HEALTH AND ENVIRONMENTAL SCIENCES AND EXPLORATION AND PRODUCTION DEPARTMENTS

API PUBLICATION NUMBER 4600

JANUARY 1995

Metals Criteria for Land Management of Exploration and Production Wastes:

Technical Support Document for API Recommended Guidance Values

STEP
Strategies for Today's Environmental Partnership

American Petroleum Institute

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Health and Environmental Sciences Department
Exploration and Production Department

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PREPARED BY:

AMERICAN PETROLEUM INSTITUTE
PRODUCTION WASTE ISSUE GROUP
METALS MANAGEMENT WORKGROUP

JANUARY 1995

American Petroleum Institute

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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACTS

Harley H. Hopkins, Health and Environmental Sciences Department
Mark Rubin, Exploration and Production Department

MEMBERS OF THE API METALS MANAGEMENT WORKGROUP

John D. Admire, Phillips Petroleum
Stuart Cagen, Shell Oil Company
George M. Deeley, Shell Development Company
Bob L. Huddleston, Delta Environmental Consultants
Dave J. Lowe, BP Exploration Alaska
Ross Macdonald, Shell Oil Company
Terry J. Moore, ARCO Exploration and Production Technology
Jeffery S. Ralston, Exxon Company, USA
Michael J. Scott, Exxon Production Research

Michael Scott and Terry Moore are acknowledged for their role as the principal authors of the report. Jeff Ralston and George Deeley also authored sections of the report. The contributions of the current workgroup leader, Jeff Ralston, and past leaders, Bob Huddleston (formerly with Conoco) and Terry Moore, are recognized.

API would also like to thank the following individuals for reviewing the report and providing many valuable suggestions:

Kirk W. Brown, K.W. Brown Environmental Services, Inc.
Rufus L. Chaney, U.S. Department of Agriculture
Lloyd E. Deuel, Jr., Soil Analytical Services, Inc.
Thomas C. Granato, Metropolitan Water Reclamation District of Greater Chicago

ABSTRACT

This document provides the technical support for recommended maximum concentrations for 12 metals of environmental concern in land-managed exploration and production waste. The guidance values for arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc were adopted directly from the EPA's regulations for the land application of sewage sludge. EPA's risk-based approach was used to calculate values for barium and boron which were not addressed by the sewage sludge regulations. General guidelines for sampling and analysis of metals are also provided. Also, formulae for calculating the application rate for exploration and production (E&P) wastes containing metals are included. A comparison of these guidance values with metals concentrations from three E&P waste databases indicated that E&P wastes do not generally have levels of metals that are of environmental concern.

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EXECUTIVE SUMMARY

In 1992, the American Petroleum Institute (API) initiated a study to develop guidelines for land-management of exploration and production (E&P) waste containing metals. This report documents the scientific basis for the API-recommended metal concentration limits for soils to which E&P waste has been applied.

In February 1993, the United States Environmental Protection Agency (EPA) completed an update of its 1980 study on land treatment technology for sewage sludge. The EPA employed exposure assessment models for 14 possible exposure pathways to develop risk-based numerical pollutant limits for sewage sludge application to land. Specifically, the 1993 update recommended maximum metals concentration limits for sewage sludge application which were protective of human health and the environment.

With respect to metal constituents, the land application of E&P waste is very similar to the land application of sewage sludge. Therefore, EPA's scientifically valid application guidelines for metals can be used for E&P wastes. Where the EPA study had not addressed a metal contained in E&P waste, the EPA methodology was used to establish a guidance value.

Specific numerical guidance has been established for 12 metals of potential environmental concern for E&P operations. These guidance values are shown in Table 4. It should be noted that these values are general guidance and will not necessarily be appropriate in all situations. In general, due to the nature of the EPA approach, these numbers should be considered conservatively low. Site-specific factors such as current and future land use, background soil concentrations, native vegetation, etc., may allow for different levels of metals to be applied to land and still be protective of human health and the environment. Specific numerical guidance was not established for tin, which may be found in E&P wastes. Technical evaluation indicated that tin is not of environmental concern in the form and concentrations in which it occurs in E&P wastes.

The level of environmental concern for a given total metal concentration is dependent on the physical and chemical state of the metal and its surroundings, which dictates the metal's form (species) and mobility. With the exception of boron, the metals levels included in this report are based on the total metals concentration as determined by various low pH extraction methods. This generally leads to a conservatively low guidance level since much of the total metals content of a given waste is not in a dissolved or bioavailable form and therefore is not available to cause toxic effects. The overwhelming current regulatory practice is to regulate the total metals content and not to consider the forms and fate of the metal in the environment where it is found. If regulatory agencies begin to regulate based on dissolved or bioavailable metals content, API will consider modifying these proposed metals levels.

INTRODUCTION

BACKGROUND

The petroleum industry generates approximately 21 billion barrels per year of waste from the exploration and production (E&P) of oil and natural gas. The vast majority of this waste (98% by volume) is water produced in conjunction with the oil and gas and is typically disposed via re-injection. The balance of E&P wastes is made up of wastes from the drilling and completion of wells (< 2%) and other wastes associated with the production of petroleum hydrocarbons (0.1%) (ERT, 1987).

Drilling wastes and these "associated" wastes (e.g., crude oil-impacted soil and tank bottoms) are disposed of in a variety of ways. Often, the most economically attractive method for their disposal is on-site land application in the form of land treating (e.g., land farming, land spreading, or composting). If these types of cost-effective land application methods are to continue, it is important to understand the nature of these wastes and the potential environmental impact from any constituents contained in them.

Organic compounds, salts and metals are constituents of possible environmental concern in drilling and associated wastes. API recommends that soil pH be maintained between 6 and 9, soil conductivity be less than 4 mmho/cm, and oil and grease content be less than one percent in the final soil-waste mixture (SAS, 1993, 1995). In 1992, API initiated this study to address the environmental concern associated with metals found in these wastes. The level of environmental concern for a given total metal concentration is dependent on the physical and chemical state of the metal and its surroundings, which dictates the metal's form (species) and mobility. The fate and impact of metals in the environment is a complex subject and, although there has been a significant body of work completed on this subject, the focus of previous studies has not been on E&P wastes.

OBJECTIVES

Practical experience has shown that many E&P wastes which contain metals can be successfully managed on-site in ways that are protective of human health and the environment. The objective of this report is to provide the scientific basis for API-recommended metal concentration limits for land-managed waste/soil mixtures. A secondary objective is to identify any knowledge gaps that may require further study to refine the suggested concentration limits.

METALS IN E&P WASTE

METALS - DEFINITION

Metals are a class of elements which may be of concern if present in a medium (such as, soil or groundwater) in a form and concentration considered to pose a risk to some receptor. Metals are defined as those elements with atomic numbers between 21 and 92 with the exception of the halogens (atomic numbers 35, 53, and 85), the noble gases (atomic numbers 36, 54, and 86), non-metals (atomic numbers 34 and 52), and a semi-metal (arsenic, atomic number 33). Although they are not defined as metals, beryllium, boron, aluminum, arsenic, selenium, and tellurium are included in this study due to their environmental importance. The resulting 67 naturally occurring metals included in this broad definition are shown on Figure 1.

Metals, as with all natural chemical elements, are ubiquitous in the environment. Any water, soil, or waste sample, if examined to a sufficient degree, will be found to contain these elements. Therefore, a measurable concentration of a metal is not, by itself, justification for concern.

PRESENCE OF METALS IN E&P WASTES

Metals content of drilling wastes and associated wastes have been analyzed by EPA (1987) and API (ERT, 1987). Together, they analyzed for 59 separate elements and identified 24 metals within drilling waste. The remaining 35 metals tested for by the EPA were not detected as they are rare elements not normally found in most geological formations at detectable levels. Table 1 lists the concentration range for each metal found in drilling wastes. Also listed is the normal range of metal concentrations typical for soils of the United States.

METALS OF CONCERN

Of the metals found in E&P wastes, the following are not considered to limit the disposal of drilling or associated wastes because of their presence at typical or low concentrations, and/or their non-toxic/non-accumulative nature: aluminum, antimony, silver, beryllium, cobalt, iron, manganese, strontium, titanium, vanadium, and yttrium. Guidance values for these metals were not developed in this study. Tin was initially of concern, but a risk evaluation indicated that a guidance value was not needed (see Appendices C & D)

The remaining metals are considered to be of potential environmental concern and guidance values were developed in this study. These metals are:

arsenic (As)	cadmium (Cd)	lead (Pb)	nickel (Ni)
barium (Ba)	chromium (Cr)	mercury (Hg)	selenium (Se)
boron (B)	copper (Cu)	molybdenum (Mo)	zinc (Zn)

