have been observed by Treshow[805] and Weinstein.[857]

Plants exhibit a broad range of tolerances to foliar injury by F pollution. Several lists of the tolerant and susceptible plant species are given in the literature. Commonly listed as tolerant are asparagus, bean, cabbage, carrot, and willow; while barley, corn, gladiolus, apricot, pine, and larch are classified as susceptible. However, a great variability in plant response to F accumulation in tissues is observed even between cultivars or genotypes of the same species. The response of plants is also highly dependent on several environmental and biologic factors. Based on Weinstein's report,[857] it can be generalized that susceptible plants would be injured by foliar F concentrations that ranged between 20 and 150 ppm (DW), intermediate plants can probably tolerate an F content in excess of 200 ppm, and highly tolerant plants do not exhibit injury below 500 ppm.

The effects of plant F on humans and, particularly, on animals is of the greatest concern. Opinions vary as to the toxic threshold values of F in forage, but 30 to 40 ppm (DW) is commonly reported.[166,288,766] More tolerant animals (e.g., lambs and turkeys) may tolerate a higher F concentration in their rations. Direct ingestion of sludge and soil with elevated levels of F by grazing cattle may be as important a source of dietary F as that ingested in herbage.

3. Concentrations in Plants

The F content of plants has been investigated for a number of reasons such as assessing its hazard to grazing animals, the diagnosis of plant injury, and for monitoring airborne F pollutants. Most of the information on F accumulation in plants has been determined for forage crops and native vegetation. Data on F concentrations in food plants are rather limited (Table 148). Higher concentrations of F have usually been reported for the aerial parts of plants. The F content of plants grown in uncontaminated areas is very unlikely to exceed 30 ppm (DW).

According to general opinion, plant F seems to be positively correlated with the concentration of F in rainwater. Davison et al.[173] discussed a method of the prediction of F concentrations in pasture using multiple regression techniques and including data on aerial deposition of F and rainfall. Several plants, especially forage vegetation, when growing in polluted areas are reported to contain large amounts of F (Table 149). Most of the F pollution is likely to be deposited on the leaf surface, which has been shown by findings of Fuge and Andrews.[1001] They reported F in unwashed grasses from an area of china clay industry to range from 756 to 3240 ppm (DW), whereas F ranged from 330 to 1410 ppm in grasses from the same area washed in distilled water. Results of the pot experiment,

Table 148 Fluorine Content of Food and Forage Plants (ppm DW)

	F Range or Mean Content as Given for Different Countries				
Plant	Tissue Sample	West Germany[710]	Sweden[568]	U.S.[288]	Other Countries[73,146,173,381]
Barley	Grains	1.7	0.5–5.5	<1–2	—
Oats	Grains	0.5	0.2–0.9	<1–2	—
Wheat	Grains	1	0.4–1.4	<1–2	—
Corn	Grains	0.2–0.4	—	—	—
Cabbage	Leaves	1.5	—	—	311[a]
Lettuce	Leaves	4.4–11.3	—	—	—
Spinach	Leaves	1.3–28.3	—	—	—
Carrot	Roots	2	—	—	—
Beet, red	Roots	4–7	—	—	<300[a]
Onion	Bulbs	3	—	—	<300[a]
Potato	Tubers	1.5–3	0.1–1.1	—	69[a]
Apple	Fruits	1.3–5.7	—	—	7
Pear	Fruits	2.1–4.4	—	—	—
Peach	Fruits	0.21	—	—	—
Alfalfa	Aerial parts	—	1.5–3.2	1–9	—
Clover	Aerial parts	6.7	2.8–7.8	—	—
Grass	Aerial parts	6.8	—	3–6	5–18, 310[a]
Forages	Aerial parts	—	0.3–1.3	4–17	36–98

[a] AW basis.

Table 149 Excessive Levels of Fluorine in Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Maximum or Range of Content	Country	Ref.
Mine waste	Grass, tops	130–5450	Great Britain	146
Al-processing industry	Vegetation, foliage	396	Canada	478
	Shrub,[a] leaves	150–500	Australia	557
	Cereals, grains	14–36	Poland	63
	Clover, tops	14–173	Poland	768
	Grass, tops	1330	Czech Republic	500
	Grass, tops	75–340	Poland	381
	Birch, leaves	230	Norway	261
	Pine, needles	48	Norway	261
	Lichens	27–241	Great Britain	606
Brick kilns	Pasture plants	160	Great Britain	166
China clay industry	Grass,[d] tops	576–3240	Great Britain	1001
Fiberglass plant	Vegetation, foliage	945	Canada	478
Phosphate rock processing	Tree,[b] foliage	71–900	Canada	782
	Vegetation, foliage	70	Canada	478
	Sagebrush, tops	100–360[c]	U.S.	278
	Pine, needles	60	Former S.U.	923
Fumigation with F	Alfalfa	1327	—	857
	Grass	496	—	857

[a] *Melaleuca nodosa.*

[b] Balsam fir.

[c] AW basis.

[d] Unwashed samples.

however, clearly indicate that soil F is not an important source of this element to red maple and orchard grass.[1243] Pine needles are common and good indicators for F pollution (Table 149). Pine needles from the vicinity of an aluminum smelter contain above 1000 ppm F, while the background value for F in pine needles in Poland is below 20 ppm.[1260] The toxicity limits for F in orange leaves range from 75 to 125 ppm, and some trees of orchards in Spain have F greater than this limit.[1210]

III. CHLORINE

A. Soils

Cl is a common halogen element under terrestrial conditions. Its concentrations are variable, especially in sedimentary rocks, the lowest being in sandstones (Table 145). There are not many stable Cl minerals. Most often it is associated, together with F, with micaceous minerals, apatite, hornblende, and some feldspars. Cl is very mobile during both hydrothermal and hypergenic processes. Under specific conditions, mobile Cl^- anions are easily associated with some metals forming such minerals as AgCl, $PbCl_2$, $Cu_2Cl(OH)_3$, etc.

Most commonly, however, Cl^- and complex Cl anions are easily soluble, leached from soil profile, and transported to water basins. Thus, Cl geochemistry, similar to Br geochemistry, is closely related to water chemistry and to evaporite deposits. Bodek et al.[948] described that almost no soil retention occurs, and therefore Cl in solution moves through soil at virtually the same speed as the displacing solution.

In soils of humid climate zones, Cl^- is leached down the profile and transported with drainage waters, whereas in soils of arid and semiarid climates, Cl^- is known to be concentrated in surface horizons. Cl is typically the predominant anion in saline soils. Solonetz and solonchaks are highly enriched in NaCl as well as in other salts which are inherited from parent material. Concentrations of Cl in solonchaks usually vary from 0.0X to 0.X%. In soil solutions, the Cl content may reach the level of X.0%.

Like other halogens, the distribution of Cl in soils exhibits a clear trend of decreasing concentration with increasing distance from the sea. Låg and Steinnes[445] found in Norwegian forest soils close to the sea a Cl range from 475 to 1806 ppm with an average of 920 ppm, while soils farther from the sea contained Cl within the range 174 to 375 ppm with an average of 265 ppm. Yuita et al.[1194] also found Cl in Japanese forest soils (in surface horizons) from the coastal plain to range from 91 to 486 ppm with an average of 228 ppm. In topsoils from upland fields, Cl ranged from 56 to 305 ppm with an average of 114 ppm.[1194]

Excessive amounts of salt (NaCl) applied to soils has resulted in increasing concern for environmental quality.[1159] Salt-affected soils due to anthropogenic activities result, in most instances, from the application of de-icing salt to roadways, field irrigation with highly mineralized waters, salt water spills associated with the extraction of oil, natural gas deposits, and some coals. Wind erosion of salt evaporites is also known to affect the Cl enrichment in soils.

Extremely high loadings of Cl in the soils have highly deleterious effects on both soils and vegetations. Increased levels of Cl^- in soil solutions influence behavior of several cations. As Hahne and Kroontje[1021] calculated, the solubility of $Zn(OH)_2$ and $Hg(OH)_2$ is significantly greater in 1.0 M chloride solution than their conditional solubility. Cl affinity for forming easily soluble complexes with Cd in soil is of environmental concern.

B. Plants

The availability of Cl to plants is related to the associated cations. The Cl^- ions are more readily absorbed in the presence of monovalent cations than di- and trivalent cations. The soluble Cl fraction in soils is taken up passively by roots, and is easily transported in plants. Cl can also be absorbed directly by plant leaves from aerial sources, and some plant species are capable of extracting their total Cl requirements from aerial sources via their leaves. Plants may accumulate relatively large amounts of Cl, especially halophytes occurring in coastal regions and in arid or semiarid climate zones.

Cl contents are reported to be in cereal plants from about 10 to 20 ppm (DW). In sugar beet leaves, the Cl range is 100 to 200 ppm, and in potato tubers from 1300 to 5500 ppm.[943] Several other plants can also contain high levels of Cl depending on growth conditions. For example, leaves of coconut palm growing at distances up to 25 km from the sea coast contain up to 7000 ppm Cl.[943]

Cl is considered a micronutrient for higher plants. Plants require a relatively low level of Cl for metabolic processes. Cl plays a role in photosynthesis and is significantly concentrated in chloroplasts. However, the requirement for Cl in photosynthesis remains in doubt.[1184] These anions also participate in phosphorolysis processes and in the activity of cytochromoxidase.[943]

Cl deficiencies are not observed often, but may occur when plants are growing in soils with Cl contents below 2 ppm. Generally, Cl is present in sufficient quantities in most soils to meet its requirement for most crops. But for some crops (e.g., tobacco), the Cl level of 10 to 15 ppm in soils is beneficial. Common symptoms of Cl deficiency are chlorotic leaves and brown edges.

Toxic Cl levels in plants vary depending on plant tolerance. Bergman[943] reported that a general threshold concentration of Cl is 2700 ppm (DW). Plants may suffer from too high Cl contents in soil solutions or water cultures. The less tolerant plants (e.g., beans, apple trees) are inhibited by Cl concentrations from 460 to 673 mg L^{-1}, whereas resistant plants (e.g., tobacco, cereals, tomato, cotton, beets, and spinach) can grow at Cl contents from 887 to 3546 mg L^{-1}.[943] The most toxic to plants are HCl and Cl_2 gases emitted from industrial sources. Strong necrosis of leaf edges is the most common symptom of these injuries. High levels of Cl associated with KCl fertilization can also adversely affect crops, especially potato tuber quality, in particular due to forming mobile complexes with Cd.

IV. BROMINE

A. Soils

The common abundance of Br in the Earth's crust varies within the range of 0.2 to 10 ppm, being the highest in argillaceous sediments (Table 145). Most Br compounds are similar to their corresponding Cl compounds, and therefore the close correlations of Cl and Br in various rock types have often been reported. The Br:Cl ratio is an important factor for defining various geological units.[855]

There are very few naturally occurring Br minerals (e.g., bromyrite, AgBr, iodobromite Ag(Br,Cl,I)), and several polyhalides which are known to be unstable in hypergenic environments. Br is a very volatile element and its salts are readily soluble. Therefore, its geochemistry is closely related to water chemistry and to evaporite deposits.

Coal and organic matter are known to accumulate Br, and a strong correlation of Br with organic carbon has been reported for both superficial sediments and soils.[855,875] Låg and Steinnes[445] assumed, however, that Br enrichment in top soil horizons is principally an effect of its precipitation with rain. This conclusion is supported by the findings of Yuita et al.[897] that a considerable part of the Br accumulated in soils of the temperate monsoon climate is directly due to the long retention period of Br from rainwater by soils. Despite the observed sorption capacity of hydroxides of Al and Fe, organic matter, and clays for Br, it is known as the element most easily leached from soil profiles, and its transportation to ocean basins in large amounts is often reported.

The few studies of the Br contents of soils show that its common range varies from 5 to 40 ppm (Table 150). According to recent data, the range for Br in the reference soils from China is from 2.6 to 7.2 ppm, and in the soils from the U.S. is from 1.4 to 7.8 ppm.[1313] Soils of Finland contain 10 ppm Br at the 90th percentile range.[1368] Gerzabek et al.[1308] calculated an arithmetic mean content at 5.7 ppm Br in about 40 topsoils of Austria (range 2.4–11.9 ppm). According to these data, Br reveals a significant positive correlation with exchangeable calcium and organic carbon, but only in calcareous soils. The highest Br amounts are reported for Japanese soil derived from volcanic ash or andesite and also different Norwegian soils from the north.[445,890] In both cases, the source of the large amounts of Br in topsoils is apparently related to atmospheric inputs either from volcanic exhalation and sea evaporation or from human activities. Yuita[1194] reported that soils at the Sea of Japan coast may accumulate significant Br, up to 495 ppm, mainly in the top horizon.

The main anthropogenic source of Br is its release in automobile exhaust, but some Br used agriculturally as a soil fumigant (methyl bromide) and as a component of K fertilizers may also add to

Table 150 Bromine Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols	Poland	7.9–8.2	—	181
Volcanic ash soils	Japan	50–104	—	897
Gleysols	Great Britain	—	34	875
Brown earths	Great Britain	—	52	875
Forest soils	Japan	68–130	—	897
Various soils	Great Britain	10–515	74	818, 875, 1000
	Norway, Northern	16–100	45	445
	Norway, Eastern	5–14	7	445
	Czech Republic	0.7–4.6	1.6	938
	U.S.	<0.5–6	—	706

Table 151 Bromine Content of Plant Food and Forage Plants (ppm DW)

Plant	Tissue Sample	Mean or Range of Content	Ref.
Barley	Grain	5.5	710
	Grain	2.1–6.4[a]	441
Oats	Grain	3.1	710
Triticale	Grain	33.0	492
Corn	Grain	0.9–1.7	462, 710
Beans	Seed	15	197
Peas	Seed	3.3	462
Lettuce	Leaves	20–22	751, 753
Cabbage	Leaves	0.37[b]	574
Radish	Roots	24–26	751, 753
Celery	Stalk	17	753
Carrot	Roots	0.85[b]	574
Potato	Tubers	4.2–14.3	462, 710
Cucumber	Fruits	10–20	751, 753
Tomato	Fruits	10	751, 753
Apple	Fruits	0.002[b]	574
Orange	Fruits	0.04[b]	574
Fruits of Central America	Fruits	0.2–1.0	197
Legumes	Hay	2.1–6.4	710
Clover	Tops	19–52	875
Cheatgrass	Tops	2.8	462
Grass	Tops	17–119	875
Mushroom[c]	Edible parts	2–36	94

[a] For inland and coastal districts, respectively.

[b] FW basis.

[c] Kind not specified.

the total soil Br. Although the amount of methyl bromide that is transformed to Br^- in soil is reported to be relatively small, it may significantly increase the Br concentration in the solution of treated soil.[106]

B. Plants

Marine plants, in general, contain more Br than do land plants, and may concentrate this element up to the range of X000 ppm (DW). Although Br is reported to occur in all plant tissues, it is not yet known whether it is essential for plant growth. Wyttenbach et al.[1553] found a high concentration of Br in Norway spruce needles at polluted and maritime sites, and very low at continental prealpine sites. The mean Br value in spruce needles from remote continental sites was 0.1 ppm.

The natural Br content of plants seems not to exceed about 40 ppm, and some higher values should apparently be related to pollution (Table 151). Stärk et al.[753] found that Br was usually higher in leaves than in roots and that it was easily soluble from tissues. Wilkins[875] concluded that the Br concentrations in herbage do not correlate with the concentrations in the soil or with soil properties such as type, drainage status, or pH. However, plants are known to take up Br readily when grown in soils enriched in Br. The method of Br^- transportation from soil to plants has not yet been described.

Yamada[890] found as much as 2000 ppm (DW) Br in plants grown in volcanic ash soil, and Staerk and Suess[751] reported Br concentrations from 267 ppm (DW) in celery roots to 9515 ppm (DW) in lettuce leaves that were cultivated in a greenhouse after fumigation with Ch_3Br at the rate of 75 g m^{-3}. Methyl bromide and other Br organic compounds used as fumigants for soils, grain, and fruits may be serious sources of Br in human diets.

Br can substitute for part of the Cl^- requirement of plants; therefore, its excess is toxic to plants. Plant species differ in their tolerance to soil Br, but several vegetables and flowers are known as sensitive plants (potato, spinach, sugar beet, onion, carnation, and chrysanthemum). Symptoms of Br toxicity resemble excess salt effects, so chlorosis followed by leaf tip necrosis is the common feature. As Gough et al.[279] reviewed, citrus seedlings have been satisfactorily used as an indicator of Br toxicity since the reduction in their growth correlated positively with water-soluble soil Br. Plants resistant to Br toxicity (carrot, tobacco, tomato, celery, and melon) can accumulate more than 2000 ppm (DW) Br without showing any effects.

V. IODINE

A. Soils

Geochemical characteristics of I resemble those of Br; however, its abundance in the Earth's crust is less than that of Br. The I content of most rocks varies from 0.01 to 6 ppm, being the highest in shales rich in organic matter (Table 145). Few new data are presented by Muramatsu and Wedepohl.[1434] They give the following concentrations of I in rocks (in ppm): sandstones, 0.05–0.33; limestones, 0.26–3.87; and shales rich in organic carbon, 0.41–6.15. These values are relatively close to those reported earlier (Table 145). According to the calculation, nearly 70% of I exists in ocean sediments. There is a significant difference in I content in andosols in Japan (range, 24.2–44.9 ppm) as compared to the I concentration in other soil orders, acrisols, fluvisols, and gleysols (range, 0.63–11.8 ppm).[1436] In each soil type, however, there is observed a greater abundance of I content in soils than in their parent material. Microorganisms and their products were found to play an important role in the fixation of both stable and long-lived radioactive I in soils.[1435]

I occurs as a minor constituent of various minerals, but does not form many separate minerals. The known I minerals include iodides of some metals such as AgI, CuI, $Cu(OH)(IO_3)$, and polyhalides, iodates, and periodates.

The high I content of some nitrate deposits, especially of Chile saltpeter (up to about 400 ppm, mean 200 ppm) has been the subject of much discussion. Apparently, the suggestion of an atmospheric origin seems to be most reasonable.[855]

All I compounds are readily soluble; therefore, weathering of rocks results in the release of much of their I content. Although I is known to be easily transported by waters to ocean basins, its great sorption by carbon, organic matter, and clays greatly influences I cycling.

The geochemistry of I, a biophile element, is strongly connected to its involvement in biological processes. The high I content of sediments and soils is mostly due to uptake of I by plankton or is due to fixation of I by organic matter. Like Br, the I content is reported to be closely correlated with organic carbon content of sediments. As Prince and Calvert[632] stated, sediments of reducing environments contain greater amounts of I than do oxidized sediments.

It is most unlikely that I occurs in soils in the form of I minerals. The association between I and organic matter, hydrous oxides of Fe and Al, and clay of the chlorite-illite group has been noted by several workers. However, as Selezniev and Tiuriukanov[700] and Whitehead[868] reported, organic matter is most responsible for I sorption in soil and therefore I is accumulated mainly in topsoil horizons. Soil microorganisms are believed to play a significant role in the I cycle owing to their great capability to accumulate this element. Letunova et al.[1062] calculated that the microorganism biomass contains from 0.012 to 3.24% of the I present in surface soil layers. Some fungi occurring in soils (e.g., *Penicillum chrysogenum*) are known to accumulate even much higher amounts of I.

The influence of soil reaction on the I status in soil is diverse. Soil acidity favors I sorption by soil components such as organic matter, hydrous oxides of Fe and Al, and illitic clays.[402,868] On the other hand, in alkali soils of arid and semiarid regions, I is known to be greatly accumulated (e.g., solanchak soils of Baraba Steppe, the former Soviet Union, is reported by Anikina[30] to contain as much as 340 ppm I). This is, however, due both to salinity processes and to the low degree of I mobilization occurring under alkaline pH conditions.

The oxidation of iodide to iodate and further alteration to elemental I may occur in soils and also the exchange of volatile I compounds between soil and atmosphere is reported to be possible.[166] Several ionic forms (I^-, IO_3^-, I_3^-, IO^-, IO_6^{3-}, $H_4IO_6^-$) may occur in the aquatic phase of soil, of which the first two are most common.[256]

The behavior of I in soils has been studied in relation to its availability to plants. Hartmans[308] and Whitehead[869] reported relatively few effects of chalk, N, and P on the uptake of I by plants. However, liming is known to reduce the solubility of iodides, iodates, and iodine in soils and thus to also reduce I bioavailability. When I was applied to peat soils, only about 4% of the added amount was taken up by plants. Fuge and Johnson[1002] reported that only a small fraction of the total I is easily mobile in soils. The relative proportion of mobile I (cold or hot water extractable) ranges from <1 to 25% of its total content in soils. Thus, most I occurs in fixed forms being sorbed by humic and fresh organic matter as well as being fixed in or on clays and crystal lattice of minerals. Studies conducted by Yuita[1194] indicated that absorption rate of radioiodine by soils is influenced by several soil factors (e.g., moisture, pH) and by the chemical forms of I, being higher for I^- than for IO_3^-. Although I is scarcely solubilized under most soil conditions, in some extreme situations, (e.g., submerged soils), I can be mobilized by a factor of 10,000 as compared with regular soil conditions.