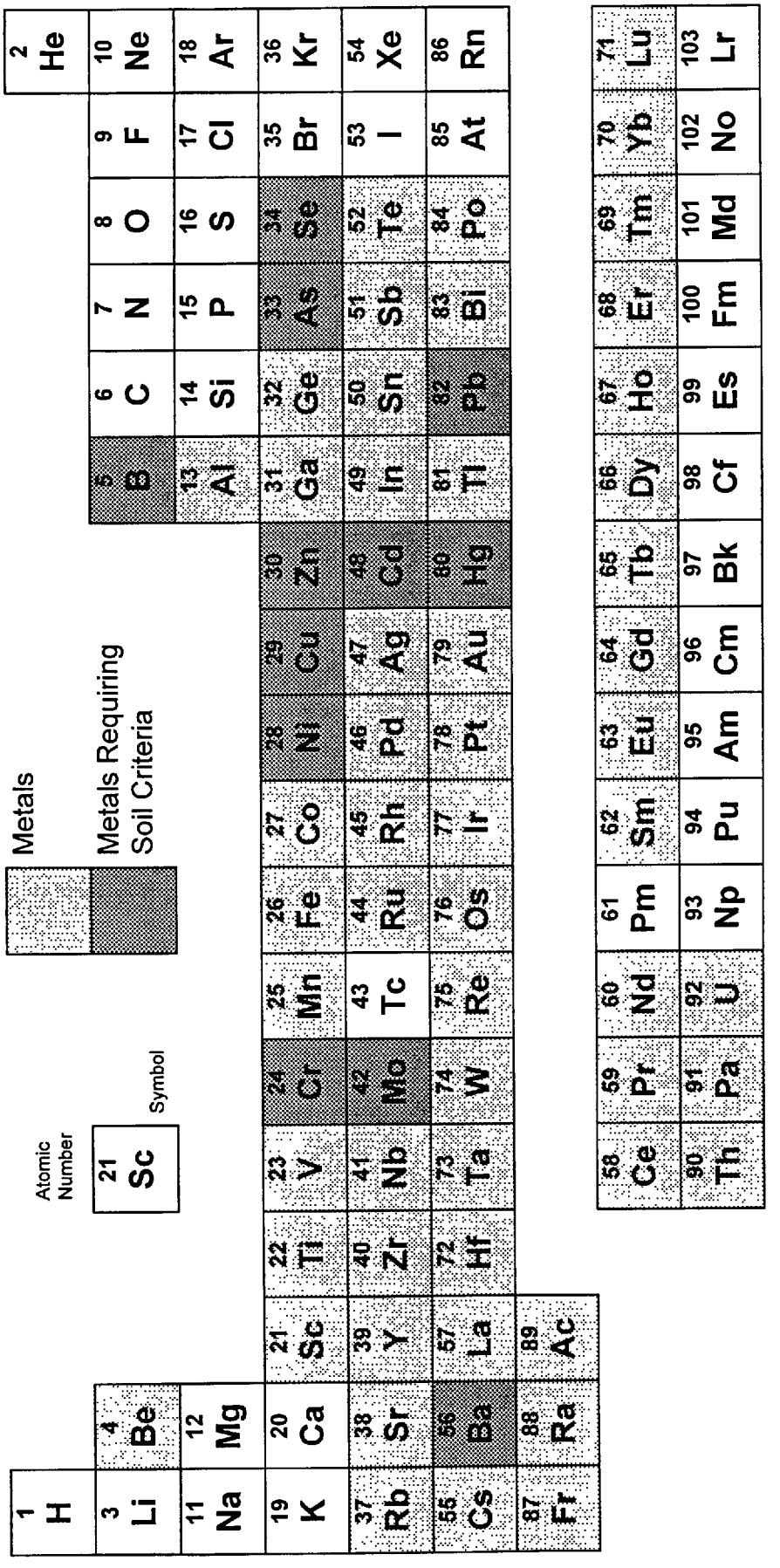

Figure 1: Periodic Table showing naturally occurring elements defined as "metals" and having soil criteria developed in this document for E&P waste.

Table 1

Metals in Drilling Waste and Soils

Metal	Drilling Waste (EPA, 1987)			Drilling Waste (ERT, 1987)			Soil (Lindsay, 1979)	
	Detections per 21 samples	Mean (mg/kg)	Maximum (mg/kg)	Detections per 19 samples	Mean (mg/kg)	Maximum (mg/kg)	Average (mg/kg)	Range (mg/kg)
Al	21	9,153	20,900	19	7,860	20,800	71,000	10,000 - 300,000
Ag	6	< 0.1	9.1	0			0.05	0.01 - 5
As	11	5.3	29	19	10	27.9	5	1 - 50
B	18	83.3	290	19	18.4	73.6	10	2 - 100
Ba	21	7,190	56,200	19	6,440	24,500	430	100 - 3,000
Be	3	0.2	3	10	0.4	1.5	6	0.1 - 40
Cd	12	2.5	14	3	0.2	1.5	0.06	0.01 - 0.7
Co	5	3.4	17	19	8.7	20.3	8	1 - 40
Cr	20	42.9	368	19	28.5	145	100	1 - 1,000
Cu	18	23.5	82	19	22.5	124	30	2 - 100
Fe	21	22,100	56,800	19	17,200	46,100	38,000	7,000 - 550,000
Hg	3	< 0.130	2.1	3	0.1	1.1	0.03	0.01 - 0.3
Mn	21	352	940	19	296	495	600	20 - 3,000
Mo	2	1.4	16	13	4.1	9	2	0.2 - 5
Ni	15	19.6	61	19	17.9	40.6	40	5 - 500
Pb	12	60.9	446	19	71.5	302	10	2 - 200
Sb	0			2	1.97	23.6	0.66	< 1 - 8.8
Se	0			1	0.03	0.58	0.3	0.1 - 2
Sn	8	16.5	101	2	3.8	60.3	10	2 - 200
Sr	8	180	1,090	19	282	885	200	50 - 1,000
Ti	21	167	554	19	110	318	4,000	1.000 - 10,000
V	15	17	74	19	19.2	37.3	100	20 - 500
Y	2	0.952	12	0			50	25 - 250
Zn	21	209	823	19	131	413	50	10 - 300

METHOD FOR DETERMINING METALS GUIDELINES FOR LAND APPLICATION OF E&P WASTES

The only specific regulatory guidelines for the land application of metals in E&P wastes are those established by the State of Louisiana Statewide Order 29-B. These guidelines, suggested by Freeman and Deuel (1984), are based on a 1980 EPA study on land treatment technology for sewage sludge and hazardous waste (EPA, 1980). The EPA has recently updated its study using a more technical, risk-based approach (EPA, 1993b). It selected an approach based on risk to *highly exposed individuals* (HEIs) and consideration of health protection for higher risk populations (i.e., an aggregate risk assessment). This is more realistic than the worst-case *most exposed individual* (MEI) approach used in the past in many regulatory studies. The EPA set new standards based not only on cancer risk but on a series of other health and environmental effects. The EPA employed exposure assessment models to develop risk-based numerical pollutant limits for sewage sludge when it is applied to land.

With respect to metal constituents, the land application of E&P waste is equivalent to the land application of sewage sludge. Metals are found predominately in both types of wastes in either an unavailable form (e.g., insoluble metals) or a potentially available form (e.g., adsorbed metals, metal carbonates, metal sulfides), and therefore, environmental criteria for metals applicable to sewage sludge are also applicable to E&P wastes.

In setting these new limits, EPA conducted risk assessments for 14 exposure pathways from sewage sludge applied to agricultural land (see Table 2). These pathways address specific concerns about land application of waste. Toxic constituents from land applied wastes can (i) interfere with plant growth, (ii) move up the food chain from plants to humans or animals (including soil organisms and soil organism predators) and from plants to animals to human, (iii) leach from the recipient soils to contaminate surface and ground waters, (iv) generate contaminated airborne dust or airborne volatile pollutants that can be inhaled by humans, and (v) leave behind contaminated soils that can be ingested either by children directly or by animals that are subsequently ingested, or whose products are ingested, by humans.

The EPA initially selected 31 pollutants for consideration, 13 inorganic and 18 organic constituents. In the end, it concluded that numerical pollutant limits for all of the organic constituents and for three of the inorganic constituents were not required. The ten inorganic or metal constituents that the EPA set numerical pollutant limits for are As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, and Zn. EPA calculated the cumulative allowable application rate of a pollutant for each exposure pathway and the lowest application rate calculated was chosen as the regulatory limit (EPA, 1992). The results of EPA's risk evaluation are listed by pathway in Table 3.

Table 2

Environmental Pathways of Concern Identified for Land Application of Sewage Sludge (EPA, 1993b)

Pathway	Description of Highly Exposed Individual
1. Sewage Sludge→Soil→Plant→Human	Human ingesting plants grown in sewage sludge-amended soil.
2. Sewage Sludge→Soil→Plant→Human	Residential home gardener.
3. Sewage Sludge→Human	Children ingesting sewage sludge
4. Sewage Sludge→Soil→Plant→Animal →Human	Farm households producing a major portion of the animal products they consume. It is assumed that the animals eat plants grown in soil amended with sewage sludge.
5. Sewage Sludge→Soil→Animal→Human	Farm households consuming livestock that ingest sewage sludge while grazing.
6. Sewage Sludge→Soil→Plant→Animal	Livestock ingesting crops grown on sewage sludge-amended soil.
7. Sewage Sludge→Soil→Animal	Grazing livestock ingesting sewage sludge.
8. Sewage Sludge→Soil→Plant	Plants grown in sewage sludge-amended soil.
9. Sewage Sludge→Soil→Soil Organism	Soil organisms living in sewage sludge-amended soil.
10. Sewage Sludge→Soil→Soil Organism→Soil Organism Predator	Animals eating soil organisms living in sewage sludge-amended soil.
11. Sewage Sludge→Soil→Airborne Dust→Human	Tractor operator exposed to dust while plowing large areas of sewage sludge-amended soil.
12. Sewage Sludge→Soil→Surface Water→Human	Water Quality Criteria for the receiving water for a person who consumes 0.04 kg/day of fish and 2 liters/day of water.
13. Sewage Sludge→Soil→Air→Human	Human breathing volatile pollutants from sewage sludge.
14. Sewage Sludge→Soil→Ground Water→Human	Human drinking water from wells contaminated with pollutants leaching from sewage sludge-amended soil to ground water.

Table 3

Limiting Results for Each Pathway for Metals, Reported as Reference Cumulative Application Rate of Metal (kg/ha)

	Exposure Pathway													
Pollutant	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Arsenic	6,700	930	41			1,600	3,100				400	66,000		1,200
Cadmium	610	120	39	1,600	68,000	140	650			53	8,000	63,000		unlimited
Chromium			79,000				190,000	3,000			5,000	unlimited		12,000
Copper			10,000			3,700	2,000	1,500	2,900			unlimited		unlimited
Lead			300			11,000	1,200			5,000	10,000	unlimited		unlimited
Mercury	180	370	17	1,500	24,000						10,000	1,100		unlimited
Molybdenum			400			18*	530							
Nickel	63,000	10,000	820			1,800	5,400	420			3,000	unlimited		13,000
Selenium	14,000	1,200	100	15,000	13,000	790	130							
Zinc	16,000	3,600	16,000	150,000	2,200,000	12,000	36,000	2,800						

Notes: Definitions and descriptions of each pathway are given in Table 2. All results are rounded down to two significant figures.

"Unlimited" is defined as no concentration limit for the particular metal in soils for the specific pathway.

A blank cell indicates that the metal was not of concern for that exposure pathway and a risk analysis was not performed.