The fact that soils contain several times as much I as do the parent rocks has been confirmed by numerous analyses. Also, an accumulation of I in surface and/or subsurface soil horizons is usually reported. In gleyed water-rich soils, however, a higher I concentration in the lower soil horizons can be expected.

Studies of I distribution in soils have been closely related to the occurrence of endemic goiter. Data collected in Tables 9 and 152 show that, on the whole, the most common I concentrations in soils range from <0.1 to around 10 ppm and that the grand mean is 2.8 ppm. However, in certain soils of islands (e.g., Ireland, Japan, and New Zealand), a higher I accumulation, up to around 80 ppm, is reported.[166] Data published by Yuita[1194] show a higher I accumulation, up to 135 ppm (average 46 ppm) in the top horizon of mountain soils at the Sea of Japan coast, while Fuge[1000] reported even higher I content, up to 149 ppm, in soils close to the coast of Wales (Table 152). As reported by Govindaraju,[1313] the range for I in the reference soils from China is from 1.3 to 19.7 ppm, and in the reference soils from the U.S., from 1 to 35 ppm. Gerzabek et al.[1308] gave an arithmetic mean content of 3.1 ppm I in about 40 topsoils of Austria (range, 1.1–5.6 ppm). According to these data, I is positively correlated only with clay content of noncalcareous soils, whereas in calcareous soils the positive relation was observed for clay, exchangeable calcium, and organic carbon. Usually, light soils of humid climatic regions are I poor, whereas high humus and clayed soils are I rich. This may vary greatly because the I level in soils is known to be dependent on atmospheric precipitation. Also, the distance from the sea and recent glaciations influence the soil I status. Since I released into the atmosphere from sea water seems to be a significant source of this element, soils from coastal districts are known to be enriched in this element.[445] Soils derived from recent glacial

Table 152 Iodine Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Israel	0.3–0.4	—	644
	Great Britain	2.3–8.5	4.1	1003
	Poland	0.8–10.0	—	139
	Russia	—	1.1	913
Loess and silty soils	Israel	4.4–5.8	—	644
	Russia	0.3–7.6	1.5	913
Loamy and clay soils	U.S.	<0.5–8.3	1.8	706
	Russia	0.7–4.9	1.7	503, 913
Soils on glacial till	Russia	<0.1–6.3	1.7	913
Fluvisols	Israel	10.6–11.6	—	644
	U.S.	<0.5–3.5	1.4	706
	Russia	0.6–6.7	2.0	386, 503, 913
Volcanic ash soils	Japan	32–41	—	897
Rendzinas	Israel	4.1–4.9	—	644
	Great Britain	2.5–9.5	6.5	1003
	U.S.	<0.5–4.5	1.7	706
	Russia	0.3–2.8	1.2	913
Kastanozems and brown soils	Israel	6.4–7.3	—	644
	Russia	0.3–5.3	2.8	503, 621, 760, 913
Ferralsols	Israel	—	7.8	644
Solonchaks	Russia	<0.1–6.0	2.1	503, 760
Chernozems	U.S.	<0.5–4.3	1.1	706
	Russia	0.4–10.8	3.8	419a, 503, 621, 760, 913, 1123
Meadow soils	Russia	0.4–3.4	1.7	503, 621, 760, 913
Histosols	Israel	3.3–3.7	—	644
	Russia	1–10	4.6	386, 503, 760, 913
Forest soils	Japan	20–23	—	897
	Norway	9.1–23.5	13.1	444, 445
	Russia	0.06–25.4	3.4	419a, 503, 621, 913
Various soils	Bulgaria	1.9–4.1	3.0	177
	Great Britain[a]	1.5–149	14.7	1000
	Great Britain[b]	1.3–26	5.4	1000
	Norway, northern	5.4–16.6	9.0	444, 445
	Norway, eastern	2.8–7.6	4.4	444, 445
	U.S.	<0.5–5.4	1.2	706
	Russia	0.1–16.0	1.7	503, 760, 913
	Lithuania	1.5–2.4	—	983

[a] Wales, <20 km from the coast.

[b] N. England, >80 km from the coast.

(Pleistocene) deposits are usually I poor because this element has not yet been highly accumulated from atmospheric precipitation.

The I levels in soils are likely to be elevated in areas of coal and/or kelp burning and around busy roads.[830] Also, some sewage sludges applied on fields can add I to surface soil. Because I is readily leached from soils under humid temperate climates, its concentrations in surface horizons do not have a significant environmental impact.

Iodine radionuclides ^{129}I and ^{131}I are present in the environment principally as a result of nuclear weapons testing and nuclear reactor accidents. The occurrence in soils of these two radionuclides has recently become a great environmental concern, especially after the reactor accident in Chernobyl in 1986. The impact of the ^{131}I emission from the Chernobyl reactor can be illustrated by its levels in soils near Warsaw (Poland); a few days after the accident, the level of its radiation was 19.9 kBq m^{-2}, and 2 weeks later was 3.7 kBq m^{-2}.[1315] Schimmack et al.[1140] observed a relatively fast migration of ^{131}I down the soil profile after its deposition by the fallout from the reactor accident in Chernobyl.

The emission of much more stable ^{129}I has slowly continued from different sources, which can be easily observed in the increasing ratio of ^{129}I to stable ^{127}I in soils and other compartments of the environment.[1434,1468] Koch and Kay[1053] studied the transportability of the long-lived and potentially hazardous nuclide ^{129}I in organic soil. The proportion of I losses from the solution phase differ widely with the kind of organic matter used in the experiment. The authors concluded that the long-term processes that operate in the field to immobilize I are highly variable between soils and within a large body of soil. Muramatsu et al.[1437] observed that ^{125}I$^-$ added to soils is readily sorbed in the soil solid phase. However, it is slowly desorbed into soil solution with passing time, and under the enhancing impact of organic substances.

For the assessment of the impact of nuclear techniques on the level of radioisotopes of I in surface soils, data are necessary on ^{129}I, the only naturally occurring radioisotope, and on the ratio of ^{129}I:^{127}I. As Muramatsu et al.[1096] reported, some ^{129}I is also added to the environment due to nuclear weapons tests, and therefore the ratio of ^{129}I to stable ^{127}I has increased in recent times in orders of magnitude from 10^{-12} to about 10^{-8}.

B. Plants

I has not been shown to be essential to plants, and reports on stimulating effects on plant growth at low concentrations have not been explained. Mengel and Kirkby[531] wrote that the stimulating effect of I was observed at 0.1 ppm I in nutrient solutions, whereas toxic effects occur at an I concentration of 0.5 to 1.0 ppm. The toxic concentration is higher than the normal soluble I content of soils; therefore, I toxicity is seldom present in plants under natural field conditions. Yuita[1193] reported, however, a physiological disease of rice plants, “Akagare,” induced by excessive absorption of I from soils enriched in easily soluble I when land was converted for submerged paddy fields.

Opinions seem to differ regarding the relation between the I content of plants and the I status of soils, but apparently the variation in the I content of plants appears to be generally unaffected by soil kind and type. On the other hand, some data cited by Fuge and Johnson[1002] show a marked variation of I content of spruce and larch twigs with soil type. Groppel and Anke[1017] stated that both parent material and the distance from the North Sea influence I content of plants. In general, soluble forms of I seem to be easily available to plants; therefore, terrestrial plants contain much less I than do marine plants, which are known to concentrate I from 53 to 8800 ppm (DW).[709] The mechanism of I uptake by plants is not understood. It has been shown, however, by Selezniev and Tiuriukanov[700] that organically bound I is scarcely available to cultivated plants, but that after the decomposition of organic matter by bacteria, soil I becomes available. Muramatsu et al.[1437] studied the volatilization of ^{129}I from the soil-plant system and observed a marked emission of this radionuclide, in a methylated form (CH_3I), from the rice plant shoot into the atmosphere. It was presumed that I in the flooded soil was methylated by the action of roots or microorganisms.

Shacklette and Cuthbert[709] studied I distribution among a variety of plant groups from various soils and stated that although I contents of individual plant species may vary considerably, the range in amount seems to be a species characteristic. Generally, vegetables and fleshy mushrooms contain more I than other land plants (Table 153). Some authors have found a higher I content in tops than in roots and also found a seasonal variation in I levels.[166,230,308] I levels are reported to be the lowest during the summer season. The highest I concentrations are in algae and seem to be associated with the pigmentation; for example, green algae contain, on average, 5, red 380, and brown 3490 ppm. About 65% of total I is bound to proteins.[1333]

Plants are capable of absorbing I directly from the atmosphere, both through the cuticle and as adhesive particles on the surface of hairy leaves. The atmospheric I can contribute significantly to the I content of plants. Gurievich[295] reported that in the Baltic regions, higher plants accumulated I to as much as 40 to 50 ppm (DW) and mosses contained 360 to 410 ppm (DW). However, Rühling et al.[1135] gave a quite different range for I in mosses from the Scandinavian countries, from 1.5 to 3.5 ppm (DW).

Table 153 Iodine Content of Food Forage Plants (ppm DW)

Plant	Tissue Sample	Country	Range	Mean	Ref.
Barley	Grain	Norway	0.005–0.038[a]	—	441
	Grain	U.S.	3.4–7.1	—	709
Cereal	Grain	Germany	0.06–0.1	—	1017
Snap beans	Pods	U.S.	5.7–9.5	—	709
Cabbage	Leaves	U.S.	9–10	—	709
Lettuce	Leaves	U.S.	—	<0.01[b]	709
Asparagus	Stems	U.S.	5.6–5.9	—	574
Carrot	Roots	U.S.	—	0.025[b]	709
Onion	Bulbs	U.S.	7.8–10.4	—	709
Potato	Tubers	U.S.	2.8–4.9	—	709
Apple	Fruits	U.S.	—	<0.003[b]	574
Orange	Fruits	U.S.	—	<0.01[b]	574
Garden vegetables	Edible parts	U.S.	2.8–10.4	6.6	709
Grass	Tops	Great Britain	0.10–0.28	0.20	166
	Tops	Finland	<1–4[c]	—	221
	Tops	Germany	0.3–1.6	0.80	316
	Tops	U.S.	4.3–7.1	5.5	709
	Tops	Former S.U., Armenia	0.03–0.08	0.06	386
Legume	Tops, clover	Great Britain	0.14–0.44	0.31	166
	Tops, clover	Germany	0.11–0.5	—	316,1017
	Tops, vetch	Former S.U., Armenia	0.06–0.12	0.1	386
Mushrooms	Stalks and caps	U.S.	5.2–9.5	6.7	709

[a] For inland and coastal districts, respectively.

[b] FW basis.

[c] For low I and high I areas, respectively.

Adequate I levels in food and feed plants are required in animal nutrition and in human diets; therefore, some scientists have investigated I as a fertilizer for soil or foliar application.[166] These techniques, however, do not appear to be of any practical importance.

The I toxicity to plants due to pollution is not often reported. As Gough et al.[279] reviewed, large applications of kelp to soil as fertilizers (practiced on some coastal fields) may cause symptoms of I toxicity which are similar to those caused by Br excess—margin chlorosis in the older leaves, while the younger leaves become dark green in color.

Radioiodine is, among other radionuclides, a subproduct of atomic reactors and is released in various proportions into the environment. Its cycling, and especially its ready bioavailability, are a recent growing concern.

VI. MANGANESE

A. Soils

Mn is one of the most abundant trace elements in the lithosphere, and its common range in rocks is 350 to 2000 ppm (Table 145). Its highest concentrations are usually associated with mafic rocks.

Mn forms a number of minerals in which it commonly occurs as the ions Mn^{2+}, Mn^{3+}, or Mn^{4+}, but its oxidation state +2 is most frequent in the rock-forming silicate minerals. The cation Mn^{2+} is known to replace the sites of some divalent cations (Fe^{2+}, Mg^{2+}) in silicates and oxides.

During weathering, Mn compounds are oxidized under atmospheric conditions and the released Mn oxides are reprecipitated and readily concentrated in the form of secondary Mn minerals. The behavior of Mn in surfacial deposits is very complex and is governed by different environmental factors, of which Eh-pH conditions are most important. Mn is easily removed, under cold climatic conditions, from the zone of weathering and from soils by acid solutions as bicarbonate or as a complex with organic acids (derived from decaying plants). Under tropical and subtropical conditions, however, Mn may be concentrated in various forms, often as concretions and nodules.

The complex mineralogical and chemical behavior of Mn results in the formation of the large number of oxides and hydroxides which give a continuous series of composition of stable and metastable arrangements of atoms. The physical features of Mn oxides and hydroxides, such as small size of crystals and consequently a large surface area, have important geochemical implications. The negatively charged $Mn(OH)_4$ and MnO_2 are responsible for the high degree of association of Mn concretions with some heavy metals, in particular with Co, Ni, Cu, Zn, Pb, Ba, Tl, W, and Mo. In addition, the oxidation of As, Cr, V, Se, Hg, and Pu by Mn oxides is likely to control the redox behavior of these elements in soils.[933]

There is great progress in research on the chemical controls of the solution and deposition of Mn in both soils and sediments. The intensive studies on Mn behavior in soils have been carried out by a number of scientists, and their findings are reviewed in Chapter 4, Section III.B.

McKenzie[524,526] and Bartlett[933] have summarized the present knowledge relating to soil Mn. They stated that Mn is likely to occur in soils as oxides and hydroxides in the form of coatings on other soil particles and as nodules of different diameters. The nodules often exhibit a concentric layering that is suggestive of seasonal growth. The Mn concretions in soils are reported to accumulate Fe and several trace elements (Table 22).

Mn may form a number of simple and complex ions in the soil solution and also several oxides of variable composition (Figure 95). The Mn oxides in soils are mostly amorphous, but crystalline varieties have also been identified in several soils. As Norrish[570] stated, lithiophorite, $(Al, Li)MnO_2(OH)_2$, is most likely to occur in acid and neutral soils, while birnessite (unconfirmed composition, $Na_{0.7}Ca_{0.3}Mn_7O_{14}2.8H_2O$) was reported to be in alkaline soils. However, a number of other crystalline forms of Mn oxides were observed in soil horizons. Of all the Mn oxides, the most stable under oxidizing conditions are pyrolusite (βMnO_2), manganite ($\gamma MnOOH$), and hausmannite (Mn_3O_4). McKenzie[524] concluded that birnessite, lithiophorite, and hollandite are the most common crystalline forms, whereas todorokite and pyrolusite are less common.

Bartlett[933] described the redox cycling of Mn in soils, and emphasized its role as scavenger for biodestructive free radicals at interfaces and as a redox transformation system. The following sequence for Mn-redox cycling is proposed by this author:

1. The reduction of Mn^{3+} to Mn^{2+} by Fe^{2+}, Cr^{3+}, reduced S, phenols, and other easily oxidized organic compounds.
2. The Mn^{2+} is either adsorbed by MnO_2 or oxidized to Mn^{3+} or Mn^{4+}. The last oxidation is most likely to be spontaneous by atmospheric oxygen or hydroxyl free radicals.
3. The reverse dismutation at the presence of organic or phosphate ligands produces Mn^{3+}.
4. The Mn^{3+}, as an extremely reactive redox species, quickly disappears, either by accepting or by donating an electron (see step 1).

As Sparks (*vide* Bartlett[1219]) stated, "Soil Mn, or its lack, appears to be the key to the entire spectrum of soil redox behavior and status." The behavior of various Mn cations as the most important metallic redox catalysts in soils has been broadly reviewed by these authors.

All Mn compounds are very important soil constituents because this element is essential in plant nutrition and controls the behavior of several other micronutrients. It also has a considerable effect on some soil properties, and in particular on the poising system of Eh and pH. The Mn compounds are known for their rapid oxidation and reduction under variable soil environments and thus oxidizing conditions may greatly reduce the availability of Mn and associated micronutrients, whereas reducing conditions may lead to the ready availability of these elements even up to the toxic range. The reduction of Mn oxides has dual effects on soil cation exchange. Not only does the oxide exchange surface disappear, but the newly formed Mn^{2+} ion enters into exchange competition with other cations. Activity and susceptibility to leaching of Ca, Mn, and several other metals increases as Mn reduces. Bartlett[933] also suggested a possible role of Mn oxides in nonmicrobial conversion of nitrite to nitrate, although no one has shown that such a reaction can occur in soils.

The solubility of Mn in soils is highly dependent on the pH and redox potential; therefore, the most common reactions occurring in soils are oxidation-reduction and hydrolysis. Although the solution of Mn species as a function of Eh-pH conditions is demonstrated on the diagrams by Lindsay,[477] the comparison of actual Mn levels in soil solutions with those predicted by the chemical equilibrium reactions has not met with success. The mixed and metastable composition of Mn oxides and hydroxides, organic complexes of Mn, and variable Eh-pH soil conditions are the main factors responsible for the lack of correspondence between actual and predicted Mn levels.

Because of the low solubility of Mn compounds in oxidizing systems at pH levels near neutrality, small shifts in the Eh-pH conditions can be very important in the Mn content of the soil solution. The abundance of soluble species of Mn in the soil solution is reported to range from 25 to 8000 $\mu g\ L^{-1}$ (Table 16). For solutions of neutral and acid soils, the Mn range is reported to vary from 1 to 100 $\mu M\ L^{-1}$.[320]

Hodgson et al.[320] reported that the soluble Mn in soil solutions is mainly involved in organic complexing. In the surrounding soil of plant roots, the reduction of MnO_2 forms, and complexing by root exudates is apparently a significant factor controlling Mn mobility.[270] Cheshire et al.[136] found that Mn in topsoil was largely associated with fulvic acid, but the Mn^{2+} bound to these compounds was highly ionized.

Microbiological soil activity is also known to be largely responsible for the oxidation and reduction of Mn compounds, as well as for the formation of Mn concretions as described by Letunova et al.,[466] Bromfield,[103] Wada et al.,[836] and Aristovskaya and Zykina.[36] Zajic[898] and Weinberg[856] reviewed several microbiological processes which directly or indirectly affect the transformation of Mn compounds in soils. The microbial dissolution of Mn compounds in soils, especially due to the enzymatic reduction of oxidized Mn (+3 and +4) and due to the production of CO_2 and organic acids, is of great importance. These processes are likely to occur at acid pH and appropriate Eh in soils. Where Fe accompanies Mn compounds in a solid phase, microbes may separate Mn from Fe by preferential solubilization. Some microorganisms, on the other hand, can precipitate Mn by oxidizing Mn^{2+} to Mn^{3+} and Mn^{4+} or stimulating the precipitation of carbonates, sulfides, etc.

The geochemistry of Mn hydroxides is closely related to the behavior of Fe hydroxides, and cross-interaction during redox reactions should be expected. As McKenzie[526] described, the formation of ferromanganese nodules in acid soils reflects this relationship.

The solubility of soil Mn is of significance since the plant supply of Mn depends mainly on the soluble Mn pool in the soil. In well-drained soils, the solubility of Mn always increases with the increase of soil acidity. However, the ability of Mn to form anionic complexes (Figure 95) and to complex with organic ligands may contribute to increased Mn solubility in the alkaline pH range (Figure 96).

Several extractants have been widely investigated for soil testing analysis. The best correlation with Mn uptake by plants was usually obtained for the water-soluble, the exchangeable, and the reducible fractions of soil Mn. It appears that most work has been done with the easily reducible Mn (the fraction extractable with hydroquinone), but the effects vary widely.

The soil Mn has been the object of much research, and a great proportion of the studies has been related to the Mn available to plants. Many data are also reported for total Mn in soils. The availability of a good Mn supply to crop plants is of growing concern for some soils, and as Finck[995] stated, an increase of the mobilization rate by soil acidification proves to be effective. In soils that have to be heavily limed for structural reasons, the availability of Mn is limited. On the other hand, in soils with an increased mobility of Mn (e.g., well-drained soils at pH levels below 5.5, poorly aerated soils at pH of about 6.0 or higher), Mn toxicity can occur.[998a] Highly alkaline soils (at about pH 8) can also produce Mn toxicity.