*On February 25, 1994 (59 FR 9050), EPA rescinded this result due to technical errors and has not yet re-established a limit for this pathway.

Reference: EPA, 1992. Technical Support Document for Land Application of Sewage Sludge: Volume I. EPA 822/R-93-001a.

Three metals identified in E&P waste (ERT, 1987; EPA, 1987) that were not included in the EPA sewage sludge risk evaluation are barium, boron, and tin. The risk associated with the land application of wastes containing these metals was evaluated using the same methodology. Summaries of environmental chemistry for each metal may be found in Appendices A-C, respectively. Risk evaluation calculations are contained in Appendix D. The evaluation for tin indicated very low risk; therefore, a guidance value is not warranted.

CALCULATION OF E&P WASTE / SOIL CONCENTRATION LIMITS

Using the results and methods from EPA's risk assessment for sewage sludge, guidelines for metals concentrations in waste/soil mixtures of land-managed E&P waste can be calculated. The results in Table 3 are expressed as reference cumulative application rates of pollutant in units of kilograms per hectare. These values are converted to a post-application maximum soil concentration by the following equation (p. 5-40, EPA, 1992):

$$MSC = \frac{CPLR}{2}$$

where:

MSC = maximum soil concentration (mg/kg)

CPLR = cumulative pollutant loading rate from Table 3 (kg/ha)

The conversion factor of 2 is based on the assumption that the soil in which the sewage sludge is incorporated weighs 2,000 metric tons dry weight per hectare based on an assumed bulk density of 1.33 g/cm^3 and a soil incorporation depth of 15 cm.

However, for exposure pathways 3, 5, and 7, the risk was associated with the ingestion of whole (undiluted) sewage sludge. For these pathways, the maximum soil concentration is equivalent to the maximum waste concentration as calculated by the following equation (derived from Equation 1, EPA, 1993b):

$$MSC = MWC = \left(\frac{CPLR}{MWAR}\right) \times CF$$

where:

MWC = maximum waste concentration (mg/kg)

MWAR = maximum waste application rate (metric tons/ha) = 1000

CF = a conversion factor ((mg/kg)/(kg/metric tons)) = 1000

The API guidance for the twelve E&P metals of concern is listed in Table 4. The methodology for determining the limiting pathway and maximum soil concentration for barium and boron is discussed in Appendix D.

Table 4

API Metals Guidance: Maximum Soil Concentrations

Metal	Extraction Method	Maximum Soil Concentration (mg/kg)
Arsenic	EPA Method 3050[1]	41
Barium	LDNR True Total Barium[2]	180,000
Boron	Hot Water Soluble (Carter, 1993)[3]	2 mg/L[4]
Cadmium	EPA Method 3050	26
Chromium	EPA Method 3050	1,500
Copper	EPA Method 3050	750
Lead	EPA Method 3050	300
Mercury	EPA Method 3050	17
Molybdenum	EPA Method 3050	see below
Nickel	EPA Method 3050	210
Selenium	EPA Method 3050	see below
Zinc	EPA Method 3050	1,400

[1]EPA, 1986. Testing Methods for Evaluating Solid Waste, SW-846, Third Edition.

[2]Louisiana Department of Natural Resources, 1989. Laboratory Procedures for Analysis of Oilfield Waste, Statewide Order No. 29-B.

[3]Carter, 1993. Soil Sampling and Methods of Analysis, Boca Raton: Lewis Publishers, pp. 91-93.

[4]Guidance for boron is based on the soluble concentration with units of mg/L rather than the total concentration (mg/kg).

Molybdenum: On February 25, 1994 (59 FR 9050), EPA rescinded the risk-based maximum soil concentration for Mo of 9 mg/kg due to technical errors and established a non risk-based interim ceiling limit of 37 mg/kg. Under certain conditions this interim level may not be protective of grazing livestock. These conditions are alkaline soils under arid and semi-arid conditions with deficient levels of copper in the soil (see Discussion of Limiting Exposure Pathways).

Selenium: The limiting pathway concentration of 100 mg/kg was generated by EPA using the risk-based multipathway analysis (see Table 3). However, the potential for plant uptake of Se may be high in alkaline soils under arid and semi-arid conditions. Plants that accumulate Se in these soils may pose a threat to grazing animals. Therefore, if elevated levels of Se are found in the waste, the operator should consider site conditions that control its availability (see Discussion of Limiting Exposure Pathways).

DISCUSSION OF RESULTS

DISCUSSION OF LIMITING EXPOSURE PATHWAYS

The limiting exposure pathway for five of the metals of concern (As, Ba, Pb, Hg, and Se) is soil ingestion by children (Pathway 3, see Table 2). The EPA selected a soil ingestion rate of 0.2 grams per day of pure waste to derive the numerical limitations. This soil ingestion rate is over-protective for several reasons, and as a result it is ultimately conservative. The entire 0.2 grams of soil ingested per day was assumed to be composed of pure waste; however, it is likely that only a portion of the 0.2 grams per day of soil is from pure waste since children are exposed to other sources of household dust and dirt, and from sources of soil away from the home. It is also unlikely that a child would ingest 0.2 grams of pure waste every day (Paustenbach *et al.*, 1993). A third assumption is that the biological availability of waste-amended soil-bound pollutants was assumed to be equal to that of the metals in drinking water and food. There is evidence that desorption from the soil particles is a very slow process that generally requires more time than is available to material that is traversing the alimentary canal. Such desorption would have to take place before the metal could cross the membranes into the blood stream and be transported to sites in the body where it could cause toxic effects. The last conservative assumption is the use of lifetime reference doses (RfDs) which represent 70 year chronic exposure. This overpredicts the metal dose the child receives relative to the toxic threshold (RfD) used because the lifetime RfDs protect the child for 70 years from ingesting metals in the waste when in actuality the child would grow out of soil eating behavior in approximately 5 years.

The risk-based maximum soil concentration for selenium (100 mg/kg) is extremely high relative to typical levels found in drilling wastes (maximum 0.58 mg/kg) and soils (average 0.3 mg/kg). It has been known for many decades that excessive soil selenium can poison livestock. Generally, livestock toxicity problems occur in alkaline soils under arid and semi-arid conditions where rainfall is insufficient to leach selenium from the root zone and selenium accumulator plants (e.g., *Astragalus, Haplopappus, Stanleya, Xylorhiza, Atriplex, Castilleja, Machaeranthera, Sideranthus, Aster, Mentzelia*, Bainbridge *et al.*, 1988) take up and concentrate soil selenium which then becomes available to the animals that eat the plants. If such conditions (arid and alkaline soils on land that may be used for grazing, high selenium waste, and naturally occurring selenium accumulator plants) exist, then it is recommended that special precautions be taken to prevent poisoning of any livestock. Such precautions may include emplacement of waste below the root zone of the soil or active promotion of a good stand of "selenium-safe forage crops." The US Department of Agriculture (USDA) has recommended that EPA use a maximum soil concentration of 14 mg/kg instead of 100 mg/kg (Chaney, 1994). This non-risk-based value represents the 98th percentile selenium concentration in the National Sewage Sludge Survey. The USDA is comfortable that this lower limit is both protective and practical based on their experience with land application of sewage sludge.

The limiting exposure pathway for five other metals (B, Cr, Cu, Ni, and Zn) is phytotoxicity (Pathway 8, see Table 2). The maximum soil concentration (threshold value) is the metal concentration that would be associated with a low probability (1×10^{-4}) of a 50 percent reduction in young plant growth. This concentration was established from scientific data relating the growth of young plants to soil metal concentrations. Phytotoxicity by metals is sensitive to changes in soil pH, to the type of plant species, and to the degree of metals' binding in the soil/waste matrix. Metals that partition onto the soil/waste matrix are biologically less available. Phytotoxicity from boron is directly related to its soluble form, and it is for this reason that the guidance for boron is based on a hot water extraction rather than a total metal extraction (see Appendix B).

In the sewage sludge regulations, the limiting pathway for molybdenum (Mo) was livestock ingestion of plants grown in waste-amended soils (Pathway 6, see Table 2). Excessive soil molybdenum in neutral pH soils has been shown to cause nutrient imbalances in livestock through uptake by forage crops (EPA, 1992). The toxicity mechanism is well understood: molybdenum is transformed in the rumen to thiomolybdate, which binds copper and prevents both copper adsorption from the intestines and copper utilization within the animal. The most sensitive livestock are cattle and sheep. On February 25, 1994 (59 FR 9050), EPA rescinded the value from this pathway due to technical errors discovered in the data. After livestock ingestion, the next limiting pathway would be soil ingestion by children, which would yield a maximum soil concentration of 400 mg/kg. EPA chose instead to set a non-risk-based interim level of 37 mg/kg based on the 99th percentile concentration of Mo in the National Sewage Sludge Survey while it redetermined a value for the livestock ingestion pathway. The USDA has recommended that EPA use a maximum soil concentration of 27 mg/kg based on the 98th percentile concentration in the National Sewage Sludge Survey (Chaney, 1994). The difference between the EPA's and USDA's approach is simply a matter of policy.

Generally, livestock toxicity problems occur in alkaline soils with excessive molybdenum relative to copper under arid and semi-arid conditions where rainfall is insufficient to leach molybdenum from the root zone. If such conditions exist, then it is recommended that special precautions be taken to prevent poisoning of any livestock. Such precautions may include emplacement of waste below the root zone of the soil or irrigation of the site. However, a review of the copper and molybdenum content of drilling wastes and associated wastes (EPA, 1987; ERT, 1987) indicates that molybdenum toxicity due to E&P wastes should not occur.

The limiting pathway for cadmium is predators consuming soil organisms from waste-amended soils (Pathway 10, see Table 2). Earthworms (soil organisms) bioaccumulate cadmium to concentrations above that in soils in which they live, and research has demonstrated that soil cadmium (Cd) constitutes a risk to birds and mammals that ingest earthworms as a significant part of their diet. The EPA examined four approaches. The first approach used the standard methodology for Pathway 10 and considered four factors to calculate a maximum soil concentration (MSC): the threshold pollutant intake level, the fraction of diet considered to be soil organisms, a bioavailability factor, and a

bioaccumulation factor. This approach resulted in the calculation of a cadmium MSC of 236 mg/kg. Three alternative approaches examined the correlation between sewage sludge use and toxicity to specific wildlife species or exposure to a sensitive species from a contaminated site. The results of these approaches are summarized below:

Sensitive Species	Soil Contamination	MSC (mg/kg)
Shrews	Sewage Sludge	740
Shrew-moles	Sewage Sludge	296
Moles	Zinc Smelter	26

The Pathway 10 limiting result for cadmium is a MSC of 26 mg/kg.