Mn is not distributed uniformly in soil substrata and, in addition to various nodules, is known to be also concentrated at certain spots which are usually enriched in several other trace elements. Colloidal Mn oxides reveal a great affinity for adsorption of cationic and anionic forms of elements as well as inorganic and organic substances. Thus, Mn oxides have a great impact on the immobilization of trace

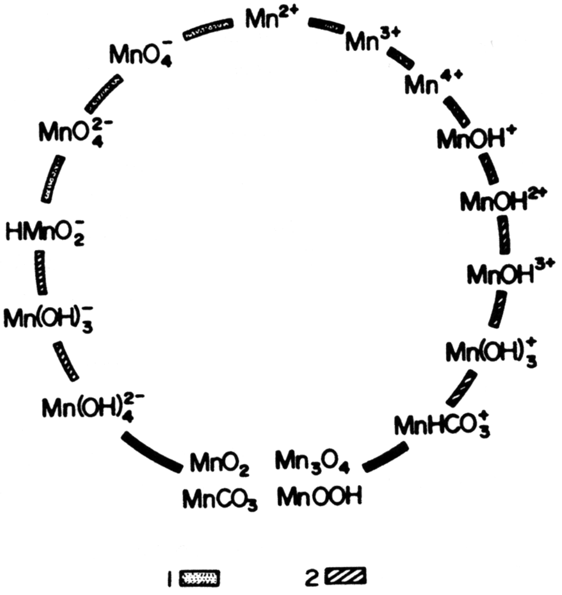

Figure 95 Ionic species and transformation of manganese compounds in soils. (1) Redox reactions; (2) redox and hydration reactions.

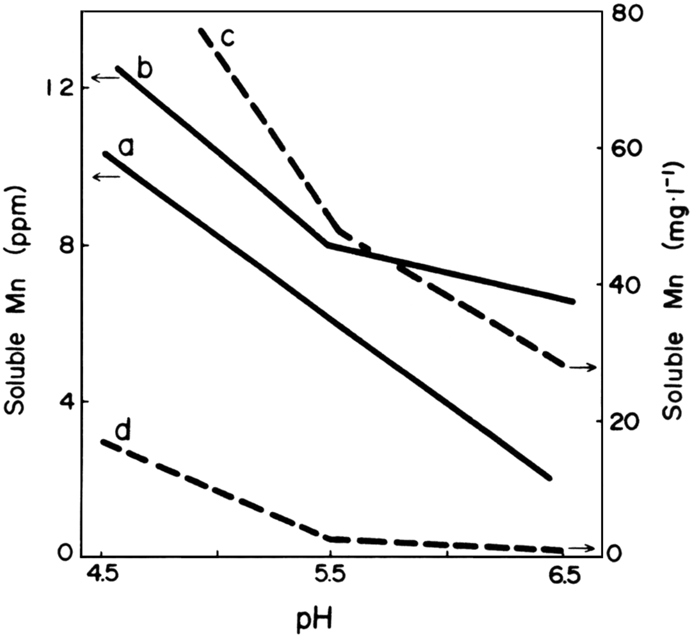

Figure 96 Solubility of soil Mn at different pH values. (a) In 0.01 M $CaCl_2$ from bulk soil; (b) in 0.01 M $CaCl_2$ from rhizosphere soil; (c) in 0.01 M citrate solution; (d) in root exudates, after 72 hr.[270]

metals in soils. On the other hand, however, due to both reducing and oxidizing properties, Mn oxide can increase the mobilization of some metals under specific soil conditions.

The variation of Mn content of surface soils rarely seems to be correlated with soil typology, but is positively associated with clay contents (Tables 9 and 154). However, higher Mn levels are

Table 154 Manganese Contents of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Australia	900–1000	—	792
	Austria	9–59	—	6
	Bulgaria	451–883	—	545
	Norway	—	165	443
	Germany	25–200	—	689
	New Zealand	1200–1900[a]	—	861
	Poland	15–1535	—	91, 378, 382
	U.S.	7–2000	345	706
	Former S.U.	135–310	217	74, 432, 493
Loess and silty soils	Germany	775–1550	—	689
	China	680–1700	844	1068
	New Zealand	1600–1800[a]	—	861
	Poland	110–1060	470	378, 382
	U.S.	50–1500	525	706
	Belarus	—	370	493
Loamy and clay soils	Austria	107–133	—	6
	Germany	500–1500	—	689
	Mali Republic	75–600	—	39
	New Zealand	670–9200[a]	—	861
	Poland	45–1065	420	91, 378, 382
	U.S.	50–2000	580	706
	Former S.U.	270–1300	475	74, 345, 432
Soils on glacial till	Denmark	—	268	801
	Poland	284–680	343	974
Fluvisols	Austria	152–1030	554	6
	India	350–780	—	641
	Mali Republic	165–250	—	39
	Poland	150–1965	1085	378
	Belarus	—	240	493
Gleysols	Australia	1200–1900	—	792
	Austria	—	765	6
	Great Britain	—	530	876
	Madagascar	900–2650	—	557a
	Norway	—	80	443
	Poland	85–890	495	91, 378
	Ukraine	—	190	432
Rendzinas	Austria	—	1315	6
	Poland	50–7750	440	378, 685
	U.S.	70–2000	470	706
	Germany	—	425	689
Kastanozems and brown soils	Australia	850–3150	—	792
	Austria	253–1675	511	6
	Bulgaria	2190–3907	—	545
	China	340–1000	270	1068
	India	924–2615	—	78
	Former S.U.	390–580	460	74, 343
Ferralsols	Australia	1350–4250	—	792
	China	200–3000	915	1068
	India	925–2065	—	78
	Madagascar	850–3400	—	557a
	Spain	10–315[b]	—	253a
Solonchaks and solonetz	Madagascar	—	850	557a
	Former S.U.	265–1100	645	74, 351, 432
Chernozems	Poland	380–700	560	91, 378
	U.S.	100–2000	600	706
	Former S.U.	340–1100	745	4, 346, 351, 432

(*Continued*)

Table 154 Manganese Contents of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Meadow soils	Former S.U.	690–1250	950	74, 432
	China	480–1300	940	1068
Histosols and other organic soils	Canada	240–540	338	243
	Denmark	43–200	100	1, 801
	Poland	20–2200	150	382
	U.S.	7–1500	260	706
	Former S.U.	510–1465	1005	74, 432
Forest soils	China	—	840	225
	Hungary	120–600[b]	—	207
	U.S.	150–1500	645	706
	Former S.U.	—	710	4, 351
Various soils	Austria	190–600	388	6
	Canada	80–850	325	629
	Canada	100–1200[b]	520	521
	Denmark	—	279	801
	Great Britain	70–8423	1055	818, 876
	Italy	12–3410	873	946
	Germany	520–1800[b]	—	61
	Madagascar	680–3500	—	557[a]
	Poland	37–1415	297	1045
	Romania	194–1870	755	43
	U.S.	20–3000	490	706

[a] Soils derived from basalts and andesites.

[b] Data for whole soil profiles.

often reported for soils over mafic rocks, for soils rich in Fe and/or organic matter, and for soils from arid or semiarid regions. Although Mn can be concentrated in various soil horizons, particularly in those enriched in Fe oxides or hydroxides, usually this element is also accumulated in topsoils as the result of its fixation by organic matter.

On a world scale, the range of Mn average content of soil units varies from 270 (podzols) to 525 ppm (cambisols) (Table 9). The grand mean calculated for world soils is 437 ppm, while for the U.S. soils the calculation is 495 ppm. The concentration of acid-soluble Mn in Finnish soils, at the 90th percentile, is 280 ppm, whereas total Mn (H_2F_2 fusion) is 600 ppm.[1368] Median contents of Mn in soils of Lithuania vary, depending on the kind of parent material, from 245 ppm in soils derived from eolian sediments to 605 ppm in soils on loamy clay glacial sediments.[1359]

Mn has not been considered to be a polluting metal in soils, yet Hemkes et al.[314] reported the increase of Mn from 242 to 555 ppm (DW) in sludge-amended soil in 5 years. MAC value for Mn in agricultural soils is estimated at 1500 ppm. Grove and Ellis[289] found more water-soluble Mn in soil after fertilization with sludge, whereas Diez and Rosopulo[176] observed a lower Mn uptake by plants from soil after sludge application. When Mn has accumulated in topsoil due to Mn application over a long period of time, toxic effects in some plants might be observed.

B. Plants

1. *Absorption and Transport*

Numerous studies have been carried out on Mn uptake by plants and on Mn distribution among plant tissues. All findings give ample evidence that Mn uptake is metabolically controlled, apparently in a way similar to that of other divalent cation species such as Mg^{2+} and Ca^{2+}. However, passive absorption of Mn is also likely to occur, especially in the high and toxic range of this metal in solution. Generally, Mn is known to be rapidly taken up and translocated within plants; therefore, it is likely that Mn is not binding to insoluble organic ligands, either in root tissue or in xylem fluid.

Mn is reported to occur in plant fluids and extracts mainly as free cationic forms.[789,798] It appears, therefore, that Mn is likely to be transported as Mn^{2+}, but its complexing compounds with organic molecules of 1000 to 5000 mol wt have also been found in phloem exudates.[822] Van Goor[820a] reported a much lower Mn concentration in phloem exudate than in leaf tissue and concluded that a slight transport of Mn through the phloem vessels is responsible for the low concentration of Mn in fruits, seeds, and storage roots.

Mn is preferentially transported to meristematic tissues, thus its concentration is mostly observed in young expanding tissue. Heenan and Campbell[309] reported that at a high Mn supply, the leaves accumulated higher concentrations with age, but small amounts of Mn were translocated from old leaves when young expanding leaves were Mn deficient. Thus, Mn appeared to have a low mobility when the supply of the plant was limited. The Mn concentration fluctuates greatly within the plant parts and within the vegetative period. Scheffer et al.[688a] reported a relatively low Mn level in barley during intensive growth and further Mn accumulation in old leaves and sheaths.

It should be emphasized, however, that the Mn content of plants is not only an effect of plant characteristics, but also of the pool of available Mn, which is highly controlled by soil properties. Generally, the most readily available Mn is in acid and flooded soil. More than a tenfold increase in the Mn content of lucerne (alfalfa) was observed in plants grown on flooded soil, compared to background values.[531] Therefore, the reducing ability of root exudates and of bacteria in the rhizosphere apparently is of direct importance in Mn nutrition of plants.[270]

Because Mn seems to be easily taken up by plants when it occurs in soluble forms in soils, the Mn content of plants should be a direct function of the soluble Mn pool in soils. And indeed, Mn concentration in plants shows a negative relationship with increasing soil pH and a positive relationship with soil organic matter (Figure 97).

An excess of phytoavailable Mn is associated with several soil properties:

1. Strongly acid soils (pH levels of 5.5 or below)
2. Anaerobic condition and poor aeration (flooded, waterlogged, or compact soils)
3. Heavily limed soils (raised pH levels up to about 8)

Foy[998a] discussed correcting or preventing Mn toxicity by conventional liming or soil drainage practices and emphasized that the most reasonable approach to the problem is to select or breed plant genotypes having greater tolerance to excess Mn in soils.

2. Biochemical Functions

All plants have a specific requirement for Mn and apparently the most important Mn function is related to the oxidation-reduction process. The functions of Mn in plants have been widely reviewed by Shkolnik,[718] Boardman,[83] and Mengel and Kirkby.[531] Mn^{2+} is known to be a specific component of two enzymes, arginase and phosphotransferase, but this metal can also substitute for Mg in other enzymes. The mechanism by which Mn^{2+} activates several oxidases is not yet known precisely, but it appears to be related to the valency change between Mn^{3+} and Mn^{2+}.

Mn appears to participate in the O_2-evolving system of photosynthesis and also plays a basic role in the photosynthetic electron transport system. Apparently, the Mn fraction that is loosely bound in chloroplasts is associated with O_2 evolution, whereas the firmly bound Mn fraction is involved in the electron pathway in photosynthesis. Bartlett[993] described Mn as a key to life in the following words: "Its essentiality for H_2O oxidation and O_2 evolution in photosynthesis is well-established, although the mechanism of its function in this vital link in life's most basic processes is still an important area of research. Thermodynamically, Mn^{3+} ion (or the Mn^{4+} ion) appears to be a likely candidate for accomplishing this difficult oxidation."

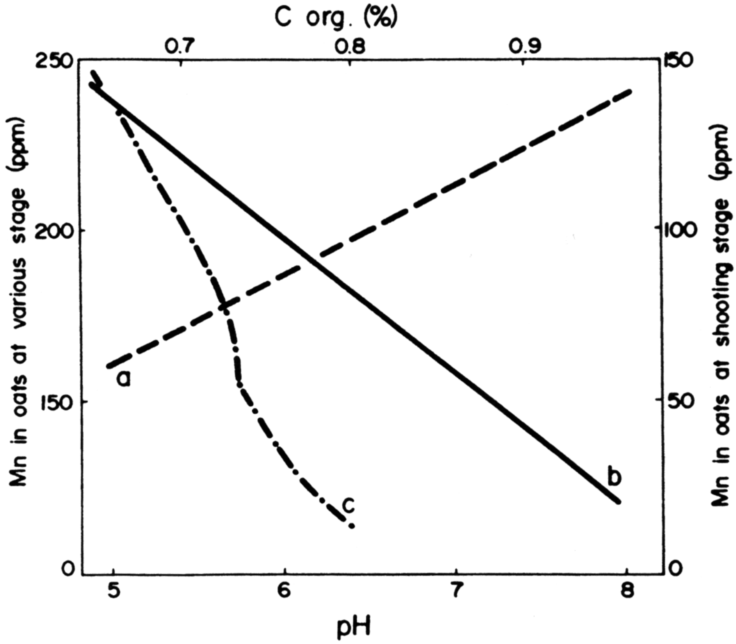

Figure 97 Influence of soil factors on the Mn content of oats. (a) Organic matter added as slurry, oats at various stages of growth; (b) pH adjusted with H_2SO_4 or CaO, oats at various stages of growth; (c) pH resulting from fertilization with different N-fertilizers, oats at shoot stage.[437,693]

The role of Mn in the NO_2^- reduction step is not yet clear, but it appears to be a kind of indirect relationship between the Mn activity and N assimilation by plants. Adequate levels of available Mn are necessary in plant nutrition. Chloroplasts are the most sensitive of all cell components to Mn deficiency and react by showing structural impairment.[83] The deficiency symptoms occur first in younger leaves as interveinal chlorosis. At further stages, necrotic spots on leaves and browning of roots appear. Plants deficient in Mn apparently are less frost hardy.[383,511] The growth of Mn-deficient plants is retarded, the turgor is reduced, and the affected leaves break. Crops and plant species differ in their susceptibility to Mn deficiency—the most sensitive are oats (gray speck symptom), peas (marsh spot symptom), sugar beet, and some fruit trees and bushes.

Although Mn deficiency is relatively common in certain crops grown on neutral and calcareous soils, diagnosis and correction of the deficiency is not well-defined. Since soil analysis is not very reliable in diagnosing the Mn supply to plants, tissue tests should be considered together with soil and field observations. The correction of Mn deficiency in crops may be done by both soil and foliar application. The optimum rates and the method of Mn application is extensively reviewed in several textbooks.[556,649,847] A high rate of Mn application or its inappropriate form (e.g., Mn-EDTA for certain fields), as well as variable soil conditions, can easily result in toxic effects on plants.

Toxicity of Mn to some field crops might be expected on acid soils of pH around 5.5 or lower and with a high Mn level. However, the critical Mn content and unfavorable soil pH range depend upon several other environmental factors. Mn toxicity is also known to occur at higher pH levels in poorly drained (poorly aerated) soils. However, if acid soils are very low in total Mn, plants are not subjected to Mn toxicity. As Beckwith et al.[60] reported, flooding did not always increase Mn uptake by rice shoots, since flooding may also increase soil pH and therefore decrease Mn uptake. As reviewed by Andersson,[921] there are great differences between species in the sensitivity to Mn. For example, most sensitive false oat grass showed a significant decrease in biomass at the Mn concentration of 5 mg L^{-1}, while marsh bent grass was unaffected even by 200 mg L^{-1} in the solution. Most often, plants growing on acid soils tolerate high Mn concentrations. Foy[998] described that Mn tolerance is related to several characteristics and metabolic processes, such as:

1. Oxidizing power of plant roots, possible oxidation of Mn to MnO_2, which is stored as inactive fraction
2. Mn absorption and translocation rates
3. Complexation of Mn by low-molecular-weight compounds produced by plant roots or soil microorganisms
4. Mn entrapment in nonmetabolic centers
5. Interactions with other elements, especially with Ca, Fe, Al, Si, and NH_4

Steam sterilization of greenhouse soils is known to increase the available Mn to levels toxic to certain plants. This phenomenon is closely linked with soil biological activity (Chapter 4, Section IV). Foy[998a] reviewed Mn-microbial relationships and emphasized remedial effects of various microorganisms (especially *Rhizobia* and *Mycorrhiza* strains) on resistance of plants to Mn toxicity.

Foy et al.[241] described the physiology of Mn toxicity in plants and emphasized its complex character and interrelation with other elements. Foy[998] reported impaired effects of high levels of Mn on the activity of some enzymes and hormones (e.g., auxin, giberellin) and also on the proportion of amino acids. The response of plants to excessive Mn levels is highly controlled by differences between genotypes. Brown and Devine[105] stated that the control of tolerance to excess Mn appeared to be multigenic and was apparently related to Fe metabolism in plants. Legumes appear to be more sensitive, because Mn excess affects rhizobia nodule numbers and thus the efficiency of N fixation. Common symptoms of Mn excess are brown spots on leaves where Mn is concentrated. The results of studies carried out by Watanabe et al.[1539] show that the Mn in leaf tissues occurs as a mixture of soluble salt $Mn\ (OH)_6^{2+}$ and organic components containing Mn-porphyrins, but is translocated in xylem mainly as free divalent cation. Leaves with bronzing symptoms contain large amounts of Mn; for example, in injured bean leaves, the Mn level was >760 ppm.[1309]

The most common symptoms of Mn toxicity are Fe chlorosis and brown spots on leaves. Leaf puckering, necrotic brown spots, and an uneven distribution of chlorophyll in older leaves are also symptoms of Mn toxicity. In severely injured plants, browning of roots occurs. Plants resistant to Mn excess have an ability to accumulate Mn in root tissues or to precipitate MnO_2, which is deposited mainly within the epidermis. Also, an increased Fe uptake by these plants has been observed.[114,340] Symptoms of Mn toxicity are more pronounced in warm and hot weather.

3. Interactions with Other Elements

Mn is known to be involved in both biological and geochemical interactions (Figure 30). The most prominent geochemical interference is observed in the strong affinity of Mn oxides for Co. This reaction is so marked that most of the native Co in soils may be unavailable to plants in the presence of moderate amounts of Mn.[524,526] The strong absorption capacity of Mn oxides for other heavy metals may also highly govern the availability of these metals to plants.

Mn-Fe antagonism is widely known and is observed mainly in acidic soils that contain large amounts of available Mn. In general, Fe and Mn are interrelated in their metabolic functions, and their appropriate level (the Fe:Mn ratio should range from 1.5 to 2.5) is necessary for the healthy plant. Below this range, symptoms of Mn toxicity and Fe deficiency may occur; and above 2.5, toxic effects of Fe, associated with the Mn deficiency, will be observed. Alvarez-Tinaut et al.[16] reported that both deficient and normal Mn levels antagonize Fe absorption, but the reverse influence was true when Mn reached toxic concentration in plants. In certain field and crop conditions, both Mn or Fe toxicity can be remedied by Fe or Mn application.[241]

Interactions between Mn and other heavy metals are not confirmed, although there are reports of either antagonistic or synergistic effects of Mn on the uptake of Cd and Pb,[381] and Zn depressing effects on the Mn uptake.[1074] The interactions of Mn and P may be cross-linked with Fe-P antagonism or related to both the variation in the Mn-phosphate solubility in soils and the Mn influence on P metabolic reactions.[3,241] Depending on soil conditions, P fertilizers are known to either aggravate Mn deficiency in oats or to increase Mn uptake by other plants. These phenomena are closely related to the soil pH and soil sorption capacity.

Interactions of Mn and Si have been reported by several authors. An adequate Si supply to plants is reflected in the easy transport of Mn and a more homogeneous Mn distribution in the plant.[326] Plants deficient in Si are known to accumulate more Mn than Si-sufficient plants. There are several indications that an available Si supply reduces the Mn toxicity to plants.[241] Antagonistic effects of Ca and Mg on Mn uptake seem to have a complex character. Foy[998] found that the excess of Mn induces Ca deficiency because it inhibits the transport of Ca within plants, and Ca, under certain conditions, reduces Mn toxicity.[1098] Antagonistic interactions are also observed between Mn and K, Na, and N (Table 43). Although there are evidences of both antagonistic and synergistic interactions, apparently more data are required in this field.[921]

4. Concentrations in Plants

Loneragan[489] stated that Mn showed a particularly wide variation among plant species grown on the same soil, ranging from an average of 30 ppm (DW) in *Medicago truncula*ta to around 500 ppm (DW) in *Lupinus albus*. Similarly, a wide range of Mn has been observed in forage plants as reported for different countries (Table 155). Worldwide background contents of Mn range from 17 to 334 ppm in grass and from 25 to 119 ppm in clover.

Plant foodstuffs are also reported to contain variable amounts of Mn, being the highest in beet roots (36 to 113 ppm DW) and the lowest in tree fruits (1.3 to 1.5 ppm DW) (Table 156). The Mn content shows a remarkable variation for plant species, stage of growth, and different organs as well as for different ecosystems. A relatively small variation has been observed in the Mn content of cereal grains, which average from 15 to 80 ppm throughout the world (Table 157).

The critical Mn deficiency level for most plants ranges from 15 to 25 ppm (DW), whereas the toxic concentration of Mn to plants is more variable, depending on both plant and soil factors. Generally, most plants are affected by a Mn content around 500 ppm (DW) (Table 36). However, the accumulation above 1000 ppm (DW) also has been often reported for several more resistant species or genotypes.[279,345] Foy[998] reviewed reports on differential Mn tolerance within plant species of cereals, legumes, apples, cotton, and flax.

VII. TECHNETIUM

Technetium is a by-product of nuclear fuel processing. ^{99}Tc is an unstable radionuclide and possibly also present, in minute quantities, in natural conditions (mainly in U ores). It is geochemically associated with Mo and Re. Due to its great dispersion, it cannot be easily determined. The disposal of Tc-enriched wastes is an environmental hazard since it is easily included in the biocycle. Echevarria et al.[1287] studied ^{99}Tc behavior in the soil-plant system. It is subjected to microbial oxidizing and reducing processes and is easily taken up by plants, possibly as the complex anion TcO_4^-, and is accumulated mainly in leaves. The average transfer factor (BAC value) of Tc from soil to edible parts of vegetables (on dry basis) ranges from 0.3 to 17, being the lowest for tomato and the highest for spinach.[1560] Organic and nitrogen fertilizers inhibit its phytoavailability. The mobile TcO_4^- in soils is readily changed to less soluble forms, such as TcO_2, TcS_2, and organically

Table 155 Mean Levels and Ranges of Manganese in Grass and Clover at the Immature Growth Stage from Different Countries (ppm DW)

	Grasses		Clovers		
Country	**Range**	**Mean**	**Range**	**Mean**	**Ref.**
Australia	67–187	120	33–43	38	266
Great Britain	79–160[a]	—	31–65[a]	—	67
Czech Republic	24–130	71	17–42	25	154, 562
Finland	41–144	77[b]	34–140	87[c]	388, 727
	—	—	33–205	119[d]	727
Germany	51–128	82	29–200	53	31, 65
Germany	35–106	70	24–420	71	576, 596
Hungary	67–309	161	55–126	82	803
Ireland	77–116	86	18–39	26[e]	235
Japan	20–330	127	15–436	89	770
New Zealand	49–139	114	29–165	77	536
Poland	20–665	98	16–260	58[c]	1045
U.S.	80–1840	334[1]	—	—	15
Russia	26–493	44	19–165	70	338
Yugoslavia	16–18	17	—	—	755

[a] From freely and poorly drained soils, respectively.

[b] Timothy.

[c] Dry hay of red clover.

[d] Fresh grown red clover.

[e] Alfalfa.

[f] Sample from grass tetany pasture.

Table 156 Mean Manganese Content of Plant Foodstuffs (ppm)

		FW Basis			DW Basis			AW Basis
Plant	**Tissue Sample**	**(574)**	**(705)**	**(395, 1187)**	**(705)**	**(381)**	**(727)**	**(705)**
Sweet corn	Grains	—	0.9	5.1	3.6	—	—	140
Bean	Pods	0.28	2.3	5.0[a]	21	—	21[a]	300
Cabbage	Leaves	1.2	1.1	2.6	14	28	—	150
Lettuce	Leaves	0.1	1.2	4.0[b]	29	—	—	210
Beet	Roots	—	—	—	—	36[c]	92, 113[d]	—
Carrot	Roots	0.15	1.0	1.5	8.5	14	28	120
Onion	Bulbs	0.6	1.6	1.2	16	17	24	390
Potato	Tubers	0.3	0.7	2.9	3.6	15	8	86
Tomato	Fruits	0.94	0.6	1.1	12	—	—	100
Apple	Fruits	0.01	0.2	—	1.3	—	—	74
Orange	Fruits	0.05	0.2	0.5[e]	1.5	—	—	43

Note: References are given in parentheses.

[a] Pea seeds or other pulses.

[b] Spinach.

[c] Red beet.

[d] Sugar and red beet, respectively.

[e] *Citrus unshiu* (Satsuma orange).

bound fractions. The N cycle in the soil might have a strong influence in ^{99}Tc transfer to crops, since N has an impact on the formation of the mobile anion TcO_4^-.[1285]

The source of ^{99}Tc is mainly global fallout. As Tagami and Uchodo[1512a] reported, concentrations of this radionuclide in paddy soils of Japan varies from 6.6 to 110 mBq kg^{-1}, and is likely to be accumulated in surface paddy fields.

Table 157 Manganese Content of Cereal Grains from Different Countries (ppm DW)

Country	Cereal[a]	Range	Mean	Ref.
Australia	Wheat	17–84	43	867
Great Britain	Barley	—	49	112
	Oats	—	94	112
Canada	Oats	—	76	867
Czech Republic	Barley (w)	12–16	15	562
	Oats	40–60	48	562
	Wheat (w)	23–52	34	562
Egypt	Wheat	7.5–24.2	13.7	213
Finland	Barley	18–30	24	727
	Oats	47–93	70	727
	Rye	31–47	39	727
	Wheat (w)	29–103	80	508,727
	Wheat (s)	28–84	55	508
Germany	Oats	22–45	—	65
	Wheat	30–44	—	65
Japan	Rice, unpolished	—	26	395
	Wheat, flour	—	2.3	395
Poland	Rye	9–76	26	424,1045
	Oats	17–121	45	1045
	Triticale	—	26	424
	Wheat (w)	10–50	28	267, 335
Sweden	Wheat (w)	22–38	31	21
U.S.	Rye	11–75	—	484,492
	Triticale	—	55	492
	Wheat	32–38	35	492
	Rice	4–39	12[b]	1187
Russia	Barley	13–22	17	337
	Oats	23–76	36	337
	Rye	25–87	30	337,501
	Wheat	16–46	36	337

[a] Spring, s; winter, w.

[b] FW basis.

VIII. RHENIUM

Re is a highly dispersed element in the Earth's crust, but it is known to be associated with some granitoids and pegmatites. Its average abundance is estimated at about 5 ppb in magmatic rock and 0.5 ppb in sedimentary rocks.[552] Two ionic forms, Re^{4+} and Re^{6+}, reveal its similarity to Mo cations and they are likely to substitute for this element in geochemical processes. Therefore, Re may be expected to be concentrated in Mo minerals (e.g., molybdenite contains Re from <1 ppm to about 2%). Higher amounts of Re are also observed in some minerals of the rare earth elements.

During weathering, Re seems to be readily soluble as the anionic form (ReO_4^-) and is known to be concentrated in certain sediments such as bituminous copper shales, in black pyritic shales, and also to be enriched in some coals. Shacklette et al.[710] reviewed data on Re occurrence in plants and gave the range in Re concentrations in native vegetation of the U.S. as 70 to 300 ppm (AW).

CHAPTER 13

Elements of Group VIII

I. INTRODUCTION

Group VIII metals form chemical subgroups (triads) with somewhat similar behavior. Geochemical properties of the first triad, Fe, Co, and Ni, are very similar, and due to the small differences in atomic radii, they are likely to form a wide range of mixed crystals.

The terrestrial abundance of Fe is so great that it is not considered a trace element in rocks and soils. However, Fe plays a special role in the behavior of several trace elements. This metal is also in an intermediate position between macro- and micronutrients insofar as its content in plants is concerned.

Both Fe and Co play significant roles in the biochemistry of plants, but the function of Ni is still not clear. However, all these metals are essential to animals.

Further elements of Group VIII belong to the so-called “platinum metal” group. They are conventionally separated into the middle weight Pd subgroup (Ru, Rh, and Pd) and the heaviest Pt metals (Os, Ir, and Pt). All these metals are highly dispersed in the Earth’s crust and are known to be mostly inactive in geochemical and biochemical processes.

According to the new Periodic Table of the Elements, the metals of this group belong to three separate groups: Group 8: Fe, Ru, Os, and Hs; Group: 9: Co, Rh, Ir, and Mt, and Group 10: Ni, Pd, and Pt. The old system, however, refers to chemical and geochemical properties of the elements, and therefore will be followed in this text.

II. IRON

A. Soils

Fe is one of the major constituents of the lithosphere and comprises approximately 5%, being concentrated mainly in the mafic series of magmatic rocks (Table 158). However, the global abundance of Fe is calculated to be around 45%.

The geochemistry of Fe is very complex in the terrestrial environment and is largely determined by the easy change of its valence states in response to the physicochemical conditions. The behavior of Fe is closely linked to the cycling of O, S, and C.

The reactions of Fe in processes of weathering are dependent largely on the Eh-pH system of the environment and on the stage of oxidation of the Fe compounds involved. The general rule governing the mobilization and fixation of Fe are that oxidizing and alkaline conditions promote the precipitation of Fe, whereas acid and reducing conditions promote the solution of Fe compounds. The released Fe readily precipitates as oxides and hydroxides, but it substitutes for Mg and Al in other minerals and often complexes with organic ligands.

Table 158 **Iron, Cobalt, and Nickel in Major Rock Types (values commonly found, based on various sources)**

Rock Type	Fe (%)	Co (ppm)	Ni (ppm)
Magmatic Rocks			
Ultramafic rocks Dunites, peridotites, pyroxenites	9.4–10.0	100–200	1400–2000
Mafic rocks Basalts, gabbros	5.6–8.7	35–50	130–160
Intermediate rocks Diorites, syenites	3.7–5.9	1–10	5–55
Acid rocks Granites, gneisses	1.4–2.7	1–7	5–15
Acid rocks (volcanic) Rhyolites, trachytes, dacites	2.6	15	20
Sedimentary Rocks			
Argillaceous sediments	3.3–4.7	14–20	40–90
Shales	4.3–4.8	11–20	50–70
Sandstones	1.0–3.0	0.3–10	5–20
Limestones, dolomites	0.4–1.0	0.1–3.0	7–20

In soils, Fe is believed to occur mainly in the forms of oxides and hydroxides as small particles or associated with the surfaces of other minerals. However, in soil horizons rich in organic matter, Fe appears to be mainly in a chelated form. Certain fractions of Fe in soils reveal magnetic properties. The increased ratio of magnetic Fe to regular Fe in a soil, as compared to mother rock, indicates the impact of industrial pollution.

Free Fe minerals that occur in soil are used as a key characterization for soils and for soil horizons. Fe minerals that are known to also form pedogenically are:

1. Hematite, α-Fe_2O_3, occurs mainly in soils of arid, semiarid, and tropical regions and is most often inherited from parent materials.
2. Maghemite, γ-Fe_2O_3, is formed in highly weathered soils of tropical zones and most often occurs in concentrations accompanied by hematite, magnetite, or goethite.
3. Magnetite, Fe_3O_4, is mostly inherited from parent materials; in soils, it is strongly associated with maghemite.
4. Ferrihydrite, $Fe_2O_3 \cdot nH_2O$, is apparently a common, but unstable soil mineral and is easily transformed to hematite in warm regions and to goethite in humid temperate zones.
5. Goethite, α-FeOOH, is the most common Fe mineral in soils over broad climatic regions, from temperate to tropical. The crystallinity and composition of goethites vary and may reflect the environment in which they have formed.
6. Lepidocrocite, γ-FeOOH, is common in poorly drained soils (e.g., paddy soils) and in soils of humid temperate regions. The formation of this mineral in soils is favored by lower pH, lower temperature, and the absence of Fe^{3+}.
7. Ilmenite, $FeTiO_3$, does not occur commonly in soils. As a mineral resistant to weathering, it is usually inherited from igneous parent rocks.
8. Pyrite (FeS_2), ferrous sulfide (FeS), and jarosite, $KFe_3(SO_4)_2(OH)_6$, are widely distributed in submerged soils containing S (e.g., acid sulfate soils).

Both mineral and organic compounds of Fe are easily transformed in soils, and organic matter appears to have a significant influence on the formation of Fe oxides. These oxides may be amorphous, semicrystalline, or crystalline, even under the same conditions.

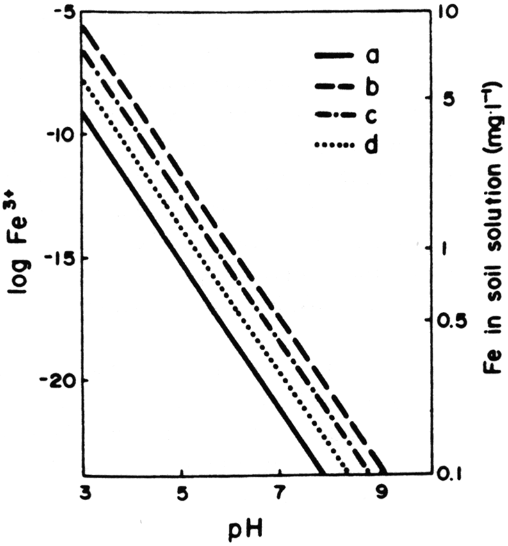

Figure 98 Influence of soil pH on the activity of Fe^{3+} maintained by Fe oxides. (a) α-FeOOH, goethite; (b) $Fe(OH)_3$, amorphous; (c) $Fe(OH)_3$, soil constituent; (d) Fe concentration in soil solution.[477,1045]

Transformations of Fe compounds are also affected by microorganisms. Some bacteria species (e.g., *Metallogenium* sp.) are involved in Fe cycling and are known to accumulate this metal on the surfaces of living cells.[36,809,856]

General characteristics of soil Fe are given in Chapter 4, Section III.B. Detailed descriptions of the role and behavior of Fe in soils have been presented by Krauskopf,[427] Norrish,[570] Schwertmann and Taylor,[699] Lindsay,[477] and Bloomfield.[81]

Soils developed on coastal sediments or on acid sulfate soils have very poor agricultural productivity because of their acidity. This acidity is a result of the oxidation of pyrite. At high pH, pyrite is oxidized chemically, but at pH values below 4.5, it is mediated microbially. These processes may bring up a very low pH of soil and greatly influence the release of metals.[1137]

Many reactions are involved in the solubility of Fe in soil, but hydrolysis and complexed species appear to be most significant. Lindsay[477] reported that the mobility of Fe in soils is largely controlled by the solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides (Figure 98). However, the formation of other Fe compounds, such as phosphates, sulfides, and carbonates, may greatly modify Fe solubilities.

The content of soluble Fe in soils is extremely low in comparison with the total Fe content. Soluble inorganic forms include Fe^{3+}, $Fe(OH)_2^+$, $FeOH^{2+}$, Fe^{2+}, $Fe(OH)_3^-$, and $Fe(OH)_4^{2-}$. In well-aerated soils, however, Fe^{2+} contributes little to the total soluble inorganic Fe, except under high soil pH conditions. The concentration of Fe in soil solutions within common soil pH levels ranges from 30 to 550 μg L^{-1}, whereas in very acid soil it can exceed 2000 μg L^{-1} (Tables 15 and 16). The soluble Fe level reaches a minimum in the alkaline pH range (Figure 98). Acid soils are therefore higher in soluble inorganic Fe than are neutral and calcareous soils. Thus, Fe^{2+} cations when in acid anaerobic soils may become toxic, but in alkaline well-aerated soils, the low concentration of soluble Fe species may not meet plant requirements for this metal.

When soils are waterlogged, the reduction of Fe^{3+} to Fe^{2+} takes place and is reflected in an increase in Fe solubility. This process of Fe reduction is strongly related to metabolism of bacteria and can result in a high Fe^{2+} concentration in some submerged soils (e.g., paddy soils). A high rate of Fe mobility in soils under anthropogenic stress (acid rain, acid fertilizers, high input of organic matter) may affect an increase of Fe mobility in various hypergenic zones. In consequence, the accumulation of Fe in certain horizons of different soils may significantly change the geochemical cycling.[1196]

Fe is known to be readily mobile in acid periodically submerged soils. The distribution of this metal in soil profiles is highly variable and reflects several soil processes. The Fe compounds that are produced are largely responsible for the color of soils and have been used for the description of soil processes and for soil classification. Zonn[1196] broadly described geochemical, geographical, and environmental aspects of Fe in soils. He emphasized a suitability of speciation and distribution of Fe compounds in soils for the typology and diagnosis of soil properties.

Like Mn compounds in soils, Fe compounds are greatly involved in the behavior of some macronutrients and of many trace elements. The degree to which soil Fe is responsible for trace metal solubility and availability is strongly governed by several soil factors. Conversely, heavy metals are also known to influence the bioavailability of Fe.

Soil Fe exhibits a great affinity to form mobile organic complexes and chelates. These compounds are largely responsible for the Fe migration between soil horizons and for Fe leaching from soil profiles and also are important in the supply of Fe to plant roots.

The Fe content of soils is both inherited from parent rocks and the result of soil processes. The most common range of Fe in soils in from 0.5 to 5%. Even in Fe-poor soil, there is no absolute deficiency of Fe for plants, but only a deficiency of readily soluble amounts.

Areas of Fe deficiency in soils for certain crops are relatively widespread (Table 39), but most occur under aridic climates and are related to calcareous, alkaline, or other specific soils (e.g., manganiferous soils). In the humic climatic zone with a predominance of acid soils, Fe deficiency in soils is most unlikely to occur unless anthropogenic factors disturb the natural chemical balance.

Soil testing and the correction of the Fe deficiency have been the subjects of several studies, and all authors have stated that caution should be used in formulating methods for determining plant-available levels of Fe.[151,279,847] There is still a lack of suitable methods to assess the Fe availability to plants. The chelating agents DTPA and EDTA appear to be most often recommended for measuring the availability of Fe to plants. Kreij et al.[1379] reported that the correlation between Fe in all substrate extracts (H_2O, EDTA, DTPA, and $CaCl_2$) and Fe in the test plant (chrysanthemum) was poor. It is assumed that during winter the plants were able, at a low growing rate, to absorb enough Fe even at low contents in the substrate.

B. Plants

1. Absorption and Transport

The mechanisms of Fe uptake and transport by plants have received much study because they are the key processes in the supply of Fe to plants. The present knowledge on this topic has been extensively reviewed by Moore,[548] Chaney et al.,[128] Tiffin,[789] Mengel and Kirkby,[531] and Tinker.[798] Almost all instances of Fe deficiency in plants are considered to occur because of soil factors that govern Fe solubility. Soil conditions that render Fe unavailable are summarized in Table 39.

The Fe uptake by plants is metabolically controlled, although it may be absorbed as Fe^{3+}, Fe^{2+}, or as Fe chelates. The ability of roots to reduce Fe^{3+} to Fe^{2+} is believed to be fundamental in the absorption of this cation by most plants. At normal soil pH levels, Fe organic complexes apparently play an important role in plant nutrition. With Fe deficiencies, roots of cereal plants release mugineic acids that are effective in mobilizing Fe and other trace metals, even from calcareous soils.[1004a] The separation of chelated Fe prior to the absorption step appears to require reduction of Fe^{3+} to Fe^{2+} at the surface of the root. Generally, roots absorb the Fe^{2+} cation.[128] In xylem exudates, Fe appears to occur unchelated; however, its transport is mediated largely by citrate chelates. In plant tissues, mobile Fe has been identified as citrates and soluble ferredoxins. Fe is not readily transported in plant tissues, and therefore its deficiency appears first in younger plant parts. As Scheffer et al.[688a] reported, the amount of Fe is relatively low in plant parts of intensive growth.