Since the promulgation of the sewage sludge regulations, USDA has found errors in EPA's cadmium evaluation for Pathways 2 and 3 (Chaney, 1994). The USDA evaluation of cadmium would establish Pathway 2 (Home Gardener) as limiting at a maximum soil concentration of 10 mg/kg. The USDA's evaluation of Pathway 3 yielded a higher value (182 mg/kg) than calculated by EPA (39 mg/kg). The USDA admits that assumptions used to develop the Pathway 2 limit are extremely conservative. These assumptions, and therefore, this pathway are not valid for E&P waste application because:

- no individual gardener would use E&P wastes to amend garden soils for 50 years as assumed by USDA,
- metal concentrations in E&P waste-amended soils would be diluted over time due to the addition of necessary garden soil amendments, and
- gardeners would not be able to produce 50% of their diet from a garden with a soil pH which favors cadmium uptake (soil pH < 6.0).

While the USDA recommends a limit that is based on Pathway 2, the API guidance is based on Pathway 10.

A risk evaluation performed in this study for tin illustrated that inorganic tin (Sn) is of very low risk (see Appendix D). The limiting pathway for tin is inhalation of dust by a tractor operator, but the resulting limit is a concentration of 200,000 mg/kg (20 percent tin). A soil containing 20 percent tin would be considered a high quality ore and mined for its economic benefit. It is improbable that wastes containing such a large concentration of tin would be associated with E&P wastes. As a result, there is no need to analyze for or establish metals criteria for tin.

CONSIDERATIONS FOR SITE-SPECIFIC ASSESSMENTS

One final consideration is the use of this guidance for site-specific assessments. While future land use is difficult to accurately predict, one (or more) of the exposure pathways may be eliminated from consideration if it (they) can be reasonably excluded because of present and future land use of a specific site. For example, in remote areas that lack hospitable environments (i.e., Arctic regions, desert areas with little or no potable water supplies), the chance that a child will inhabit the site and consume 0.2 grams of soil per day is remote. Therefore, the soil ingestion by children pathway can be eliminated for sites in these areas. If the limiting pathway can be eliminated from concern, then criteria can be re-evaluated for the next most appropriate limiting pathway.

COMPARISON OF GUIDANCE VALUES TO E&P WASTE CHARACTERIZATIONS

A survey of three characterization studies of E&P wastes indicates that only four out of 1007 chemical analyses (71 samples) had a result greater than the API guidance concentrations (Table 5). Three of these analyses had a total lead concentration greater than 300 mg/kg while one analysis had a total arsenic concentration greater than 41 mg/kg. The excess lead was found in two drill solids (mud and cuttings) samples and one tank bottom sample. The excess arsenic was found in a drill solids sample. This comparison of the waste data with the guidance criteria indicates that, generally, E&P wastes contain non-toxic levels of metals. When managed properly, these wastes can be disposed of safely by land application.

COMPARISON WITH OTHER SOIL CRITERIA

API recommended maximum soil concentration values from this study are shown in Table 6, along with those from Louisiana State Wide Order 29-B and the Canadian Interim Soil Remediation Criteria for Agriculture. The Louisiana 29-B criteria were developed primarily from previous EPA work on metals in sewage sludge (EPA, 1980) and was confirmed to be protective in field studies. This work has been superseded by the recent EPA work. The Louisiana 29-B criteria for barium was based on agricultural studies (Freeman and Deuel, 1984) which, unfortunately, utilized inconsistent barium analysis (Deuel and Freeman, 1989).

In 1991, the Canadian Council of Ministers of the Environment (CCME) adopted a set of interim criteria from values that were currently in use in various jurisdictions across Canada in response to its urgent need to begin remediation of high priority "orphan" contaminated sites (Environment Canada, 1991). Many of these criteria do not have complete scientific rationale and therefore the criteria are considered to be only interim. The CCME considers the criteria to be generally protective of human and environmental health for agricultural uses of soil based on experience and professional judgment. The CCME is currently developing scientifically validated criteria. The API guidance criteria are the result of a quantitative risk assessment, in combination with best available data, which provides more certainty and warrants less conservative guidelines than those proposed by CCME. Implementation of a risk-based approach typically results in higher

allowable maximum soil concentrations. Even with the conservativisms noted for EPA's approach, this study provides higher maximum soil concentrations than the Louisiana and the Canadian regulations for all metals except lead and boron (Table 6). The API guidance criteria, used in conjunction with proper sampling and analytical techniques, should provide reasonable operational guidelines in addition to protecting human health and the environment.

Table 5

Total Metals Analyses of E&P Waste Solids

Metal	*Study*	*# Samples*	*# Non Detect Samples*	*# Positive Samples*	*# Samples > API Guidance*	*Max Conc. (mg/kg)*
As	EPA 87	21	10	11	0	29
	ERT 87	19	0	19	0	27.9
	PWIG 95	31	14	17	1	140
Ba	EPA 87	21	0	21	0	56,200
	ERT 87	19	0	19	0	24,500
	PWIG 95	31	8	23	0	10,700
B	EPA 87	21	3	18	---	290
	ERT 87	19	0	19	---	73.6
Cd	EPA 87	21	8	13	0	14
	ERT 87	19	16	3	0	1.5
	PWIG 95	31	26	5	0	3
Cr	EPA 87	21	1	20	0	368
	ERT 87	19	0	19	0	145
	PWIG 95	31	13	18	0	54
Co	EPA 87	21	16	5	---	17
	ERT 87	19	0	19	---	20.3
	PWIG 95	31	25	6	---	6
Cu	EPA 87	21	3	18	0	82
	ERT 87	19	0	19	0	124
	PWIG 95	31	6	25	0	210
Pb	EPA 87	21	9	12	1	446
	ERT 87	19	0	19	1	302
	PWIG 95	31	15	16	1	970
Hg	EPA 87	21	18	3	0	2.1
	ERT 87	19	16	3	0	1.1
	PWIG 95	31	27	4	0	1.4
Mo	EPA 87	21	19	2	0	16
	ERT 87	19	6	13	0	9
Ni	EPA 87	21	6	15	0	61
	ERT 87	19	0	19	0	40.6
	PWIG 95	31	12	19	0	100
Se	EPA 87	21	21	0	0	3 (DL)
	ERT 87	19	18	1	0	0.6
	PWIG 95	31	29	2	0	1.4
Ag	EPA 87	21	15	6	---	9.1
	ERT 87	18	18	0	---	0.3 (DL)
	PWIG 95	31	30	1	---	10 (DL)
Tl	EPA 87	21	21	0	---	3 (DL)
	ERT 87	19	19	0	---	0.2 (DL)
	PWIG 95	31	30	1	---	0.7
Sn	EPA 87	21	13	8	---	101
	ERT 87	19	17	2	---	60
	PWIG 95	31	29	2	---	13
V	EPA 87	21	6	15	---	74
	ERT 87	19	0	19	---	37
	PWIG 95	31	14	17	---	25
Zn	EPA 87	21	0	21	0	823
	ERT 87	19	0	19	0	413
	PWIG 95	31	6	25	0	400

DL = Detection Limit

--- = Element not included in analysis

Table 6

Comparison of API, Louisiana 29-B, and Canadian Maximum Soil Concentration Values for Metals

Element	*API Guidance*[1]	*Louisiana 29-B*[2]	*Canadian Agriculture*[3]
Arsenic	41	10	20
Barium[4]	180,000	20,000 40,000 100,000	750
Boron	2 mg/L	---	2 mg/L
Cadmium	26	10	3
Chromium	1500	500	750
Copper	750	---	150
Lead	300	500	375
Mercury	17	10	0.8
Molybdenum	see footnote 5	---	5
Nickel	210	---	150
Selenium	see footnote 5	10	2
Zinc	1400	500	600

1 All concentrations in mg/kg unless specified and extracted from soils by methods listed in Table 4.

2 All concentrations in mg/kg (LDNR, 1990).

3 All concentrations in mg/kg unless specified (Environment Canada, 1991).

4 Louisiana 29-B barium values for wetlands, uplands, and commercial landfarming facilities, respectively.

5 API Guidance does not recommend a specific value for this metal; see Table 4 and Discussion of Limiting Exposure Pathways for further details.

GUIDELINES FOR SAMPLING AND ANALYSIS

CHARACTERIZING SOILS AND WASTES

Accurate characterization of the metals concentrations of soils and waste is essential for managing the materials according to the API guidance criteria. The largest source of error in this characterization is inadequate sampling. The following sections contain a synopsis for sampling, analysis, and reduction of data from a hypothetical waste site. References are supplied for readers requiring additional detail.

DOCUMENTATION OF BACKGROUND SOILS

The risk-based API guidance criteria were developed by assuming typical agricultural soil concentrations for background. In some instances, native soils will exceed the API guidance criteria. In general, land treatment of wastes due to their metals content may be unnecessary if the metal concentration is below that of background. For this reason it is essential that background concentrations of metals in soils be characterized when planning waste management activities or site closure.

SOIL SAMPLING

The goal of sampling is to obtain soils or wastes for testing that: i) are representative of the unit being sampled, and ii) have minimum variability between samples. The details of designing and executing a sampling plan can be obtained from a number of documents (Wilding and Drees, 1983; Petersen and Calvin, 1986; Crepin and Johnson, 1993; Deuel and Holliday, 1994). Rules of thumb for sampling a hypothetical site are summarized below.

Pits and Background Soils

Pits contents and background soils should be characterized prior to excavation to allow determination of waste application rates. A grid (e.g., 50 X 50 feet) should be developed to avoid sampling bias. Composite sampling is a very cost-effective way to control sampling variability. Pit subsamples should be collected over 2 foot intervals to a depth to one sample below the waste body. Subsamples from similar depths may be composited from a number of locations to form samples for analysis. A sketch must be developed to identify areas where composites were collected.