Both Fe uptake and transport between plant organs are highly affected by several plant and environmental factors, of which soil pH, concentration of Ca and P, and ratios of several heavy metals are most pronounced. In general, a high degree of oxidation of Fe compounds, Fe precipitation on carbonates and/or phosphates, and competition of trace metal cations with Fe^{2+} for the same binding sites of chelating compounds are responsible for a low Fe uptake and for a disturbance in Fe transport within plants. Usually, the more Fe deficient, the greater the ability of plant roots to extract Fe from minerals and from chelating agents.

2. Biochemical Functions

The metabolic functions of Fe in green plants are relatively well-understood, and Fe is considered the key metal in energy transformations needed for syntheses and other life processes of the cells.[83,564,630,1184] The essential role of Fe in plant biochemistry can be summarized as follows:

1. Fe occurs in heme and non-heme proteins and is concentrated mainly in chloroplasts.
2. Organic Fe complexes are involved in the mechanisms of photosynthetic electron transfer.
3. Non-heme Fe proteins are involved in the reduction of nitrites and sulfates.
4. Chlorophyll formation seems to be influenced by Fe.
5. Fe is likely to be directly implicated in nucleic acid metabolism.
6. Catalytic and structural role of Fe^{2+} and Fe^{3+} are also known.

This summary is oversimplified and too generalized, but it gives some information showing that, in addition to the active Fe roles in redox reactions of chloroplasts, mitochondria, and peroxisomes, Fe also performs other functions in the plant.

Fe deficiency affects several physiological processes and therefore retards plant growth and plant yield. The deficiency of Fe is a major worldwide problem with many crops since a large number of cultivated soils are low in available content. The control of Fe deficiency often is not sufficiently effective and therefore much effort has been made in screening plants for iron efficiency. Brown[104a] reviewed the current approach to the Fe deficiency problem and stated that genotypes and plant species should be selected for their efficient absorption of Fe.

The symptoms of Fe deficiency may occur at very different Fe levels in plants, and this deficiency is highly dependent on soil, plant, nutritional, and climatic factors. The most common initial symptom of Fe deficiency is interveinal chlorosis of young leaves (Table 38). Several fruit trees and, of all the cereals, oats and rice in particular, are very susceptible to Fe chlorosis.

On soil rich in the soluble Fe fraction, an excessive Fe uptake can produce toxic effects in plants. Plant injury due to Fe toxicity is most likely to occur on strongly acid soils (ultisols, oxisols), on acid sulfate soils, and on flooded soils. High concentrations of Fe in the soil solution is almost always related to Fe toxicity. This toxicity is also often associated with salinity and a low phosphorus or base status of soils. It has been reported in countries of both tropical and arid regions.[622] The concentration of about 500 ppm Fe^{2+} in the soil solution of paddy soil was reported to kill rice seedlings.[241] It should be emphasized that both an excessive Fe uptake and a low tolerance to a high concentration of Fe in plant tissues is significantly complicated by several nutritional factors.

Symptoms of Fe toxicity are not specific and usually differ among plant species and stages of growth (Table 40). Injured leaves or necrotic spots on leaves indicate an accumulation of Fe above 1000 ppm (3 to 6 times as high as the Fe content of healthy leaves). However, the most pronounced symptom is the ratio of Fe to other elements and to heavy metals in particular. The proper Fe:Mn ratio seems to be the most obligatory factor in the tolerance of plants to Fe toxicity.

Foy et al.[241,998] reviewed the physiology of Fe toxicity and of plant resistance. Based on this review, it may be stated that:

1. Plants high in nutrients, especially in Ca and SiO_2, can tolerate higher internal levels of Fe.
2. Rice roots are able to oxidize Fe and deposit it on root surfaces.
3. Root damage by H_2S or any other factor destroys the oxidizing power of roots and thus aggravates Fe toxicity.

Fe tolerance of plants is most often associated with oxidation and immobilization and/or exclusion of soluble Fe by roots. Plants adapted to waterlogged conditions are commonly more tolerant to high Fe levels than plants grown in well-aerated soils.

Plant response to Fe toxicity, as well as to Fe deficiency, is highly variable among genotypes and plant species. Therefore, genetic manipulation through plant breeding seems to be one of the most promising lines of research on the iron problem in plant nutrition. Toxicity symptoms in bean leaves are reported to occur at Fe concentrations >3080 ppm.[1309]

3. Interactions with Other Elements

Antagonistic interaction between Fe and heavy metals has been observed in several crops, and results of several studies suggest that chlorosis brought about by heavy metal excess is apparently the result of induced Fe deficiency.[16,105,778] Excess amounts of heavy metals, and of Mn, Ni, and Co in particular, caused a reduction in absorption and translocation of Fe and resulted in a decrease of chlorophyll. On the other hand, high levels of Fe compounds in soil are known to greatly decrease trace metal uptake (Figure 30). Reactions between Fe and Mn (see Chapter 12, Section VI.B.3) are commonly observed, and the ratio of these two metals in both growth medium and plant tissue seems to be more important to plant metabolism than their concentrations.

Pulford[633] suggested that the interaction of Fe-Zn is apparently associated with the precipitation of franklinite ($ZnFe_2O_4$) that depressed the availability of both metals. Fe-P interactions commonly occur in both plant metabolism and soil media. The affinity between Fe^{3+} and $H_2PO_4^-$ ions is known to be great, and therefore the precipitation of $FePO_4 \cdot 2H_2O$ can easily occur under favorable conditions. Furthermore, P anions compete with the plant for Fe, and thus P interferes with Fe uptake and with the internal Fe transport. High Fe concentrations are known to cause P deficiency. The appropriate P:Fe ratio in plants is fundamental to plant health. The details of this subject are reviewed by Olsen,[581] Adams,[3] Dekock,[174] and Wild and Jones.[1184] K deficiency is also often associated with Fe toxicity because plants are not capable of oxidizing Fe^{2+} to Fe^{3+}.[921] The antagonistic effect of Ca on Fe is very complex and is related to both the growth medium and intracellular metabolism.

Other interactions between Fe and macronutrients (Table 43) are not well-understood. Thus, Fe chlorosis in plants on calcareous soils may be thought to reflect a low Fe availability in such soils because of the present insufficient evidence of Fe-Ca metabolic interferences. Interaction between Fe and S seems to be erratic in that low soil S levels may depress Fe uptake, whereas a high S content may also result in low Fe availability, depending on soil environments.

4. Concentrations in Plants

The appropriate content of Fe in plants is essential both for the health of the plant and for the nutrient supply to man and animals. The variation among plants in their ability to absorb Fe is not always consistent and is affected by changing conditions of soil and climate and by the stages of plant growth. Generally, certain forbs, including legumes, are known to accumulate more Fe than are grasses. However, where Fe is easily soluble, plants may take up a very large amount of Fe. This is clearly shown by vegetation grown in soils derived from serpentine, where grass contained Fe within the range of 2127 to 3580 ppm (DW).[366]

The natural Fe content of fodder plants ranges from 18 to about 1000 ppm (DW) (Table 159). The nutritional requirement of grazing animals is usually met at the Fe concentration range from around 50 to 100 ppm (DW) in forage.

Edible parts of vegetables appear to contain fairly similar amounts of Fe, ranging from 29 to 130 ppm (DW), with lettuce being in the upper range and onion in the lower range. Fe in ash of a variety of plant species is reported to range from 220 to 1200 ppm (Table 160). The recent

Table 159 Mean Levels and Ranges of Iron in Grass and Clover at the Immature Growth Stage from Different Countries (ppm DW)

	Grasses		Clovers		
Country	Range	Mean	Range	Mean	Ref.
Australia	228–264	244	252–357	285	266
Great Britain	73–154	103	122–132[a]	—	867a
Finland	39–49	43[b]	—	—	388
Germany	79–206	126	116–253	175	31
Germany	110–430	187	—	—	596
Hungary	133–923	376	118–535	346[c]	803
Ireland	34–78	55	64–85	74[a]	235
Japan	55–157	106	75–229	152	770
Poland	60–140	92	76–136	117	838
U.S.	18–320	73	—	—	200
New Zealand	69–1510	320	105–1700	400	536

[a] Alfalfa.

[b] Timothy.

[c] Various legumes.

Table 160 Mean Iron Content of Plant Foodstuffs (ppm)

		FW Basis		DW Basis			AW Basis
Plant	Tissue Sample	(574)	(705)	(705)	(727)	(381)	(705)
Sweet corn	Grains	4.3	4.4	17	—	—	670
Bean	Pods	0.7	9.2	84	86[a]	—	1200
Cabbage	Leaves	2.4	3.3	42	—	52	450
Lettuce	Leaves	0.3	5.6	130	—	—	960
Red beet	Roots	—	—	—	71	82	—
Carrot	Roots	0.8	1.9	16	54	67	220
Onion	Bulbs	—	3.3	33	29	50	780
Potato	Tubers	2.8	3.9	21	41	58	490
Tomato	Fruits	—	3.0	58	—	—	480
Apple	Fruits	0.6	0.9	6	—	—	350
Orange	Fruits	2.2	2.0	15	—	—	430
Cucumber	Fruits	1.0	2.6	67	—	—	680
Tea	Leaves[b]	—	—	—	99	132	174

Note: References are given in parentheses.

[a] Pea seeds.

[b] Tea from Japan, India, and China, respectively.[1032]

reference for food compositions in the U.S. gives the following values for Fe in some categories of plant food (ppm FW): (1) vegetables: range 3–31, the lowest value for celery root, and the highest for spinach; (2) fruits: range 1–11, the lowest value for apples and honey melon, and the highest for black currant (European); (3) cereals: range 3–37, the lowest value for barley pearls (cooked), the highest for rye (whole grain); and (4) nuts: range 11–47, the lowest value for hazelnuts (shelled) and the highest for almonds (shelled).[1291]

Various cereal grains do not differ much in their Fe concentrations. The common average Fe content of different cereals ranges from 25 to around 80 ppm (DW). Values above 100 ppm are reported only for a few countries (Table 161). The grand mean of 48 ppm (DW) for Fe in grains was calculated by excluding the values of 100 ppm and above.

Table 161 **Iron Content of Cereal Grains from Different Countries (ppm DW)**

Country	Cereal[a]	Range	Mean	Ref.
Great Britain	Barley	—	218	112
	Oats	—	96	112
Canada	Oats	—	133	514
Egypt	Wheat	26–69	40	213
Finland	Barley	—	52	727
	Oats	—	60	727
	Rye	—	53	727
	Wheat (s)	24–50	37	508
	Wheat (w)	25–37	31	508
Norway	Barley	16–54	33	446
	Wheat	17–38	30	446
Poland	Rye	34–43	38	267, 667
	Wheat	15–30	25	267, 667
U.S.	Barley	53–160	88	200
	Oats	54–140	81	200
	Wheat (s)	28–100	48	200
	Wheat	25–43	38	200, 492
	Rye	—	100	492
	Rice	1.4–10	3.6[b]	1187
Russia	Wheat (s)	29–37	33	586

[a] Spring, s; winter, w.

[b] FW basis.

III. COBALT

A. Soils

In the Earth's crust, Co has a high concentration in ultramafic rocks (100 to 220 ppm) when compared to its content in acid rocks (1 to 15 ppm). The Co abundance in sedimentary rocks ranges from 0.1 to 20 ppm and seems to be associated with clay minerals or organic matter (Table 158). The crust of the Earth as a whole contains, on average, 25 ppm Co.

There are no common rock-forming Co minerals (formed mainly with As, S, and Se), for example, cobaltite (CoAsS) and limneite (Co_2S_4). In hypergenic zones and in soils, the formation of erythrite, $Co_2(AsO_4)_2 \cdot 8H_2O$, is likely to occur; Co is mostly hidden in various Fe minerals. In geochemical cycles, Co closely resembles Fe and Mn. However, its fate in weathering processes and its distribution in sediments and in soil profile seems to be strongly determined by Mn oxide phase formation.

In nature, Co occurs in two oxidation states, Co^{2+} and Co^{3+}, and formation of the complex anion $Co(OH)_3^-$ is also possible. During weathering, Co is relatively mobile in oxidizing acid environments, but due to a high sorption by Fe and Mn oxides, as well as by clay minerals, this metal does not migrate in a soluble phase. In soils, certain bacteria are known to mobilize Co already complexed as chelate compounds and, thus, Co^{3+} in solution can be transported away.

In soils, the weathering, transforming, and adsorption mechanisms of Co compounds and forms are extremely complicated due to variable oxidation stages of Co and due to microbial activity.[1568] The solubility and availability of soil Co is of great nutritional concern and therefore has received much study. McKenzie[523] has reviewed his research and the findings of other scientists on Co behavior in soils. Adequate amounts of Co in soil are essential to its biological activity since Co, as a component of vitamin B_{12}, is involved in methylation processes in soil.

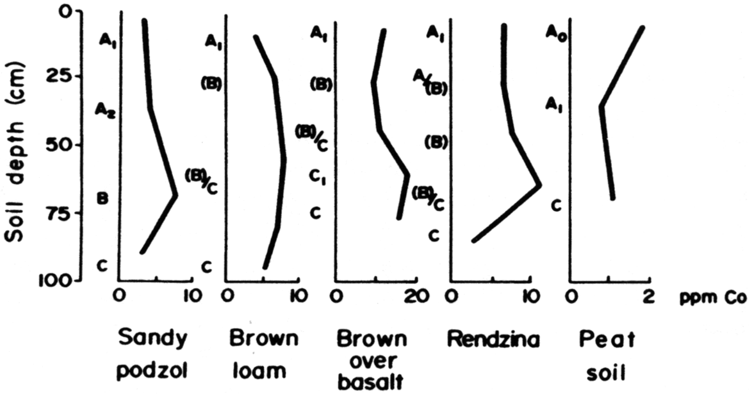

Figure 99 Distribution of Co in the profiles of different soils developed under humid climate conditions. (Letters indicate genetic soil horizons.)

Fe oxides are known to have a great affinity for selective adsorption of Co. This has been observed in most kinds of soil and is reflected in the Co distribution in soil profiles showing a general similarity between the levels of Fe and Co in soil horizons (Figure 99). However, in certain soils enriched in Mn minerals, the association of Co with Mn dominates other factors governing Co distribution.

The sorption mechanism of Co by crystalline Mn oxides apparently differs at different pH values and generally is based on the interchange of Co^{2+} with Mn^{2+} and on the formation of hydroxy species, $Co(OH)_2$, precipitated at the oxide surface. Different redox mechanisms have been proposed for the Co sorption by Mn oxides.[997] These include: (1) oxidation of Co^{2+} to Co^{3+} at the oxide interface, (2) reduction of Mn^{4+} to Mn^{3+} in the oxide crystal lattice, and (3) replacement of Mn^{3+} or Mn^{4+} by Co^{3+} (see Chapter 12, Section VI.A). In addition, the specific exchange sorption with bound H can occur over a broad pH range.[486] In soil, the sorption of Co by Mn oxides increases greatly with pH, and the reaction seems to be rapid (Figure 100). Thus, the mobility of Co in most soil conditions is greatly influenced by Mn oxides and by the Eh-pH soil intensities.

Soil organic matter and clay content are also important factors that govern Co distribution and behavior. The roles of montmorillonitic and illitic clays especially have been cited by numerous investigators as being of significance because of their great sorption capacity and their relatively easy release of Co. The mobility of Co is strongly related to the kind of organic matter in soils. Organic chelates of Co are known to be easily mobile and translocated in soils (Figure 22). Some organic ligands (e.g., citric acid) are shown to stimulate the sorption of Co on Fe-coated silica compounds, but increase Co mobility when Fe hydroxides are absent.[1244a] Although soils rich in organic matter are known to have both a low Co content and low Co availability, Co organic chelates may also be readily available to plants.[81] This is especially pronounced at higher pH and in freely drained soils. In solutions of most soils, the Co concentration is fairly low and ranges from 0.3 to 87 $\mu g\ L^{-1}$ (Table 16). In general, the behavior of Co in most soil types is relatively well-understood: therefore, a preliminary evaluation of a probable Co status and the availability of Co to plants can be made based on soil and geological information.

Factors contributing to Co deficiency for grazing animals are mainly associated with alkaline or calcareous soils, light leached soils, and soils with high organic matter content (Table 39). The Co content and distribution in soil profiles are also dependent on soil-forming processes and therefore differ for soils of various climatic zones. Usually, higher Co contents of surface soils are observed for arid and semiarid regions, whereas exceedingly low soil Co has been

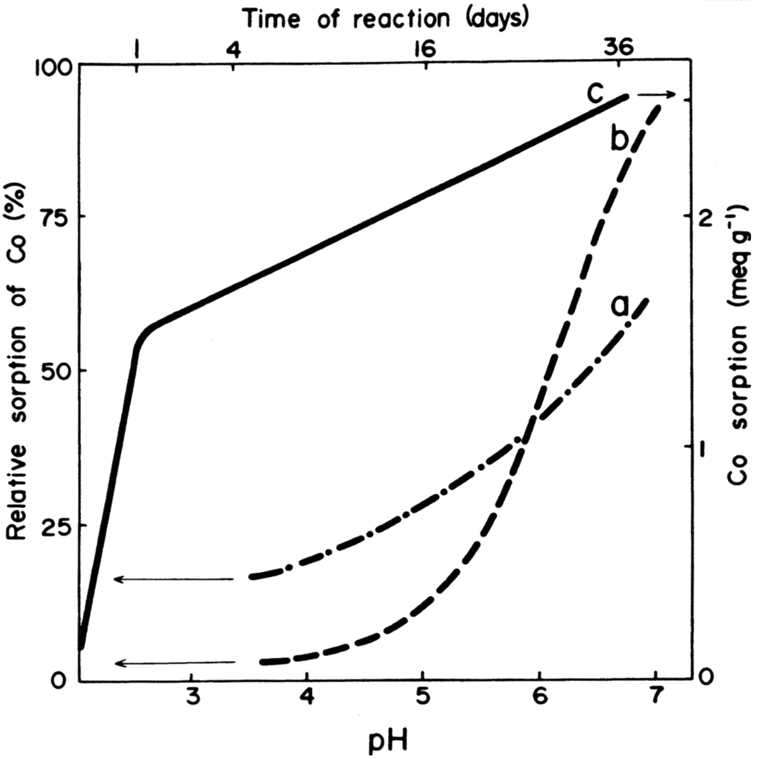

Figure 100 Effects of pH on the sorption of Co by (a) Mn nodules and (b) goethite and effects of time on the sorption of Co by (c) birnessite.[523]

reported for light soils of the Atlantic Coastal Plain and for soils of the glaciated region of the northeastern U.S.[436]

The Co concentration in soils is inherited from parent materials. Soils over mafic rocks and soils derived from clay deposits contain the highest amounts of this metal (Table 162). Other high Co concentrations reported for Australian ferralsols (122 ppm) and Japanese soils (116 ppm) are related either to pollution or to specific enrichment. The normal Co content of surface soils usually ranges from 0.1 to 70 ppm (DW), with the lowest mean values for histosols and podzols and the highest for cambisols and rendzinas (Table 9). The grand mean Co concentration for worldwide soils is 7.9 ppm, and for the soils of the U.S., it is 8.2 ppm.[433,706]

The range of Co in the reference soil samples of the U.S. is from 5.5 to 29.9 ppm (mean, 10 ppm), and in the soil samples of China is from 5.5 to 97 ppm (mean, 11.6 ppm).[1313] The total content of Co in soils of Finland, at the 95th percentile, is about 25 ppm, and the acid-soluble fraction is 13 ppm.[1368] The median value for the total Co content in soils of Lithuania is reported to be 3.4 ppm, and in forest podzolic soils of Russia, its concentration is about 5.5 ppm.[1475] In most sandy soils of Poland, the HCl-soluble Co is below 2.5 ppm, while in silty and loamy soils its concentration increases to 10 ppm.[1390]

Acetic acid-soluble Co in soils usually corresponds to readily available Co (Table 39). Soil application of Co as sulfate or EDTA chelate is the most common practice in controlling Co deficiency in ruminants.

Naturally high Co contents are usually observed in soils over serpentine rocks and ore deposits. Significant sources of Co pollution are related to nonferrous metal smelters, whereas coal and other fuel combustions are of considerably less importance; however, roadside soils and street dusts are known to be enriched in Co (Table 163).