Background soils should be analyzed from the potential land application area. Application sites should be well drained and out of floodplains and wetlands. Additional criteria for land application sites may be enforced by state regulators. Background soil samples should be collected from the "A" soil horizon or upper one foot and be composited from a number of nearby locations.

Waste-amended Soils

Following waste application, the waste-amended soil should be sampled to ensure that API guidance criteria were satisfied. Sampling could be performed on a grid basis as described above for pits and background soils.

ANALYSIS

Soils should be extracted for all of the guidance metals except barium and boron by EPA SW 846 Method 3050 (EPA, 1986). This method extracts all of the these metals from the solid phase into solution and the results are reported as "total metal." Several studies have shown Method 3050 cannot accurately or precisely measure barium at concentrations of regulatory significance (Deuel and Freeman, 1989; Kimbrough and Wakakuwa, 1991). This problem is the result of the inability of the acid extraction procedure to solubilize all of the barium in the sample. Barium in soil and waste samples should be analyzed by the "true total barium" method developed for the Louisiana 29-B regulations (Deuel and Freeman, 1989). Hot water soluble boron (HWSB) is the only boron phase of environmental concern. In order to analyze for HWSB, soil and waste samples should be extracted by hot water as described in Carter (1993). Extracted metals should then be analyzed by ion coupled photometry (ICP) or atomic absorption methodology.

The recommended guidance concentrations for barium and boron are extremely high relative to typical levels found in E&P wastes. Barium concentrations of this magnitude are only possible when high weight drilling muds are used, and due to operational limitations, the highest weighted drilling muds typically are not formulated with more than 35% barite, which corresponds to a barium concentration of 205,000 mg/kg. Boron is typically present above background concentrations only when used as a special additive. It may not be necessary to analyze for these metals unless it is known that metal-containing additives are present in a sufficient quantity to approach these guidance concentrations.

DATA REDUCTION

Application Rates

The quantity of waste that can be applied to the soil surface under API guidance is a function of the metal concentrations of the waste and background soil. The depth of incorporation is assumed to be one-half foot (can be altered as necessary). The objective is to calculate the proportion of waste that can comprise the upper one-half foot and maintain all metals concentrations below the API guidance criteria. A simple formula to calculate the depth of waste that may be applied and incorporated is as follows:

$$Dilution\ Factor = \frac{Waste\ metal\ concentration - Background\ soil\ metal\ concentration}{API\ Guidance\ Criteria - Background\ soil\ metal\ concentration}$$

If the background soil metal concentration is greater than API guidance criteria or waste metal concentration, this equation need not be used. The dilution factor should be calculated for each metal of concern. If the highest dilution factor is less than or equal to 1, the wastes are within the API guidance criteria and may be applied without any incorporation with the native soil. If the highest dilution factor is greater than 1, the thickness of waste that can be added to the soil surface is calculated by the following equation:

$$Thickness\,of\,Waste = \frac{Depth\,of\,Incorporation}{Dilution\,Factor}$$

Due to equipment limitations, the practical maximum depth of incorporation is approximately 1/2 foot (6 inches or 15 centimeters).

For example, consider a waste that has a lead concentration of 500 mg/kg and a site with a background lead concentration of 100 mg/kg. Using the API guidance criteria for lead of 300 mg/kg, the calculated dilution factor is 2. Thus the maximum thickness of waste that can be applied in this situation is 3 inches (7.5 centimeters). It should be noted that it may be physically impossible due to equipment limitations to apply the waste to a thickness of less than 2 inches.

Meeting API Guidance Criteria

The risk-based criteria apply to the waste-amended soil zone as a whole and not to every sample from within the zone. Sufficient samples should be collected for analysis in order to statistically describe the zone with a high degree of confidence. The actual number of samples is dependent upon both the size of the site and the variability of the data. Soil properties are typically either normally or log-normally distributed (Figure 2; Petersen and Calvin, 1986). The appropriate distribution should be used to determine the proper arithmetic mean and standard deviation of the sample population. The arithmetic mean plus one standard deviation theoretically contains 84 percent of samples from the population (Figure 2). The critical soil concentration of a waste-amended zone is defined as that which is equal to the arithmetic mean plus one standard deviation. The critical soil concentration should be less than the API guidance criteria. This approach is more protective than using the arithmetic mean concentration and should provide a margin of safety over the uncertainties introducing by mixing and analysis. Some native soils may exceed the API guidance criteria. If this situation occurs, the viability of exposure pathways should be re-evaluated.

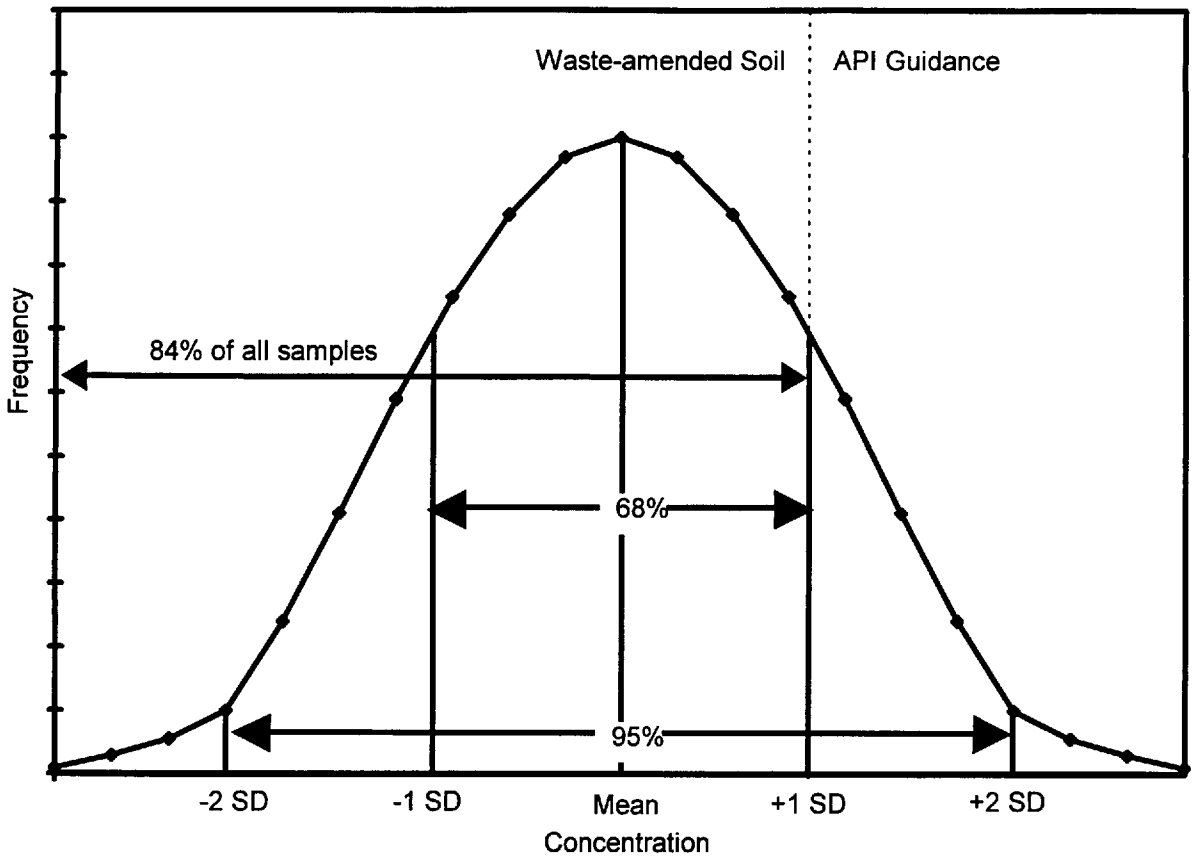

Figure 2: Normal distribution of soil properties plotted in units of standard deviation (SD). Many soil properties require log-normal transformations to resemble this distribution. API Guidance recommends that the critical soil concentration (the mean plus one standard deviation) of a metal in a waste-amended zone be less than the criteria for that metal.

CONCLUSIONS

This document provides the technical support for recommended maximum concentrations for 12 metals of environmental concern in land-managed exploration and production waste. These guidance values are based on limiting values for the land application of sewage sludge promulgated by EPA in 1993. The guidance values for arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc were adopted directly from the sewage sludge regulations. EPA's risk-based approach was used to calculate values for barium and boron which were not addressed by the sewage sludge regulations. Tin was found to exhibit a very low risk and a guidance value is not needed. A comparison of these guidance values with metals concentrations from three E&P waste databases indicated that E&P wastes do not generally have levels of metals that are of concern.

It should be noted that these maximum soil concentration values are general guidance and will not necessarily be appropriate in all situations. In general, due to the nature of the EPA approach, these numbers should be considered conservatively low. Site-specific factors such as current and future land use, background soil concentrations, native vegetation, etc., may allow for different levels of metals to be applied to land and still be protective of human health and the environment. However, the operator must determine whether the guidance values apply over the short term or long term, or whether site specific conditions warrant more or less restrictive values.

APPENDIX A.

DISCUSSION OF THE ENVIRONMENTAL CHEMISTRY OF BARIUM

Successful drilling for oil and gas requires drilling fluid systems that can carry cuttings to the surface, lubricate the bit, and maintain down hole pressures. To produce drilling fluids with sufficient weight to prevent dangerous blowouts, weighting agents must be employed. The most commonly used weighting agent is barium sulfate ($BaSO_4$). It is not uncommon for drilling wastes to contain in excess of 100,000 mg/kg Ba.

Barium is a commonly monitored element in environmental samples and is an analyte in the Toxicity Characteristic Leaching Procedure (EPA, 1990). From a historical perspective, barium salts were once marketed as rodenticides. Studies with rats, however, have shown that Ba is somewhat less toxic than magnesium, which is one of the most common soluble soil cations (Syed and Hosain, 1972).

GEOCHEMISTRY

Barium is a naturally occurring element that is found in all soils and other geologic material. However, literature describing the behavior of Ba in soils is not extensive. Barium is ubiquitous in soils, with an average concentration of 430 mg/kg and a range of 100 to 3,000 mg/kg (Lindsay, 1979). Barium may be contained in soil clays, but Ba in solution is usually controlled by the low solubility of $BaSO_4$. The equilibrium expression for $BaSO_4$ dissolution is expressed as:

$$BaSO_4 \text{ <==> } Ba^{2+} + SO_4^{=} \qquad \log K_{sp} = -10$$

Barium sulfate dissolved in water produces a solution of approximately 1-2 mg Ba/L. This Ba concentration in soil solutions and groundwater, however, is dependent upon ionic strength, redox potential, and availability of sulfate (Sposito and Traina, 1987; Deuel and Freeman, 1989; Branch *et al.*, 1990).

A typical soil solution sulfate concentration (10^{-3} M; Lindsay, 1979) minimizes the amount of Ba that can remain in solution. In reducing environments, however, microorganisms can transform sulfate to sulfide. Thermodynamics would predict that Ba in solution would increase under these conditions. A laboratory study has illustrated that drilling wastes under severely reducing conditions may produce Ba concentrations less than 3 times primary drinking water standards (Figure 3 from Deuel and Freeman, 1989). In reality, redox conditions below -200 mV rarely exist in mineral soils. An important finding by this study is that the quantity of $BaSO_4$ in the system had no influence on the soil solution Ba concentration produced. Only a small portion of the $BaSO_4$ is required to saturate the soil solution. Barium sulfate is fairly ubiquitous in soils subject to reduction and oxidation processes; therefore, addition of $BaSO_4$ through drilling waste may have no effect on soil solution Ba concentrations in many cases. Use of

gypsum ($CaSO_4 \cdot 2H_2O$) treatments for soil salinity have also been shown to drastically reduce Ba solubility in reducing environments (Branch *et al.*, 1990).

Based on the geochemistry of barium it is difficult to conceive of a soil environment that would be conducive to plant uptake or leaching of significant Ba from exploration and production waste.

REGULATIONS

Regulatory guidelines for Ba were developed from experience rather than data. Air quality criteria were adapted from a rule-of-thumb used at Sandia National Laboratories. A threshold limit value (TLV) of 0.5 mg/m^3 was adapted because it had been used at Sandia for many years without reports of incidents (EPA, 1975). Drinking water criteria were developed from this TLV, using assumptions for volumes of air and water uptake. A limit of 1 mg/L was originally established; however, EPA recently increased the limit to 2 mg/L (approximately the solubility of $BaSO_4$).

The Louisiana 29-B regulations specifically address Ba content of reserve pit closures. Although originally set at a limit of 2,000 mg/kg, changes in the Ba analytical procedure have necessitated changes in the regulatory limits. It was recognized that $BaSO_4$ was incompletely dissolved by the EPA 3050 extraction method (Deuel and Freeman, 1989). A new methodology was established and the 29-B limits were changed to 20,000 mg/kg for wetlands, 40,000 mg/kg for uplands, and 100,000 mg/kg for commercial landfill operations (LDNR, 1990).

TOXICITY

Humans and Animals

Toxicity studies of barium have been performed on both humans and animals. These studies have been performed using soluble forms of barium, both injected and oral. Rats were gavaged in most studies because they would not drink sufficient barium-containing water due to the salinity (Borzelleca *et al.*, 1988). The most common symptom of acute Ba toxicity is hypertension and reported blood pressure elevation in rats (Perry *et al.*, 1983). Studies of communities with high Ba concentrations in public water supplies, however, found no adverse health effects in humans such as hypertension, stroke, or heart and kidney disease (Brenniman *et al.*, 1984).

Studies of $BaSO_4$ toxicity are not available because the material is considered relatively non-toxic due to low solubility. Patients of a single diagnostic X-ray treatment may consume in excess of 400 grams of $BaSO_4$ as an X-ray contrast medium. This amount can be contrasted to the child eating soil risk assessment pathway. The amount of $BaSO_4$ consumed in one upper/lower gastrointestinal X-ray series would equate to 135 years of ingestion (200 mg soil/day) of a soil with a concentration of 40,000 mg Ba/kg (Louisiana 29-B limit). Based on similar information, the EPA recently deleted $BaSO_4$

from the list of toxic chemicals for which reporting is required under Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPA, 1994).

Plants

Toxicological information for plants is very species dependent and studies have utilized Ba compounds other than $BaSO_4$. Although high loading rates of drilling fluids have been shown to decrease plant yields (Miller *et al.*, 1980; Miller and Pesaran, 1980; Nelson *et al.*, 1984), no plant toxicity has been shown to exist with $BaSO_4$ additions to soil (Miller *et al.*, 1980). Studies of drilling fluid additions to soil have shown that Ba may be even more unavailable to plants when gypsum ($CaSO_4 \cdot 2H_2O$) is applied as a soil salinity treatment (Nelson *et al.*, 1984; Miller *et al.*, 1980). Loading rates as high as 260,000 mg Ba/kg soil (added as barite) have been shown to have no effect on the dry matter yield of bush beans (*Phaseolus vulgaris*) and only a 20% reduction in dry matter yield of sweet corn (*Zea may* var. *saccharata*) (Miller *et al.*, 1980).

APPENDIX B.

DISCUSSION OF THE ENVIRONMENTAL CHEMISTRY OF BORON

Appreciable boron concentrations are found in only a few materials used in exploration and production drilling fluids. Reservoir management techniques include the use of polymers to seal geologic zones and isolate fluid flow. One of the more common cross-linking agents used in these polymers is borate. Natural boron-containing materials that may also be brought to the surface during drilling include cuttings from evaporite beds or produced waters.

Boron is a commonly measured environmental parameter because the borate form is very mobile and only weakly attenuated by soils. Toxicological guidelines exist for both plant and animal uptake. The majority of soil geochemical literature, however, addresses deficiency of the essential plant nutrient boron.

GEOCHEMISTRY

Boron is a naturally occurring element that is ubiquitous in soils and other geologic materials. Average boron concentrations in soils and the lithosphere are 10 mg/kg, with a common soil range of 2-100 mg/kg (Lindsay, 1979). Groundwaters and surface waters range from 0.007 to 0.2 mg/L and from 0.001 to 5.0 mg/L, respectively (USHHS,1992b). Boron is contained in a number of soil fractions with a wide range of solubility and plant availability. The majority of soil boron is contained in silicate minerals and released slowly through weathering. The soluble portion, which is available to plants, ranges from 0.44 to 4.69 percent of total boron (Gupta, 1968). Most geochemical studies of boron have focused on the soluble boron fraction because it is mobile in the environment and an essential plant nutrient.

Borates, such as borax ($Na_2B_4O_7 \cdot 10H_2O$), are commonly found in dry lake beds in desert climates. The most common primary mineral that contains appreciable boron is tourmaline. The mobile plant-available fractions include water soluble, nonspecifically adsorbed, specifically adsorbed, and metal oxide occluded boron (Jin *et al.*, 1987).

Common environmental analyses are not well suited to the study of boron. The commonly employed EPA 3050 extraction is inadequate for boron because: i) unavailable forms of boron are extracted, and ii) contamination from borosilicate glassware can occur. Environmental and plant nutrient studies have shown that hot water soluble boron or saturation extract boron (Bingham, 1979) analytical methods are the best predictors of plant uptake and mobility (Adriano, 1986; Gupta *et al.*, 1985; Keren and Bingham, 1985; Butterwick *et al.*, 1989; EPRI, 1987).

TOXICITY

Humans and Animals

Summaries of the toxicological effects of boron on terrestrial organisms can be found in Butterwick *et al.* (1989). Concentrations above 1 mg/L, the desirable upper limit for boron in public drinking water, are common in public drinking water systems (USPHS, 1970). A mandatory upper limit of 5 mg/L has been established for these systems (USHHS, 1992). Drinking water concentrations in excess of 30 mg/L can result in digestive disorders (Adriano, 1986). Other water criteria include < 1 mg/L for aquatic life, <5 mg/L in livestock drinking water, <30 mg/kg in water fowl diets, and <100 mg/kg in livestock diets (USDI, 1990). Sheep grazing on soils with boron concentrations of 30-300 mg/kg may develop adverse effects.

Plants

The majority of soil boron literature addresses plant boron deficiency as opposed to toxicity, suggesting that deficiency is the more serious problem (Butterwick *et al.*, 1989). The range between deficiency and toxicity of boron is narrower than for other nutrients. Figure B1 illustrates that optimum plant growth occurs at soil concentrations greater than the deficiency threshold, but less than the threshold where excess boron decreases plant yield. The soil boron concentration ranges for optimal plant growth differ greatly between plant species. Table B1 illustrates optimal ranges for sensitive, semi-tolerant, and tolerant crop species (Keren and Bingham, 1985).

Reviews of boron geochemistry and plant availability in soils can be found in Keren and Bingham, 1985; Gupta *et al.*, 1985; Adriano, 1986; and EPRI, 1987. Plant uptake of boron cannot be correlated with total boron content of soils. Best correlations are obtained between hot water soluble or saturation extract boron and plant yield or plant boron uptake (Adriano, 1986; Gupta, 1985; Keren *et al.*, 1985; Bingham, 1979; Keren and Bingham, 1985). Estimates of the potential for boron toxicity from drilling waste should not be based on acid extracts but will require a more standard soil fertility methodology (Bingham, 1979).