Table 162 Cobalt Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Germany	0.8–6	—	689
	New Zealand	21–65	—	861
	Poland	0.1–12	2.0	382
	Romania	4–25	14	1127
	U.S.	0.4–20	3.5	433, 706
Loess and silty soils	Germany	4–13	—	689
	New Zealand[a]	17–24	—	861
	Poland	3–23	7.0	382
	Romania[b]	—	5.2	42
	U.S.	3–30	11	433, 706
Loamy and clay soils	Bulgaria	15–23	18.1	558
	Burma	16–19	18	575
	Germany	3–6	—	689
	New Zealand[a]	19–58	—	861
	Poland	4–29	6.0	382
	Romania	13–24	18	1127
	U.S.	3–30	8	433, 706
	Russia	—	5.9	346
Soils on glacial till	Denmark	—	2.1	801
	Ireland	1–17	—	236
	Poland	1.4–14	3.6	974
	U.S.	5–15	7.5	433, 706
Fluvisols	Bulgaria	—	6.4	558
	Egypt	16–21	18.3	213
	Poland	5.3–13	—	156
Rendzinas	Germany	—	6.1	689
	China	1–70	27	1124
	Ireland	10–12	—	236
	Poland	2.2–22	4.5	156, 685
	U.S.	3–20	9.5	433, 706
Kastanozems and brown soils	Burma	6–11	9	575
	Ireland	2–10	—	236
	Romania	5–17	12	1127
	Russia	2.3–3.8	2.9	343
Ferralsols	Australia	0.2–122	—	565
	Madagascar	3–20	—	557a
Solonchaks and solonetz	Burma	12–15	14	575
	Madagascar	15–30	—	557a
	Russia	9–14	10.4	12, 351
Chernozems	Bulgaria	9.5–18	—	558
	U.S.	3–15	7.5	433, 706
	Russia	0.5–50	12.0	346, 351, 419a, 1123
	Former S.U.[c]	0.8–2.3	1.4	1097
Paddy soils	Japan	2.4–24	9.0	395
Meadow soils	Russia	11.7–15	—	12
Histosols and other organic soils	Bulgaria	1.7–49	—	558
	Canada	3.1–13.1	6.8	243
	Denmark	—	1.6	801
	Poland	0.2–34	3	382
	U.S.	3–10	6	433, 706
Forest soils	Russia	0.6–45	8.0	12, 419a
	U.S.	5–20	10	433, 706
Various soils	Bulgaria	3.8–65	21.5	558
	Great Britain	—	17.7	818
	Canada	5–28	12.4	409

(*Continued*)

Table 162 Cobalt Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Various soils	Canada[b]	5–50	21	521
	Denmark	—	2.3	801
	Germany	—	14.5	390
	Italy[d]	4–275	14	946
	Japan	1.3–116	10	395
	Romania	1–6.9	3.1	43
	U.S.	3–50	10.5	433, 706

[a] Soils derived from basalts and andesites.

[b] Data for whole soil profiles.

[c] Kirghizya.

[d] Maximum values included contaminated soils excluded from the mean value.

Table 163 Cobalt Enrichment and Contamination in Surface Soils (ppm DW)

Site and Pollution Source	Mean or Range of Content	Country	Ref.
Soil over serpentine rock	10–520	New Zealand	495
Mining or ore deposit	13–85	U.S.	744
Metal-processing industry	10–127	Canada	150, 333
	18	Germany	390
	67	Great Britain	1005
	20–70	Norway	441
	42–154	U.S.	744
Sludged farmland	3.3–12.4	Holland	314
Roadside or airport area	7.9	U.S.	744
	6–14[a]	Great Britain	744

[a] Urban street dusts.

B. Plants

1. Absorption and Transport

Co uptake by plants is a function of the mobile Co content of soil and of the Co concentration in solution (Figure 101). During absorption, Co behaves like other heavy metals (e.g., Fe, Mn) and is transported in forms bound to complexing organic compounds with a molecular weight in the range of 1000 to 5000, with a negative overall charge.[872] Apparently, the simultaneous transport of Co^{2+} (like Fe^{2+}) with citrate cannot be precluded.

Numerous studies have been made of plant uptake of Co from soils, and it has been shown that enrichment of the soil with Co has led to increased levels of this metal in plants. Co is also easily taken up by leaves through the cuticle; therefore, foliar applications of Co in solution are known to be effective in the correction of Co deficiency.

Liming and different fertilizers influence the solubility of Co. As Klessa et al.[1365] suggest, liming is a major factor in reducing soil Co phytoavailability. This creates a risk of low Co content in herbage, which affects a dangerous Co deficiency in ruminants.

2. Biochemical Functions

The essentiality of Co for both blue-green algae and microorganisms in fixing N_2 is now well-established. It is not clear, however, whether Co is essential for higher plants, although there are some evidences of a favorable effect of Co on plant growth, as reported by Reisenauer et al.,[648] Jagodin et al.,[349] and Mengel and Kirkby.[531] Co has also been recognized as a component of a precursor of vitamin B_{12} for ruminant animals.

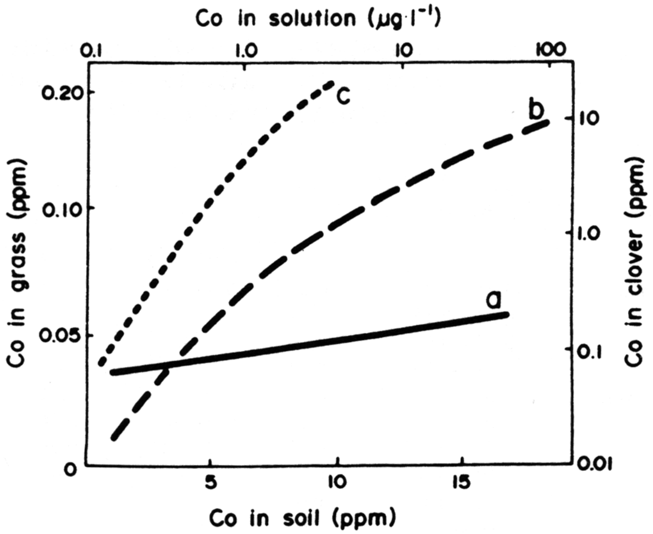

Figure 101 Co uptake by plants from soil or nutrient solution. (a) Ryegrass grown on soil; (b) clover, tops, grown in culture solution; (c) clover, roots, grown in culture solution.[147,1045]

Smith and Carson[744] compiled information from several sources on the effects of Co on nonleguminous plants, and the final opinion is inconclusive. Although traces of Co coenzymes have been detected in nonlegumes, it is not known whether these compounds might have originated from microorganisms associated with the plant.[564] Beneficial effects of low Co concentrations on plant metabolism are not yet fully understood. Presumably, several effects are cross-linked with interactions with other trace metals.

In legumes and alder (*Alnus* sp.), Co affects the ability of plants to fix N_2 from air. Co is chelated at the center of a porphyrin structure termed the cobamide coenzyme, which is effective in N_2 fixation. Nicholas[564] reviewed all recent findings on the Co function in N_2 fixation and stated that cobamide coenzymes are involved in the migration of the H atom during the formation of the NH_3 compound by the rhizobia. Although Co is known to be essential in certain bacterial functions, it is also reported to inhibit Mg uptake by some microorganisms and to exhibit antimicrobial activity.[856]

In legumes, Co deficiency inhibits the formation of leghemoglobin and hence N_2 fixation. However, the Co requirement for this process is low. As Wilson and Reisenauer[883] have found, 10 ppb Co in the nutrient solution was adequate for the growth of alfalfa. In natural conditions, Co deficiency is not known to retard the growth of either nonlegumes or legumes.

The Co deficiency in herbage has been considered mainly from the viewpoint of ruminant requirements. It has been observed that soils with a Co content of less than 5 ppm may produce herbage that is Co-deficient for the normal growth of animals. The critical Co level for ruminant diets is around 0.08 to 0.1 ppm (DW), and similar levels were found in clover from different countries (Table 163). The deficiency of Co can be controlled by the application of Co salts to the soil, and the effect of such a treatment is known to last for several years.[544,649] There are differences of opinion, however, as to whether it is better to apply Co to the soil or give directly to livestock when curing a Co deficiency. If the soil contains large amounts of Mn or Fe oxides capable of immobilizing Co, a shorter effective period should be expected.

When Co is taken up in excess by roots, it principally follows the transpiration stream, resulting in an enrichment of Co at the leaf margins and tips. Therefore, the common symptoms of Co toxicity are white, dead margins and tips of leaves. However, the primary reaction of plants to an excess of Co is interveinal chlorosis of new leaves, which is closely linked with Fe chlorosis.

Cytological effects of Co excesses were reported to be inhibited mitosis and chromosome damage, or damage to the endoplasmic reticulum of root tips, and as disorganized phloem of the minor veins.[643,744]

In nature, although plant species range widely in their content of Co, toxicity symptoms are not often observed. When a high Co level is readily available, in polluted soil in particular, it can seriously affect plant growth and metabolic functions. Kitagishi and Yamane[395] reported that the addition of 25 and 50 ppm of Co to the soil was toxic to rice plants. Anderson et al.[23] found a Co concentration of 140 μg L^{-1} in a soil solution from serpentine soils where oat plants were affected by Co toxicity.

Different concentrations of Co in plant tissues have been reported to produce toxicity symptoms, as follows: 43 to 142 ppm (DW) in bush beans,[841] 19 to 32 ppm (DW) in Sudan grass,[279] and 6 ppm (DW) in barley seedlings.[171] Kloke et al.[1052] gave a similar range of Co as toxic to sensitive plant species. However, commonly reported critical Co levels in plants range from 30 to 40 ppm (DW).[1081]

Cereals are known as the most sensitive plants to Co excess, but Anderson et al.[23] reported that toxic effects at the Co concentrations of 10 to 20 ppm are most probably associated with an excess of Ni. Case et al.[123] proposed that the Co content of herbage should not exceed 60 ppm (DW) because of the animal health hazard.

Plants are known to accumulate large amounts of Co and to develop a mechanism of Co tolerance which is basically similar to that occurring in any metalliferous plant species. Several plant species, mainly of the families Cruciferae, Caryophyllaceae, Violaceae, Leguminosae, Boraginaceae, Myrtaceae, and Nyssaceae, are known for their high accumulation of Co and are also recommended as biogeochemical indicators. These plants growing in soils over serpentine or Cu-Co ores may contain Co as high as 2500 to 17,700 ppm (AW).[613] Brooks[104] described *Hausmaniastrum* sp. as hyperaccumulators of Co, containing up to about 4000 ppm (DW) Co without having toxicity symptoms when grown in soil overlying a Co-Cu ore body. On the Co-deficient coastal sands of North Carolina, leaves of *Nyssa sylvatica* (black gum) contained from 1 to 216 ppm (DW) Co, whereas broomsedge (*Andropogon* sp.) contained only 0.05 to 0.81 ppm.[744]

3. Interactions with Other Elements

Cobalt interacts with all metals that are associated geochemically with Fe (Tables 11 and 12). However, the most significant relationship has been observed between Co and Mn or Fe in the soil and between Co and Fe in the plant. Both geochemical and biochemical antagonisms between these metals have arisen from their affinity to occupy the same sites in crystalline structures and from the similarity of their metallo-organic compounds.

4. Concentrations in Plants

In addition to soil factors highly controlling the Co levels in plants, the ability of plant species to absorb Co varies considerably. Legumes are known to accumulate more Co than do grasses. The mean Co content of clover from different countries was reported to range from 0.10 to 0.57 ppm (DW), whereas this value for grass was 0.03 to 0.27 ppm (Table 164). In general, Co concentration in legumes exceeds Co content of grasses and grain crops. The Co content of plant foodstuffs varies from around 8 to 100 ppm (DW), with cabbage being in the upper range and corn and apple in the lower range (Table 165).

The relatively great variation observed in Co levels given by different authors for cereal grains may also reflect analytical error (Table 166). It seems rather unlikely that grains would contain higher amounts of Co than are found in green parts. Therefore, values within the range of 4 to 80 ppb (DW) seem to be most reasonable. However, a higher content of Co may occur in grains of certain cereal genotypes, as well as in grains of plants growing in specific soil and climatic conditions. Sillanpää and Jansson[1491] evaluated results of analysis of wheat (before shooting stage, N = 1723)

Table 164 Mean Levels and Ranges of Cobalt in Grass and Clover at the Immature Growth Stage from Different Countries (ppm DW)

	Grasses		Clovers		
Country	**Range**	**Mean**	**Range**	**Mean**	**Ref.**
Australia	—	—	0.07–0.53	0.19	524a
Great Britain	<0.03–1.0[a]	0.27	0.06–1.7[a]	0.57	67, 544
France	0.02–0.15	0.07[b]	—	—	147
Finland	0.04–0.08	0.06[c]	—	—	829
	0.17–0.39	0.22[d]	—	—	221
Germany	0.03–0.22	0.09	0.06–0.21	0.12	31, 576a, 596
Japan	0.01–0.51	0.12[c]	0.02–0.75	0.20	770
Norway	0.02–0.04	0.03[d]	—	—	360
New Zealand	0.03–0.15	0.08[f]	—	—	863
Poland	0.01–0.24	0.08	0.05–0.26	0.10	156
Sweden	0.01–0.40	0.06	0.08–0.30	0.15	203
U.S.	<0.04–0.39	0.08	0.15–0.27	0.19	200, 436

[a] For freely and poorly drained soils, respectively.

[b] Ryegrass.

[c] Hay.

[d] Timothy.

[e] Orchard grass.

[f] Sweet vernal grass.

Table 165 Cobalt Content of Plant Foodstuffs (ppb)

		FW Basis		DW Basis	AW Basis
Plant	**Tissue Sample**	**(547, 574)**	**(705, 710)**	**(705, 710)**	**(705, 710)**
Sweet corn	Grains	6.4	2.0	8.1–31	310
Snap bean	Pods	1.0	5.9	20–51	770
Cabbage	Leaves	3.6	8.0	100–160	1100
Lettuce	Leaves	6.8	1.9	46–210	360
Carrot	Roots	3.0	4.4	37–120	520
Onion	Bulbs	—	2.8	28–80	660
Potato	Tubers	2.5	6.9	37–160	860
Tomato	Fruits	—	3.2	62–200	520
Cucumber	Fruits	0.9	3.4	87–170	880
Apple	Fruits	0.3	1.2	8.3–16	460
Orange	Fruits	0.4	2.4	19–45	520
Tea	Leaves[a]	—	—	0.18–0.24	—

Note: References are given in parentheses.

[a] Range of mean contents in tea leaves from Japan, India, and China.[1032]

and of corn (6-leave stage, N = 1892) from 30 countries. They stated that soil texture is the most significant parameter controlling the Co level in plants. The average concentration of Co in wheat plants was 0.110 ppm and in corn plants 0.148 ppm.

Plants grown on Co-enriched soils such as serpentine soils or soils over Co ore bodies contain higher amounts of this metal, even when they are not known as Co accumulators. Leaves of oats from serpentine soils contained up to about 15 ppm (DW) Co,[23] cultivated grass contained up to 96 ppm (DW),[366] and native vegetation contained from 17 to 540 ppm (AW).[494]

Data are scarce concerning Co pollution in plants, although Co is known to be released into the atmosphere from coal and fuel oil burning. However, tomato plants grown in water extracts of soils collected near a Cu-Ni smelter contained from 10 to 18 ppm (DW) Co, as cited by Hutchinson and Whitby.[333]

Table 166 Cobalt Content of Cereal Grains from Different Countries (ppb DW)

Country	Cereal[a]	Range	Mean	Ref.
Australia	Wheat	13–231	82	867
Egypt	Wheat	160–380	270	213
Finland	Barley	—	20	829
	Oats	—	10	829
	Wheat (s)	—	10	829
Norway	Barley	1–15.6	4.4	446
	Oats	<100–280[b]	—	748
	Wheat	1.5–13.7	4.7	446
U.S.	Barley	<28–44	28	200
	Oats	<24–78	41	200
	Wheat (s)	<12–48	20	200
	Wheat (w)	14–51	19	200
Russia	Oats	170–300	237	790

[a] Spring, s; winter, w.

[b] Pot experiment.

There are no reports of Co toxicity to animals attributed to consumption of natural feedstuffs. However, in certain geochemical areas, and under the influence of man-induced pollution, the excess of Co in plants may be a health risk.

IV. NICKEL

A. Soils

There is a general similarity between the distribution of Ni, Co, and Fe in the Earth's crust. Thus, Ni contents are highest in ultramafic rocks (1400 to 2000 ppm), and its concentrations decrease with increasing acidity of rocks down to 5 to 15 ppm in granites (Table 158). Sedimentary rocks contain Ni in the range of 5 to 90 ppm, with the highest range being for argillaceous rocks and the lowest for sandstones.

Geochemically, Ni is siderophilic and will join metallic Fe wherever such a phase occurs. Also the great affinity of Ni for S accounts for its frequent association with segregates of S bodies. In terrestrial rocks, Ni occurs primarily in sulfides (millerite, NiS), arsenides (niccolite, NiAs), and antimonides (breithauptile, NiSb), and most of it is in ferromagnesians, replacing Fe. Ni is also associated with carbonates, phosphates, and silicates.

Ni is easily mobilized during weathering and then is coprecipitated mainly with Fe and Mn oxides. However, unlike Mn^{2+} and Fe^{2+}, Ni^{2+} is relatively stable in aqueous solutions and is capable of migration over a long distance. During weathering of Ni-rich rocks (mainly in tropical climates), the formation of garnierite, $(Ni, Mg)\ SiO_3 \cdot nH_2O$, which is a poorly defined mixture of clay minerals, is observed. Organic matter reveals a strong ability to absorb Ni; therefore, this metal is likely to be concentrated in coal and oil. This concentration is apparently an effect of the precipitation of Ni as sulfides in sediments rich in organisms and under reducing conditions.

Although soil Ni is believed to be strongly associated with Mn and Fe oxides (Table 22), for most soils, less than 15 to 30% of the total Ni is extracted with the Mn oxides.[570] A relatively high percentage of Ni extraction with EDTA from soils suggests that Ni is less strongly fixed by soil components than is Co, as described by Berrow and Mitchell.[69]

In surface soil horizons, Ni appears to occur mainly in organically bound forms, a part of which may be easily soluble chelates.[81] However, Norrish[570] stated that the fraction of soil Ni carried in the oxides of Fe and Mn seems also to be the form most available for plants.

Ni distribution in soil profiles is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types. Concentrations of Ni in natural solutions of surface horizons of different soils vary from 3 to 25 μg L^{-1} at the boundary and at the center of the affected area, respectively.[23]

Information on the Ni ionic species in the soil solution is rather limited, but the Ni species described by Garrels and Christ[256] such as Ni^{2+}, $NiOH^+$, $HNiO_2^-$, and $Ni(OH)_3^-$ are likely to occur when the Ni is not completely chelated. Generally, the solubility of soil Ni is inversely related to the soil pH. Ni sorption on Fe and Mn oxides is especially pH dependent, probably because $NiOH^+$ is preferentially sorbed and also because the surface charge on sorbents is affected by pH.[948]

Bloomfield[81] stated that although organic matter is able to mobilize Ni from carbonates and oxides as well as to decrease Ni sorption on clays, the bonding of this metal to the organic ligands could not be particularly strong. Complexing ligands such as SO_4^{2-} and organic acids reduce the sorption of Ni. The remobilization of Ni from solid phases appears to be possible in the presence of FA and HA. Thus, Ni may be quite mobile in soils with high complexation ability (e.g., organic-rich and polluted soils).

The Ni status in soils is highly dependent on the Ni content of parent rocks. However, the concentration of Ni in surface soils also reflects soil-forming processes and pollution.

Soils throughout the world contain Ni within the broad range of from 0.2 to 450 ppm, while the range for soils of the U.S. is from <5 to 150 ppm (Tables 9 and 167). The highest Ni contents are always in clay and loamy soils, e.g., rendzinas, cambisols, and kastanozems (Table 9). This is clearly demonstrated for soils of Poland: geometric mean in light sandy soils is 5 ppm, in medium loamy soils 11 ppm, and in clay loamy soils 22 ppm. (Table 20). Geometric mean Ni content in surface soil from major agricultural production areas of the U.S. is 16.5 ppm, ranging from 0.7 to 269 ppm.[1329] The median Ni content of sandy soils of Lithuania is 9 ppm, and of loamy clayed soils is 17 ppm.[1359] The total content of Ni in soils of Finland is 60 ppm at the 90th percentile, whereas acid-soluble Ni is 30 ppm.[1368] Ni is also elevated in soils over basic and volcanic rocks, and in some organic-rich soils. Especially peaty serpentine soils are known for high Ni levels existing in easily soluble organic complexes.[566] Also, soils of arid and semiarid regions are likely to have a high Ni content. The grand mean for world soils is calculated to be 22 ppm, and 19 ppm was reported for U.S. soils.[706]

Ni recently has become a serious pollutant that is released in the emissions from metal processing operations and from the increasing combustion of coal and oil. The application of sludges and certain phosphate fertilizers also may be important sources of Ni. Anthropogenic sources of Ni, from industrial activity in particular, have resulted in a significant increase in the Ni content of soils (Table 168). In particular, Ni in sewage sludge that is present mainly in organic chelated forms is readily available to plants and therefore may be highly phytotoxic. Soil treatments, such as additions of lime, phosphate, or organic matter, are known to decrease Ni availability to plants. Ammonium acetate soluble Ni in soils of Finland did not change (ranges from 0.5 to 1. mg L^{-1}) during the period 1974 to 1987, which indicates that Ni pollution does not increase significantly in topsoils.[1431] Nevertheless, Ni cycling under anthropogenic impact is of environmental concern.