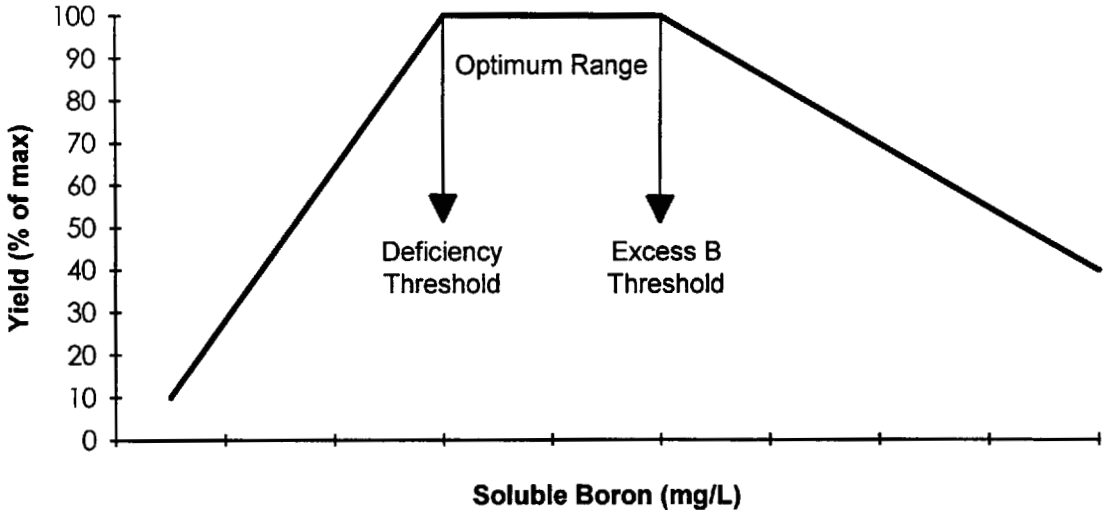

Figure B1: Idealized optimum plant growth occurs at soluble soil boron concentrations greater than the deficiency threshold, but decreases past a threshold range until it reaches toxicity. Actual optimum soluble soil boron concentration ranges for plant growth differ greatly between plant species. Modified from Gupta *et al.*, 1985.

Table B1

Threshold Soluble Soil Boron Concentration Ranges Above Which Plants Exhibit Visual Injury and/or Decreased Yields (Keren and Bingham, 1985)

Sensitive Crop Species	Threshold Concentration Range (mg/L)	Semi-tolerant Crop Species	Threshold Concentration Range (mg/L)	Tolerant Crop Species	Threshold Concentration Range (mg/L)
Lemon	0.3 - 0.5	Sesame		Sorghum	
Blackberry		Red pepper		Alfalfa	
Avocado		Pea		Purple vetch	
Orange		Carrot	1.0 - 2.0	Oat	
Grapefruit		Radish		Parsley	4.0 - 6.0
Apricot		Potato		Red beet	
Peach		Cucumber		Tomato	
Cherry		Lettuce		Sugarbeet	
Plum		Cabbage		Cotton	6.0 -10.0
Persimmon	0.5 - 0.8	Celery		Asparagus	10.0 - 15.0
Fig		Turnip			
Grape		Barley			
Walnut		Corn	2.0 - 4.0		
Pecan		Artichoke			
Cowpea		Tobacco			
Onion		Sweet clover			
Garlic		Squash			
Sweet potato		Muskmelon			
Wheat					
Mung bean					
Strawberry	0.8 - 1.0				
Kidney bean					
Lima bean					

Note: Crops listed in order of increasing tolerance

APPENDIX C.

DISCUSSION OF THE ENVIRONMENTAL CHEMISTRY OF TIN

Materials containing high concentrations of tin (Sn) are not used in the E&P industry. Examples of some Sn-containing materials that could make up very minor components of drilling wastes include: paint and plastic pigments, solders, Sn-plated metals, and brass. The environmental importance of Sn is primarily associated with its organic forms. While inorganic forms are generally non-toxic to plants or animal ingestion, organic forms are used as pesticides (Beeson *et al.*, 1977). The bulk of environmental Sn literature is oriented toward organotin compounds. All forms of Sn used in conjunction with drilling and production are inorganic.

GEOCHEMISTRY

Water and soil geochemistry of Sn are not well developed because Sn is not an essential plant or animal nutrient and, in inorganic forms, does not pose a serious environmental threat. The majority of Sn in the lithosphere occurs as minor concentrations in silicate minerals (Wedepohl, 1969). The average lithosphere concentration of Sn is 40 mg/kg, with an average soil concentration of 10 mg/kg (Lindsay, 1979). A common Sn range in soils is 2-200 mg/kg. The most stable form under oxidizing soil conditions is Sn^{4+}. Under soil conditions, SnO_2 will control solubility. Solubility decreases with increasing pH and plant studies have shown that it is unavailable in the normal pH range of soils (Romney *et al.*, 1975).

TOXICITY

Humans and Animals

Applied toxicological studies of Sn have been oriented toward tin plating on food cans, inhalation of Sn in metal refining, solder in public water systems, toothpaste additives, and organotin pesticides. In general, these studies have indicated that inorganic forms of Sn pose no appreciable risks to health and the environment (Beeson *et al.*, 1977). Drilling fluids would be expected to have only inorganic forms of Sn. Organic forms of Sn, however, are potential toxicants and carcinogens. Organotin compounds are useful as fungicides, bactericides, and insecticides and for their antihelminthic activity (Beeson *et al.*, 1977). A discussion of the toxicity of various organotin compounds can be found in Stokinger (1963).

Plants

There is no evidence that Sn is either essential or detrimental to plant growth (Beeson *et al.*, 1977). Typical crop plants do not accumulate Sn, even when added to soil in soluble form ($SnCl_2$). Yields of bush bean (*Phaseolus vulgaris*) were decreased only slightly by additions of 500 mg/kg of $SnCl_2$ (Romney *et al.*, 1975). The minor effects on

yield may have been due to Sn in solution or due to the strong reducing effect of the Sn amendment, $SnCl_2$. The reduced form of Sn is not expected to be present in drilling wastes. Barley could be affected by Sn additions (500 mg/kg) but only when elemental S was used to decrease soil pH to 4.5. In solution culture, Sn was toxic to bush beans at concentrations greater than 10^{-3} mol/L (119 mg/L). Addition of $CaCO_3$ to the solution culture negated the toxic effects (Romney *et al.*, 1975). It is important to note that Sn taken up by these crop plants was retained in root tissues and not translocated to the above-ground tissues, where consumption by livestock could occur.

Some plants have shown an affinity for Sn-containing soils. Plants can accumulate Sn with concentration ratios in plant ash:soils of 1 or more (Glazovskaya, 1964; Dobrovol'skii, 1963; Sainsbury *et al.*, 1968). Plants grown on Sn tailings at mining operations have shown uptake of large quantities of Sn with no toxic effects to the plants (Peterson *et al.*, 1976). Studies of plant Sn contents, however, may be biased because of Sn-containing dust on plant tissues originating from urban activities (Fleming and Parle, 1977).

APPENDIX D.

RISK EVALUATION OF ENVIRONMENTAL PATHWAYS OF CONCERN FOR LAND APPLICATION OF E&P WASTE CONTAINING BARIUM, BORON, AND TIN

This appendix summarizes the risk evaluation for the land application of E&P waste containing the metals barium, boron, and tin. This risk evaluation used the 14 exposure pathways identified by the EPA for land application of sewage sludge containing metals. The EPA methodology from the Technical Support Document for Land Application of Sewage Sludge: Volumes 1 and 2 (EPA, 1992) was followed using toxicological data from the US Department of Health and Human Services Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles for barium, boron, and tin (USHHS, 1992a, 1992b, 1993).

SUMMARY FOR BARIUM

In summary, there are only three exposure pathways of concern for barium containing E&P wastes: children ingesting barium contaminated soil (Pathway 3), phytotoxicity (Pathway 8), and groundwater contamination (Pathway 14). The results of risk evaluation indicated that soils can contain up to 180,000 mg/kg (18 percent) barium without causing toxic effects in children who eat excessive quantities of soil. Unlimited quantities of barium sulfate could be placed in the soil and the groundwater would not be adversely affected. Unfortunately, there is only a limited number of studies that properly assess the phytotoxicity exposure pathway for barium sulfate. The EPA has defined the threshold phytotoxic concentration as being the concentration that causes a 50 percent reduction in yield. One study shows that a soil barium concentration of 260,000 mg/kg (26 percent) depresses the dry matter yield of corn (a sensitive species) by only 20 percent. The same concentration of Ba had no effect on the yield of bush beans (Miller *et al.*, 1980). This concentration is greater than the barium concentration (205,000 mg/kg) of a maximum high weight drilling mud (35 percent barite).

SUMMARY FOR BORON

For boron, there are only two exposure pathways of concern: children ingesting boron contaminated soil (Pathway 3), and phytotoxicity (Pathway 8). The results of the risk evaluation indicated that soils can contain up to 22,000 ppm boron without causing toxic effects in children who eat excessive quantities of soil. Other evidence indicates that boron phytotoxicity occurs for sensitive plant species at concentrations of soluble boron greater than 2 mg/L (Gupta *et al.*, 1985; Adriano, 1986).

SUMMARY FOR TIN

For tin, the results of the risk evaluation indicated that the limiting concentration is 200,000 mg/kg for the exposure pathway of a tractor operator who is exposed to dust while plowing areas of E&P waste-amended soils. Tin is a very minor constituent of E&P waste and it is improbable that tin could reach these levels. It was therefore concluded that there is no need to establish a maximum soil criteria for tin.

DETAILED DISCUSSION OF INDIVIDUAL EXPOSURE PATHWAYS

Each of the 14 exposure pathways considered are briefly discussed below and calculations for the relevant exposure are included. For a more thorough description and discussion of each pathway, see the technical support document for land application of sewage sludge (EPA, 1992).

Pathway 1: Human ingesting plants grown in E&P waste-amended soil

This pathway is not relevant for exposure from land application of E&P wastes. E&P land application sites are much smaller than sewage sludge application sites (1 ha versus 1000 ha, respectively) and therefore the percentage of food in one's diet from food grown in E&P waste-amended soil would be very small (EST, 1995). The percentage of food from sludge sites was estimated by the EPA at 2.5%. By using a simple ratio of land application site size, the percentage of food from E&P waste sites would only be 0.0025%.