B. Plants

1. Absorption and Biochemical Functions

There is no evidence of an essential role of Ni in plant metabolism, although the reported beneficial effects of Ni on plant growth have stimulated speculation that this metal may have some function in plants.[531,542]

Welch[859] discussed recent reports that Ni is an essential component of the enzyme urease, and thus Ni may be required by nodulated legumes that transport N from roots to tops in forms of ureide compounds. The stimulation effects of Ni on the nitrification and mineralization of N

Table 167 Nickel Content of Surface Soils of Different Countries (ppm DW)

Soil	Country	Range	Mean	Ref.
Podzols and sandy soils	Austria	1–1.5	—	6
	Great Britain	3.5–110	20	944
	Canada	1.3–34	8	243
	Poland	1–52	7	382
	Romania	9–62	33	1127
	U.S.	<5–70	13	706
	Former S.U.	5–15	11	493, 580
	New Zealand[a]	6–370	—	861
Loess and silty soils	Poland	7–70	19	382
	U.S.	5–30	17	706
	Belarus	—	11	493
	New Zealand[a]	3.6–44	—	861
Loamy and clay soils	Austria	13–15	—	6
	Burma	27–91	50	575
	Canada	3–98	23	243
	Poland	10–104	25	382
	Romania	24–60	44	1127
	U.S.	5–50	21	706
	Former S.U.	—	24	493, 631, 714
	New Zealand[a]	9–110	—	861
Soils on glacial till	Denmark	—	6	801
	Ireland	5–25	—	236
	Poland	2.4–50	9	974
Fluvisols	Austria	20–30	26	6
	Belarus	—	10	493
Gleysols	Austria	—	6	6
	Chad	3–50	—	39
	Former S.U.	—	36	631
Rendzinas	Austria	—	39	6
	China	2–450	92	1124
	Ireland	20–45	—	236
	Poland	7–41	21	685
	U.S.	<5–70	18	706
Kastanozems and brown soils	Austria	6–25	18	6
	Burma	12–39	23	575
	Ireland	10–20	—	236
	Romania	11–61	32	1127
	Former S.U.	10–34	20	580, 714
Solonchaks and solonetz	Burma	32–72	55	575
	Chad	10–50	—	39
	Madagascar	30–80	—	557a
	Former S.U.	10–76	25	351, 580
Chernozems	U.S.	7–70	20	706
	Former S.U.	14–40	30	4, 351, 580, 714
Meadow soils	Former S.U.	27–75	42	631, 714
Histosols and other organic soils	Canada	6.6–119	29	243
	Denmark	1.9–5	4	1, 801
	Poland	0.2–50	9	91, 684
	U.S.	5–50	12	706
	Belarus	—	5	493
Forest soils	China	—	51	225
	U.S.	7–100	22	706
	Former S.U.	22–55	33	4, 631, 714
Various soils	Austria	6–38	21	6

(*Continued*)

Table 167 Nickel Content of Surface Soils of Different Countries (ppm DW) (Continued)

Soil	Country	Range	Mean	Ref.
Various soils	Great Britain	—	23	100, 818
	Canada[b]	—	20	521
	Chad	3–30	—	39
	Denmark	—	8	801
	Germany	—	19	340
	Italy[c]	5–3240	14	946
	Japan	2–660	28	395
	Madagascar	—	20	557a
	Poland	1.3–68	9	1045
	Romania	5–25	15	43
	U.S.	<5–150	19	706

[a] Soils derived from basalts and andesites.

[b] Data for whole soil profiles.

[c] Maximum values include contaminated soils which were excluded from mean content.

Table 168 Nickel Enrichment and Contamination in Surface Soils (ppm DW)

Site and Pollution Source	Mean or Range in Content	Country	Ref.
Soil over serpentine rocks	770	Australia	702
	1700–5000	New Zealand	495
	3563–7375	Rhodesia	566
Mine wastes	2–1150	Great Britain	289
Metal-processing industry	206–26,000	Canada	150, 245, 775
	500–600[a]	Great Britain	38
	304–9288	Russia	1217
	26–36[b]	Sweden	811
Sludged farmland	23–846	Great Britain	59, 959, 987
	31–101	Holland	314
	50–84	Germany	176

[a] Soluble in HCl.

[b] Needle litter and humus layer, respectively.

compounds are emphasized.[978] Dalton et al.[975] reported that microorganisms that metabolize H_2 and urea are highly sensitive to the Ni nutrition. The studies of the uptake and chemical behavior of Ni in plants are related mainly to its toxicity having possible implications with respect to animals and man.

Cataldo et al.[124] studied in detail the absorption, distribution, and forms of Ni in soybean plants. These authors showed that when Ni is in the soluble phase, it is readily absorbed by roots. Ni uptake by plants is positively correlated with Ni concentrations in solutions, and the mechanism is multiphasic (Figure 102). A strain of *Pseudomonas* was investigated by Bordons and Jofre[950] for its Ni accumulation capacity. Results indicate an extracellular, metabolically independent adsorption, and a possible displacement by Ni^{2+} of Mg^{2+} from the membrane. All Ni^{2+} retained by bacteria was accumulated externally to cells.

Like other divalent cations (Co^{2+}, Cu^{2+}, and Zn^{2+}), Ni^{2+} is known to form organic compounds and complexes. Cataldo et al.[124] reported that a large portion of Ni was composed of compounds with $<$10,000 mol wt, whereas Wiersma and Van Goor[872] found Ni complexing by compounds with a molecular weight in the range of 1000 to 5000, with a negative overall charge. Also Tiffin[789] found Ni bound to anionic organic complexes in xylem exudates. Although the transport and storage of Ni seems to be metabolically controlled, this metal is mobile in plants and is likely to be accumulated in both leaves and seeds.[176,301,860]

Ni is readily and rapidly taken up by plants from soils, and until certain Ni concentrations in plant tissues are reached, the adsorption is positively correlated with the soil Ni concentrations

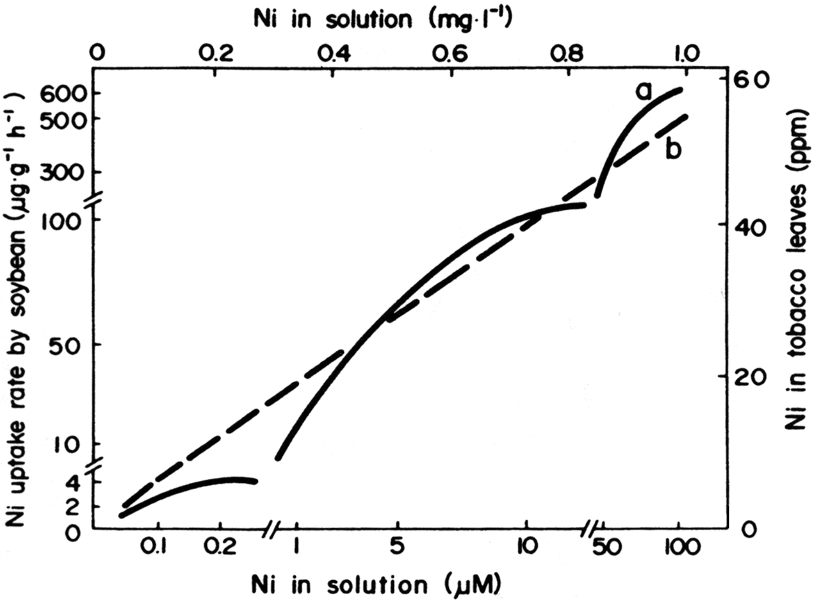

Figure 102 Effects of Ni concentration in solution on Ni uptake by plants. (a) Molar Ni concentrations on the rate of Ni uptake 21-day-old intact soybeans (whole plant); (b) Ni concentration in solution on Ni content of tobacco leaves.[124,860]

(Figure 103). Both plant and pedological factors affect the Ni uptake by plants, but the most pronounced factor is the influence of the soil pH. As Berrow and Burridge[67] found, increasing the soil pH from 4.5 to 6.5 decreased the Ni content of oats grain by a factor of about 8. Staunton et al.[1504] described that the secretion of organic anions, and modification of soil pH by roots and fungi in the rhizosphere may considerably decrease Ni adsorption by soil, and thus increase its bioavailability. The origin of the metal also plays a significant role in its availability to plants. Grupe and Kuntze[1018] reported a much higher Ni uptake by cereals from the soil with added metal than from its lithogenic source.

Ni is easily extracted from soils by plants, especially by hyperaccumulator plants such as *Alyssum* sp. Chaney[1251] was the first to suggest the possible phytoextraction of Ni from polluted soil. According to this author, and also others, *Alyssum* genotypes can accumulate over 400 kg Ni per ha.[1252] Recently, hybrid poplars were tested for phytoremediating Ni-polluted sites.[1464] This is most promising for the phytoremediation of polluted soils and for phytomining and metal recovery. Using the isotopic (^{63}Ni) exchange method, Shallari et al.[1484] showed that the ability of red clover and *Alyssum* species to increase Ni phytoavailability was not significantly different among these plants. The mechanism of the high uptake efficiency of *Alyssum* to take up Ni from soil remains to be elucidated. Krämer et al.[1377] reported that exposing a species of *Alyssum* to Ni elicits a large increase in the levels of free histidine in a Ni-accumulator phenotype. Histidine is known to be coordinated with Ni in plant cells. The authors concluded that an enhanced production of histidine is responsible for the Ni hyperaccumulation in *Alyssum* species. Nicks and Chambers[1441] described that individual plants of the same species, sampled at the same time, varied widely in Ni concentration. A great variation in Ni content (3280–7820 ppm) was also observed for the plant *Streptanthus polygaloides* (family Brassicaceae) that is endemic to serpentine soils in California, when sampled at three different times. The maximum plant mass and Ni concentration occurred just before the onset of flowering. It may be a potential plant for Ni phytomining.

The mechanism of Ni toxicity to plants is not well-understood, although the restricted growth of plants and injuries caused by an excess of this metal have been observed for quite a long time.

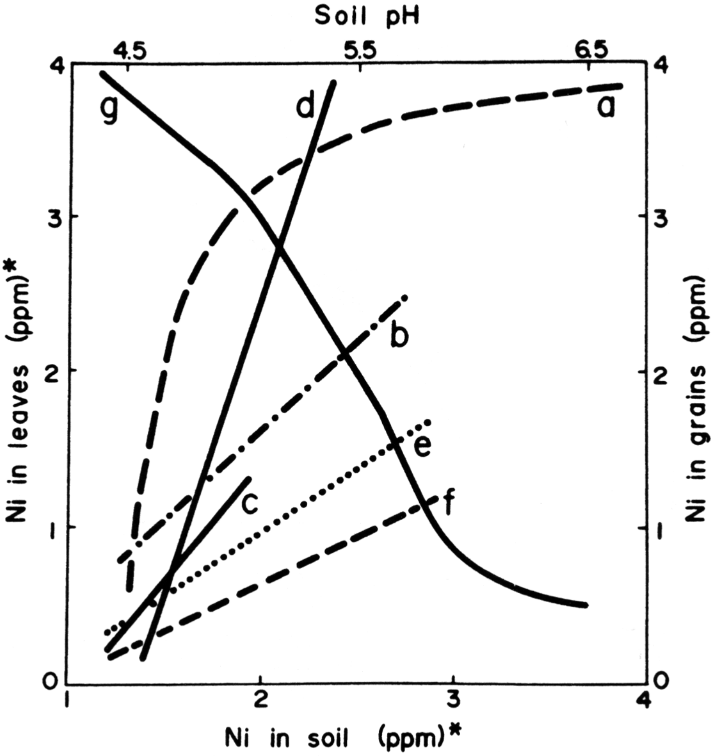

Figure 103 Ni concentrations in plants as a function of Ni content of soils. (a) Leaves of *Alyssum* sp., accumulating Ni; (b) leaves of *A. montanum*, nonaccumulating Ni; (c) wheat leaves; (d) barley grains; (e) carrot roots; (f) radish roots. The influence of soil pH on Ni concentration in (g) oat grains. *Ni concentrations in soils, leaves, and roots are given in powers of ten.[67,176,553,616]

The biological effects of Ni are highly related to its species. However, Ni speciation in the plant extract indicated that regardless of the chemical form added to the soils, Ni was only found in neutral and negative complexes.[1543] Recent findings of Molas[1422] indicated that Ni fixed with glutamic acid was the most toxic to cabbage, and the least toxic was the Ni-EDTA complex. The most common symptom of Ni phytotoxicity is chlorosis, which seems to be Fe-induced chlorosis. Indeed, Foy et al.[241] reported a low foliar Fe level at toxic concentrations of Ni in the growth medium. With plants under Ni stress, the absorption of nutrients, root development, and metabolism are strongly retarded. Before the acute Ni toxicity symptoms are evident, elevated concentrations of this metal in plant tissues are known to inhibit photosynthesis and transpiration.[56] Also, low N_2 fixation by soybean plants was reported to be caused by Ni excesses.[824]

Under natural conditions, Ni toxicities are associated with serpentine or other Ni-rich soils. Anderson et al.[23] reported that oats, a Ni-sensitive crop, when affected by this metal, contained Ni in leaves ranging from 24 to 308 ppm (DW). The phytotoxic Ni concentrations range widely among plant species and cultivars and have been reported for various plants to be from 40 to 246 ppm (DW).[279] Growth and survival of hybrid poplars show severe phytotoxicity above 1 mg Ni L^{-1} in the growth media.[1464] Davis et al.[171] found the toxic Ni content of barley seedlings to be as low as 26 ppm (DW), and Khalid and Tinsley[389] found 50 ppm (DW) Ni in ryegrass to cause slight chlorosis. Ni is the most toxic metal to microfungi of soils. Increased Ni concentration in soil, up to 1 mg L^{-1}, decreases ciliate (Protozoa, *Copoda* sp.) by about 5% of the control value. When a phosphate buffer was added, the growth rate of soil ciliate was significantly improved.[1449]

Generally, the range of excessive or toxic amounts of Ni in most plant species varies from 10 to 100 ppm (DW) (Table 36). Most sensitive species are affected by much lower Ni concentrations, ranging from 10 to 30 ppm (DW).[1052,1081] Several species are known for their great tolerance and hyperaccumulation of Ni. Usually these species, mainly of the Boraginaceae, Cruciferae, Myrtaceae, Leguminosae, and Caryophyllaceae families, are also Co accumulators. Native vegetation of serpentine soils was reported to contain up to 19,000 ppm (AW) Ni,[494] and *Hybanthus floribundus* (Violaceae family) growing on acid ferralsols accumulated 6542 ppm (DW) Ni in leaves, 5490 ppm in stems, and 221 ppm in root bark.[702] The pronounced ability of some plant species to accumulate Ni when grown in soil over Ni ore bodies may make them useful biogeochemical indicators.[417,553,899]

2. Interactions with Other Elements

The interaction between Ni and other trace metals, Fe in particular, is believed to be a common mechanism involved in Ni toxicity. Cataldo et al.[124] found that the absorption of Ni by soybean roots and Ni^{2+} translocation from roots to shoots were inhibited by the presence of Cu^{2+}, Zn^{2+}, and Fe^{2+}, whereas Wallace et al.[844] stated that Fe^{3+} (as FeEDDHA) did not depress Ni concentrations in leaves of bush beans. Nevertheless, the excess of Ni is believed to cause an actual Fe deficiency by inhibiting the translocation of Fe from roots to tops. Khalid and Tinsley[389] concluded that the Ni/Fe ratio, rather than the Ni and Fe concentrations in plants, has shown better relationships with the toxic effects of Ni. Both antagonistic and synergistic interactions have been observed between Ni and several trace metals (Figure 30).

3. Concentrations in Plants

The Ni content of plants growing on uncontaminated soils may vary considerably because it is reflecting both environmental and biological factors. However, the Ni concentrations in certain foodstuffs, cereal grains, and pasture herbage from different countries do not differ widely.

The mean levels of Ni in grasses range from around 0.1 to 1.7 ppm (DW) and in clovers range from 1.2 to 2.7 ppm (DW) (Table 169). There is not much information on Ni in vegetables. Shacklette[705] showed that the Ni content of vegetables ranges from 0.2 to 3.7 ppm (DW) (Table 170).

Mean values for Ni in wheat grains ranged from around 0.2 to 0.6 ppm (DW) and seem to be relatively stable in grains from different countries (Table 171): Oat grains apparently contained somewhat higher amounts of Ni, from about 0.3 to 2.8 ppm. The Ni content of all cereals averaged 0.50 ppm (DW) if extremely high values for oats from Canada and Lithuania are not included. Also, in oat flakes, the Ni content is 0.20 ppm (FW), and is higher than in other grain products.[1402]

Table 169 Mean Levels and Ranges of Nickel in Grass and Clover at the Immature Growth Stage from Different Countries (ppm DW)

	Grasses		Clovers		
Country	Range	Mean	Range	Mean	Ref.
Belgium	0.9–1.3	1.1	—	—	684
Great Britain	0.84–2.4[a]	—	1.3–6.2[a]	—	67
Germany	1.3–2.5	1.7	1.0–1.3[b]	1.2	769
Finland	0.15–1.08	0.4	—	—	590
Hungary	—	—	1.4–2.4[b]	1.9	769
Ireland	0.8–2.2	1.4	—	2.7	235
Poland	0.3–4.7	1.7	0.2–8.2	2.5	684, 381, 1045
U.S.	<0.07–0.67	0.13	<0.5–5	1.5[c]	200, 710
Lithuania	2.4–4.8[d]	—	—	2.6[e]	502

[a] For freely and poorly drained soils, respectively.

[b] For meadow and red clover, respectively.

[c] Calculated from AW basis for alfalfa.

[d] For meadow hay and grass crop, respectively.

[e] Clover-timothy hay.

Table 170 Nickel Content of Plant Foodstuffs (ppm)

Plant	Tissue Sample	FW Basis			DW Basis		AW Basis
		(547, 574)	(705, 710)	(696, 1187)	(705, 710)	(764)	(705, 710)
Sweet corn	Grains	0.04	0.06	0.33	0.22–0.34	—	8.5
Snap bean	Pods	0.02	0.18	—	1.7–3.7	—	24.0
Kidney bean	Seeds	—	—	—	1.1[a]	2.3[b]	—
Cabbage	Leaves	0.05	0.05	0.20	0.62–0.99	3.3	6.7
Lettuce	Leaves	0.01	0.04	0.14	1.0–1.8	1.5	7.2
Carrot	Roots	0.02	0.03	0.07	0.26–0.98	—	3.6
Onion	Bulbs	—	0.06	0.04	0.59–0.84	—	13.0
Potato	Tubers	0.04	0.06	0.56	0.29–1.0	—	7.0
Tomato	Fruits	—	0.02	0.03	0.43–0.48	—	3.6
Cucumber	Fruits	0.01	0.05	—	1.3–2.0	—	13.0
Apple	Fruits	0.003	—	0.08	0.06	—	$<$10.0
Orange	Fruits	0.008	—	—	0.39	1.2[c]	$<$10.0

Note: References are given in parentheses.

[a] From Reference 589.

[b] Peas.

[c] Figs.

Table 171 Nickel Content of Cereal Grains from Different Countries (ppm DW)

Country	Cereal[a]	Range	Mean	Ref.
Canada	Oats	—	2.79	514
Finland	Barley	0.13–0.14	0.14	829
	Oats	0.43–0.46	0.44	829
	Wheat (s)	0.21–0.27	0.24	829
Germany	Barley	—	0.9	176
	Rye	—	1.0	176
	Wheat	—	0.4	176
Norway	Oats	0.29–2.62	1.23[b]	748
Poland	Wheat (w)	0.2–0.5	0.4	267
	Oats	0.2–8.0	1.4	1045
	Rye	0.14–1.0	0.38	1045
Sweden	Wheat (w)	0.3–0.7	0.5	21
U.S.	Barley	0.10–0.67	0.20	200
	Oats	$<$0.27–0.94	0.53	200
	Rice	$<$0.2–1.2	0.29[c]	1187
	Wheat (s)	0.17–0.67	0.32	200
	Wheat (w)	0.18–0.47	0.25	21, 860, 906
Lithuania	Oat meal	—	2.55	502
	Wheat bran	—	3.60	502

[a] Spring, s; winter, w.

[b] Pot experiment.

[c] FW basis.

Oat grain accumulates more Ni than straw, while all other metals are usually accumulated more in cereal straw. The field study also showed a similar picture of Ni distribution in oats; the expected range for Ni in grain was 0.30 to 6.48 ppm, with a geometric mean of 1.39 ppm, whereas these values for oat straw were 0.55 to 3.14 ppm, and 1.31 ppm, respectively.[1045] Cereal grains collected in Poland during the period 1992 to 1996 had an average Ni content of 0.44 ppm, and potatoes—0.61 ppm. Ni in wheat flour of the U.S. is reported to be 0.18 ppm, (FW), and in rye grain of Germany—0.083 ppm (FW).[1382,1514,1549]

The easy phytoavailability of Ni to plants is demonstrated by the results of an experiment with ^{63}Ni, where the isotopic composition in soil solution was the same as in plants, during the same time.[1286]

Table 172 Nickel Content of Plants Grown in Contaminated Sites (ppm DW)

Site and Pollution Source	Plant and Part	Mean or Range of Content	Country	Ref.
Metal-processing industry	Blueberry	4.8–6.2	Sweden	811
	Blueberry, leaves	92	Canada	866
	Celery, stalks	29	Canada	775
	Horsetail, tops	140	Canada	745
	Lettuce, leaves	2.7	Australia	57
	Lettuce, leaves	84	Canada	775
	Lettuce, leaves	11	Germany	431
	Grass	3.9–9.0[a]	Germany	769
	Oats, grain	1.5	Germany	431
	Cereal, leaves	230–250	Great Britain	38
	Grass, tops	1700–32,000	Great Britain	38
	Onion, bulbs	47	Canada	775
	Spruce, twigs	6–14[b]	Sweden	811
Oil refinery	Clover, tops	2.8–14.8	Poland	605
	Grass, tops	2.4–13.3	Poland	605
Sludged soils or urban gardens	Grass, tops	15–19[c]	Holland	297
	Collard, leaves	0.1–11.6	U.S.	127
	Parsley, leaves	3.7	Poland	1015a
	Lettuce	1.8–5.8[d]	Australia	831
	Lettuce	2.4–40.3[e]	Great Britain	170
	Grass	10–24	Great Britain	68
	Cereal, straw	9.7–20.8	Germany	176
	Cereal, grain	1.6–5.2	Germany	176
	Soybean, seeds	7–26	U.S.	10
Other sources	Rice, leaves	11–20	Japan	395
	Oats, grain	60	Canada	301
	Alfalfa	44[e]	Canada	301
	Sagebrush	30[f]	U.S.	278

[a] Industrial emission and urban waste waters.

[b] Five and one-year old, respectively.

[c] Nonwashed and washed leaves, respectively.

[d] For field and greenhouse experiments, respectively.

[e] Pot experiment.

[f] AW basis.

Environmental Ni pollution greatly influences the concentrations of this metal in plants (Table 172). In ecosystems where Ni is an airborne pollutant, the tops of plants are likely to concentrate the most Ni, which can be washed from the leaf surfaces quite easily.[38] Sewage sludge has also been shown to be a serious source of Ni as a pollutant in plants. As Ni is easily mobile in plants, berries and grains are reported to contain elevated Ni concentrations.

The health hazards of exposure to Ni and its compounds have recently come to be recognized.[764] Therefore, a redistribution of this metal in the environment from the burning of fossil fuel, application of sludges to agricultural lands, and by industrial emissions should be of concern.

V. PLATINUM-GROUP METALS

The available analytical data are very limited for evaluating the Pt metal abundance in the Earth's crust. A general estimation of the range in concentration of the Pt metals in rocks is as follows (in ppb): Pd, 0.1 to 200; Pt, 0.1 to 75; Ru, 0.01 to 60; Os, 0.06 to 50; Rh, 0.01 to 20; Ir, 0.01 to 20.

It should be emphasized, however, that data for the occurrence of Pt metals are extremely subject to errors derived both from sampling difficulties and analytical uncertainties.

Pt metals are concentrated mainly in ultramafic and mafic rocks and are also known to be associated with Ni-Cu ore bodies. In sedimentary and metamorphic rocks, the Pt metals occur at a much lower level, with the exception of some Cu-bearing shales.

Pt-group metal deposits have been described by Page and Carlson.[595] The lodes usually are composed of all the Pt metals, with Pd and Pt by far the most abundant. Pt metals are both siderophile and chalcophile, and they are likely to be associated with oxide minerals. Most often, these metals occur naturally as alloys.

Pt metals are noble metals and manifest a marked resistance to oxidation and do not readily unite with other elements. Ru and Os may form easily volatile oxides (RuO_4, OsO_4). However, as a result of new physical methods of analysis, some sulfide, arsenide, and antimonide minerals are described, as for example sperrylite ($PtAs_2$) and geversite ($PtSb_2$).

Some of the Pt metals apparently are readily absorbed by plants when they occur in easily soluble forms in substrata.[248] Farago and Parsons[991] reported that all the platinum metals produced toxic symptoms in the test plant, water hyacinth. Toxicities of the metal species to this plant vary and decrease in the following order: $Pt^{2+} \simeq Pd^{2+} > Os^{4+} \simeq Ru^{3+} > Ir^{3+} \simeq Pt^{4+} > Rh^{3+}$.

A. Ruthenium

Ru is considered to be the least abundant of the platinum metals in the Earth's crust, at about 1 ppb. Ru is not a major component of platinum-metal alloys, but has been found in some Ir and Os alloys, and is associated with certain base metals (e.g., Fe, Cu). Some sulfide and arsenosulfide minerals of Ru have recently been found at very low concentrations in other sulfide and arsenide minerals.

There are not enough data to estimate Ru abundance in soils and plants. Bowen[94] reported Ru to occur in land plants at the concentration of 5 ppb (DW). Duke[197] reported Ru in food plants from a Central American tropical forest region to range from 0.4 to <200 ppb (DW).

The radionuclides ^{103}Ru and ^{106}Ru are released during nuclear reactions. Some studies of ^{106}Ru behavior in soil show that this radionuclide is largely accumulated in surface soil layers.[603] In acid soils, however, ^{106}Ru is highly mobile and is likely to migrate down the soil profile.[17] ^{103}Ru, and ^{106}Ru in particular, deposited on soils by the fallout from the reactor accident in Chernobyl, appeared to be mobile and easily migrated down the soil profiles.[1140]

The availability of this nuclide is reported to be relatively high, but a large proportion of the ^{106}Ru is concentrated in roots.[393,698] Therefore, ^{106}Ru is not likely to be strongly transferred from soil to the food chain. Nevertheless, the transfer factors for ^{106}Ru from soils to wheat suggest that under specific conditions the uptake of this radionuclide may be fairly high.[1016]

B. Rhodium

Data on Rh are too scarce to permit evaluation of its environmental abundance. Some authors consider Rh as the least frequent element of the Pt metals, whereas Wright and Fleischer[888] reported Rh in concentrations up to 20 ppb in black shales and as much as 7 ppm in pyrrhotites. This metal is known to be concentrated also in siderites on the order of 0.0X to 0.X ppm, and it may be expected to be elevated around some Fe processing industries. The only platinum-metal mineral that contains a higher amount of Rh is the arsenosulfide, hollingworthite. Rh reveals both siderophilic and chalcophilic character. Rh complexes revealed the lowest phytotoxicity among the other platinum metals.[991]

C. Palladium

Pd is more abundant and more chemically reactive than the other Pt metals and is known to form minerals such as stibiopalladinite (Pd_3Sb), arsenopalladinite (Pd_3As), and others. In addition to platiniferous lodes, it is associated with Cu and Ni sulfide ores. Mn ores and Mn concentrations are also known for their capacity to accumulate Pd, as well as coals and phosphorites that may contain large amounts of this metal. A current estimation of Pd abundance in the Earth's crust is 10 ppb.

Kothny[416] found Pd in two soils to be 40 and 140 ppb, and in leaves and twigs of various trees to range from 30 to 400 ppb (AW). This author reported a great seasonal variation in Pd concretions in leaves under different climatic conditions and stages of plant growth. Fuchs and Rose[248] gave the range of Pd in surface soils to be from around 0.5 to 30 ppb, and in limber pine to range from 2 to 285 ppb (AW).

Since Pd seems to be easily taken up by plants when it occurs in soluble forms, Kothny[416] speculated that Pd^{2+} is able to replace Mn^{2+} in a metalloenzyme due to the similar ionic radii, and Fuchs and Rose[248] suggested a significant Pd mobility in the organic cycle. Farago and Parsons[991] found Pd^{2+} to be very toxic to water hyacinth.

Smith et al.[743] extensively reviewed information on the natural occurrence, technology, and environmental behavior of Pd. These authors concluded that losses of Pd to the environment, mainly from metal processing and use, are believed to be relatively innocuous and of little environmental hazard. The metal is only slightly phytotoxic; however, when the Pd concentration in the nutrient solution was high (from 1 to around 3 mg L^{-1}), damage to the structural units of cells was observed. The inhibition of some metabolic processes has also been observed under increased Pd content in plant tissues.

D. Osmium

Like other Pt metals, Os occurs mainly in native metal alloys of variable composition. The most common alloys are of Os and Ru. In the Ru mineral laurite (RuS_2), Os has been found at about 3%. Its atypical behavior is its easy reaction with oxygen and its variable oxidation states in compounds. Smith et al.[743] summarized the available data on the geochemical, technological, and environmental behaviors of Os. There is no analytical information on Os contamination, even in the vicinity of likely sources of Os pollution. However, Os is known to be released to the environment as a volatile tetroxide (OsO_4) during metal processing. The authors concluded that Os is considered an inert metal and that OsO_4 is not a serious health hazard. When Os^{4+} occurs in soluble species, it is easily phytoavailable and relatively toxic.[991]

E. Iridium

Ir is present in the Earth's crust at about 1 ppb. Ir is concentrated in Fe-Ni core and in meteorites. Increased content of Ir in sedimentary rocks at the border layer between Cretaceous and Tertiary deposits is apparently related to an effect of the great meteorite collision about 65 million years ago.[1271]

Generally, Ir is considerably more often associated with Fe, Cu, and Ni sulfide deposits than are the other Pt metals. The environmental abundance of Ir has not been studied yet, but Bowen[94] gave the Ir content of land plants to be below 20 ppb (DW) and reported the accumulation of ^{192}Ir in the leaf margins of corn treated with that radionuclide.

F. Platinum

Pt seems to be most reluctant to enter into chemical compounds with other elements and therefore occurs mainly in alloys known as "native platinum." However, several mineral forms, such as sperrylite ($PtAs_2$) and cooperite (PtS), occur in ore bodies.

There are but few reports on Pt occurrence in soils and plants. Govindaraju[1313] presented only two analyses of Pt in the reference soils: 50 and 150 ppb. Fuchs and Rose[248] reported the Pt content of surface silty soils to range from <20 to 75 ppb, being the highest in the soil over weathered norite. The magnetic fraction of these soils seemed to contain most of the Pt, from <860 to <3000.

Twigs of limber pine growing on these soils contained Pt concentrations ranging from 12 to 56 ppb (AW). Shacklette et al.[710] gave the range in Pt concentrations in herbage growing on metamorphic and Pt-bearing ultramafic rocks to be from 3500 to 6600 ppb (AW). Pt, as a chemically inert metal, is presumed unlikely to be of any environmental concern or health hazard. However, Pt^{2+} complexes are easily taken up into the plants and are accumulated mainly in roots. Farago and Parsons[991] described the high phytotoxicity of this metal, with Pt^{4+} species being less toxic than those of Pt^{2+}.

APPENDIX

The following are common plant names used in this book, with corresponding Latin names, and families (in parentheses) to which they are assigned.

Alamo switchgrass, *Panicum virginatum* L. (Graminaceae)
Alfalfa, *Medicago sativa* L. (Leguminosae)
Amarant, *Amaranthus hypochondriacus* L. (Amaranthaceae)
Apple, *Pyrus malus* L. (Rosaceae)
Apricot, *Prunus armenica* L. (Rosaceae)
Asparagus, *Asparagus officinalis* L. (Liliaceae)
Avocado, *Persea americana* Mill. (Lauraceae)

Barley, *Hordeum vulgare* L. (Gramineae)
Bean, *Phaseolus* sp. (Leguminosae)
Beech, *Fagus* sp. (Fagales)
Birch, *Betula* sp. (Betulaceae)
Black gum, *Nyssa silvatica*
Blueberry, *Vaccinium* sp. (Ericaceae)
Brazil nuts, *Bertholltia excelsa* (Lecythidaceae)
Broccoli, *see* Brussels sprouts
Bromegrass, *Bromus* sp. (Gramineae)
Broomsedge, *Andropogon* sp. (Gramineae)
Brussels sprouts, *Brassica oleraceae* var. *gemmifera* Zenker (Cruciferae)
Buckwheat, *Fagopyrum sagittatum* Gilib. (Polygonaceae)
Bush bean, *Phaseolus vulgaris* L. (Leguminosae)

Cabbage, *Brassica oleracea* var. *capitata* L. (Cruciferae)
Carnation, *Dianthus caryophyllus* L. (Caryophyllaceae)
Carrot, *Daucus carota* L. (Umbelliferae)
Cauliflower, *Brassica oleracea* var. *botrytis* L. (Cruciferae)
Celery, *Apium graveolens* var. *dulce* DC. (Umbelliferae)
Chard, *Beta vulgaris* var. *cicla* L. (Chenopodiaceae)
Cheatgrass, *Bromus secalinus* L. (Gramineae)
Cherry, *Prunus avium* L. or *P. cerasus* L. (Rosaceae)
Chicory, *Cichorium intybus* L. (Compositae)
Chinese cabbage, *Brassica pekinensis* (Lour.) Ruprecht (Cruciferae)
Chive, *Allium schoenoprasu* L. (Liliaceae)
Chrysanthemum, *Chrysanthemum* sp. (Compositae)
Clover, *Trifolium* sp. (generally, *T. pratense* L.) (Leguminosae)
Coconut palm, *Cocos nucifera* (Arecaceae)
Collard, *Brassica oleracea* var. *viridis* L. (Cruciferae)
Comfrey, *Symphytum officinale* L. (Boraginaceae)
Corn, *Zea mays* L. (Gramineae)

Cotton, *Gossypium* sp. (Malvaceae)
Cottonwood, *Populus angustifolia* (Salicaceaa)
Cucumber, *Cucumis sativus* L. (Cucurbitaceae)

Dandelion, *Taraxicum officinale* Weber (Compositae)
Douglas fir, *Pseudotsuga menziesii* (Mirb.) Franco (Pinaceae)

Elders, *Sambucus nigra* L. (Caprifoliaceae)

False oat grass, *Arrhenan thenum eliatus* (Gramineae)
Fescue, *Festuca arundinaceae* L. (Graminaceae)
Flax, *Linum usitatissimum* L. (Linaceae)
Fodder radish, *see* Radish

Garlic, *Allium sativum* L. (Liliaceae)
Gladiolus, *Gladiolus* sp. (Iridaceae)
Grape, *Vitis vinifera* L. or *V. labruscana* Bailey (Vitaceae)

Hairy milk-vetch, *Oxytropis pilosa* L. (Leguminosae)
Heather, *Calluna vulgaris* L. (Erinaceae)
Hickory tree, *Carya* sp. (Junglandaceae)
Hops, *Humulus lupulus* L. (Moraceae)
Horse bean, *Dolichos lablab* L. (Leguminosae)
Horsetail, *Equisetum* sp. (Equisetaceae)

Indian mustard, *Brassica juncea* L. (Cruciferae)

Kenaf, Ketnia, *Hibiscus cannabinus* (Malvaceae)
Kidney bean, *Phaseolus vulgaris* cultivar (Leguminosae)

Labrador tea, *Ledum palustre* L. (Ericaceae)
Larch, *Larix* sp. (Pinaceae)
Lettuce, *Lactuca sativa* L. (Compositae)
Limber pine, *Pinus flexilis* James (Pinaceae)
Linden, *Tilia* sp. L. (Tiliaceae)
Lucerne, *Medicago sativa* L. (Leguminosae)

Maize, *Zea mays* L. (Gramineae)
Mangel, *Beta vulgaris* var. *macrorhiza* Hort. (Chenopodiaceae)
Maple, *Acer* sp. (Aceraceae)
Marsh bent grass, *Agrostis stolonifera* L. (Gramineae)
Mother wort, *Artemisia semiarida* L. (Compositae)
Mushroom, edible fleshy fungus of the Basidiomycetes
Mustard, *Brassica nigra* (L.) Koch or *B. hirta* Moench. (Cruciferae)

Narcissus, *Narcissus tazetta* L. (Amaryllidaceae)
Nettle, *Urtica* sp. (Urticaceae)
Norway spruce, *Picea abies* [L.] Karts. (Pinaceae)

Oak, *Quercus* sp. (Fagaceae)
Oats, *Avena sativa* L. (Gramineae)
Onion, *Allium cepa* L. (Liliaceae)
Orange, *Citrus sinensis* Osbeck (Rutaceae)
Orchardgrass, *Dactylis glomerata* L. (Gramineae)

Pea, *Pisum sativum* L. (Leguminosae)
Peanut, *Arachis hypogaea* L. (Leguminosae)
Perennial ryegrass, *Lolium perenne* L. (Gramineae)
Pine, *Pinus* sp. (Pinaceae), mainly *Pinus silvestris*
Potato, *Solanum tuberosum* L. (Solanaceae)
Pulses, edible seeds of various legumes

Radish, *Raphanus sativus* L. (Cruciferae)
Rape, *Brassica rapa* L. (Cruciferae)
Raya, *Brassica juncea* Coss. (Cruciferae)
Red beet, *Beta vulgaris* var. *crassa* Alef. (Chenopodiaceae)
Red clover, *Trifolium pratense* L. (Leguminosae)
Red maple, *Acer rubrum* L. (Aceraceae)
Rice, *Oryza sativa* L. (Gramineae)
Rose, *Rosa* sp. (Rosaceae)
Ryegrass, *Lolium perenne* L. or *L. multiflorum* Lam. (Gramineae)

Sagebrush, *Artemisia tridentata* Nutt. (Compositae)
Scots pine, *Pinus sylvestric* L. (Pinaceae)
Sedge, various genera and species of the Cyperaceae family
Sesame, *Sesamum* sp. (Pedaliaceae)
Snap bean, *Phaseolus vulgaris* L. cultivar (Leguminosae)
Sorghum, *Sorghum vulgare* Pers. (Gramineae)
Soybean, *Glycine max* (L.) Merr. (Leguminosae)
Spinach, *Spinacia oleracea* L. (Chenopodiaceae)
Spruce, *Picea* sp. (Pinaceae)
Strawberry, *Fragaria ananassia* Duchesne (Rosaceae)
Sudan grass, *Sorghum sudanense* (Piper) Stapf. (Gramineae)
Sugarbeet, *Beta vulgaris* var. *saccharinum* Hort. (Chenopodiaceae)
Sunflower, *Helianthus annuus* L. (Compositae)
Sweetclover, *Melilotus officinalis* (L.) Lam. or *M. alba* Desr. (Leguminosae)
Sweet corn, *Zea mays* var. *rugosa* Bonaf. (Leguminosae)
Sweet vernal grass, *Anthoxanthum odoratum* L. (Gramineae)

Tagacanth, *Astragalus bisulcatius* L. (Leguminosae)
Tea, *Thea sinensis* L. (Theaceae)
Timothy, *Phleum pratense* L. (Gramineae)
Tobacco, *Nicotiana tabacum* L. (Solanaceae)
Tomato, *Lycopersicum esculentum* Mill. (Solanaceae)
Triticale, an artificial hybrid of wheat and rye
Turkish hazel, *Corylus colurna* L. (Betulaceae)
Turnip, *Brassica napus* L. (Cruciferae)

Valencia orange, *Citrus sinensis* Osbeck cultivar (Rutaceae)

Water hyacinth, *Eichhornia crassipes* L. (Pontederiaceae)
Wheat, *Triticum aestivum* L. (Gramineae)
White clover, *Trifolium repens* L. (Leguminosae)
Willow, *Salix* sp. (Salicaceae)
Wormwood, *Artemisia* sp. (Compositae)

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