Pathway 2: Residential home gardener

The residential home gardener scenario is also not appropriate for E&P waste. Whereas some sewage sludge is processed into fertilizer for home gardens, E&P waste is not recycled in this manner. Also, it is highly unlikely that a plot of land that has had E&P waste with high metal concentrations spread upon it will be used for 50 years without further soil amendments (which would considerably dilute the metal concentrations)

Pathway 3: Children ingesting E&P waste-amended soils

The equation to calculate a risk-specific concentration limit for this soil ingestion pathway is:

$$RSC = \frac{RIA}{I_s \times DE}$$

where:

RSC = reference concentration of metal in E&P waste (μg-metal/g-waste dry weight)

RIA = adjusted reference intake of metal in humans (μg-metal/day)

I_S = soil ingestion rate (g-soil dry weight/day) = 0.2

DE = exposure duration adjustment (unitless) = 1

$$RIA = \left(\frac{RfD \times BW}{RE} - TBI \right) \times 10^3$$

where:

RfD = oral reference dose (mg/kg/day)

BW = human body weight (kg) = 16

RE = relative effectiveness of ingestion exposure (unitless)

TBI = total background intake rate of metal from all other sources of exposure (mg-metal/day)

10^3 = conversion factor (μg/mg)

For Pathway 3, the value of the risk specific concentration (RSC) is equivalent to the value of the maximum soil concentration (MSC). MSC values are rounded down to the nearest two-digit value. The values for each parameter used in the calculation of the MSC for barium, boron, and tin are listed in Table D1. The selection of values for the parameter is discussed in the following paragraphs.

Table D1

Parameter Values for Pathway 3 Calculations

Metal	RfD (mg/kg/day)	RE	TBI (mg/day)	RSC (μg/g)	MSC (mg/kg)
Barium	0.07	0.03	1.25	180,417	180,000
Boron	0.9	1	10.0	22,000	22,000
Tin	0.6	0.05	4.0	940,000	940,000

The oral reference dose (RfD) and total background intake rate (TBI) values were taken from the ATSDR toxicological profiles for the individual metals except for the RfD for boron. Use of the EPA calculated value resulted in a negative value for the adjusted reference intake (RIA) so the foundations for this RfD were re-evaluated.

The EPA Integrated Risk Information System (IRIS; EPA, 1993a) summarizes the derivation of this RfD. The RfD is 0.09 mg/kg/day and is based on a no observable adverse effect level (NOAEL) of 350 ppm in dogs. Higher levels of 1170 ppm for 38 weeks and, in a separate study, 1750 ppm for 90 days, produced testicular atrophy. Dietary exposure of dogs to 350 ppm was calculated as 8.8 mg/kg/day boron equivalents. The EPA next divided 8.8 by 100 (uncertainty factor) to arrive at the RfD of 0.09 mg/kg/day.

However, boron is ingested in the normal human diet, primarily from fruits and vegetables, at the rate of 10 to 25 mg/day. A 0.09 mg/kg/day RfD is equivalent (0.09 times 70 kg) to exposure to 6.3 mg/day or roughly one-half to one-fourth to the background exposure. Therefore, it can be concluded that an RfD dose that is less than the background exposure is clearly not expected to result in any toxic effects. Accordingly it may be expected that significantly higher values would also be nontoxic. For example, an alternative RfD of about 0.4 mg/kg/day would be equivalent to the high end of the range of background exposures (25 mg/day).

On the basis of available toxicology information and a more reasonable view of *inter*- and *intra*-species uncertainties, a case can be made for an alternative RfD of 0.9 mg/kg/day or 10 times the EPA value. To begin, a summary of toxicity results presented in IRIS are listed in Table D2.

Table D2

Summary of Toxicity Results presented in IRIS for Boron (USHHS, 1992b)

SPECIES	DURATION	NOAEL (mg/kg/day)	LOAEL (mg/kg/day)	TOXIC EFFECT
Dogs	2 years	8.8	29	Testicular atrophy
Dogs	90 days	4.4	44	Testicular atrophy
Rats	2 years	17.5	58.5	Testicular atrophy
Rats	70 days	---	23.7	Testes weight (low)
Rats	90 days	26	88	Organ weights (low)
Rats	Reproduction	17.5	58.5	Testicular toxicity
Rats	90 days-repro	0.426	---	None
Rats	60 days-repro	25	50	Reduced fertility
Mice	2 years	8.1	---	None
Mice	90 days	---	34-47	Splenic toxicity

NOAEL = no observable adverse effect level
LOAEL = lowest observable adverse effect level

These results indicate that the dog is the most sensitive of the species tested. This conclusion is reinforced in the ATSDR Toxicology Profile on Boron (USHHS, 1992b). In this profile, the NOAEL levels for oral exposure to boron are about 10 mg/kg/day or more (USHHS, 1992b Figure 2.2).

The question is then what magnitude of uncertainty factor would be needed to ensure no toxic effects in humans if, in fact, humans are more sensitive than any other species and if there are particularly sensitive individuals in the human population. Although it is obvious that an uncertainty factor of 100 is excessive because the resulting RfD would be below the background level, an alternative value is not so obvious. Nonetheless, it is recommended that an uncertainty factor of 10 (2 times 5) is sufficient because:

- All recognized species differences to date have been limited to a value of about 2.
- Inter-individual sensitivities with most compounds are not more than a factor of 3 to 5.

Therefore, an alternative boron RfD of 0.9 mg/kg/day was selected and used for the soil ingestion exposure pathway.

Relative effectiveness of ingestion exposure (RE) is a unitless factor that accounts for the differences in the toxicological effectiveness of the source. These differences include bioavailability associated with the exposure medium (water versus soil), as well as differences in absorption caused by differences in the route of exposure (inhalation versus ingestion). According to the EPA, an RE factor should be applied only where well-documented/referenced information is available on the pollutant's observed relative effectiveness. In EPA's sewage sludge assessment, the RE for all pollutants considered was conservatively set to 1.

For this study, to develop the relative effectiveness of the three metals of interest, studies reported in the ATSDR toxicological profiles that were concerned with excretion in humans were used. If a metal was reported found in feces, then it was assumed that the percentage of the metal was not bioavailable. The RE factor was calculated as the difference between the total metal intake and the amount found in feces. For boron, the RE factor was set to 1 because the ATSDR toxicological profile reported over 93% of an administered dose was excreted in the urine, but did not report any boron in the feces.

According to the ATSDR toxicological profile, barium taken by mouth is poorly absorbed and most of the dose is excreted in the feces. Studies have shown that excretion of oral doses from humans is about 3% in the urine and the remainder in the feces. The RE factor for barium was therefore set to 0.03.

No studies were reported in the ATSDR toxicological profile regarding absorption in humans after oral exposure to inorganic tin compounds. In animals, data suggest inor-

ganic tin compounds are not readily absorbed. At 48 hours after oral administration of ^{113}Sn, approximately 95% or more was recovered in feces with 1% or less in urine. The RE factor for tin was therefore set conservatively at 0.05.

Pathway 4: Farms producing a major portion of the animal products they consume and animals eat plants grown in soil amended with E&P wastes

Pathway 5: Farms consuming livestock that ingest E&P waste-amended soils while grazing

Pathway 6: Livestock ingesting crops grown on E&P waste-amended soils

Pathway 7: Grazing livestock ingesting E&P waste-amended soils

These pathways are all of very low risk because the size of the waste application sites would limit the relative exposure of farm animals to E&P waste-amended soils. Studies have shown that only 1.5 percent of a grazing animal's diet consist of sewage sludge amended soils. The fraction of the diet of animals grazing on E&P waste-amended land would only be about 0.0015 percent, assuming that E&P application sites are one-thousandth the size of sewage sludge sites. There are also no known studies that indicate any of the three metals are toxic to, or bioconcentrate in, livestock.

Pathway 8: Plants grown in E&P waste-amended soils (phytotoxicity)

The phytotoxicity of boron is well documented (Butterwick *et al.*, 1989; Gupta *et al.*, 1985; Adriano, 1986). As discussed in Appendix B, the phytotoxicity of boron has been associated with its soluble form. Thus it is not possible to use the EPA methodology which is based on observations made for the total metal in the soil. Several studies have shown that soluble boron in irrigation water is phytotoxic to boron sensitive plants at a concentration above 2 mg/L (Gupta *et al.*, 1985; Adriano, 1986). The maximum soil concentration of boron from the phytotoxicity pathway is therefore set at 2 mg/L and is based upon the soluble boron concentration (hot water extraction) and not the total boron (EPA Method 3050).

This pathway was not evaluated for tin because there is no evidence that inorganic tin is phytotoxic at normal soil pH ranges (see Appendix C).

There is not enough data to address this pathway for barium. The equation to calculate a reference cumulative application rate of barium (RP_C, kg Ba/ha) is:

$$RP_C = \frac{TPC - BC}{UC}$$

where:

TPC = threshold phytotoxic concentration (µg Ba/g plant tissue dry weight)

BC = background crop concentration (µg Ba/g plant tissue dry weight)

UC = plant uptake response slope (µg Ba/g plant tissue dry weight)/(kg Ba/ha)

The EPA defines TPC as causing a 50% reduction in crop yield. Miller *et al.* (1980) found no plant toxicity with $BaSO_4$ additions to soil (up to 260,000 mg Ba/kg soil). The only other data for barium was reported by Chaudhry *et al.* (1977). However, barium was added to the soil in a soluble form ($Ba(NO_3)_2$) that is not found in natural soils. In this report, bush bean leaves grown at a barium soil level of 2,000 mg/kg contained 2.72% Ba and this soil barium concentration caused a 63% reduction in crop yield while lower concentration levels had no significant effects on yields. The same study also reported that barley leaves grown at a 500 mg Ba/kg soil contained 2,060 mg Ba/kg dry plant material and had decreased barley yield by 38% while barley leaves grown at a 1,000 mg Ba/kg soil level contained 2,430 mg Ba/kg dry plant material and had decreased barley yield by 57%. These studies clearly illustrate the phytotoxic difference between soluble and insoluble forms of barium. Additional studies are also needed to get values for both of the other variables in the above equation (BC and UC). Currently, such data are rare and probably not reliable as result of poor analytical procedures.

Pathway 9: Soil organisms

Pathway 10: Animals eating soil organisms

These two pathways present little risk as the small size of E&P land application sites limit the exposure. Also there are no known studies indicating toxic effects to either soil organisms or soil organism predators from any of these three metals.

Pathway 11: Tractor operator exposed to dust while plowing large areas of E&P waste-amended soils

The equation used to establish the reference application rate is:

$$RP = MDC \times MS \times 10^{-9}$$

where:

RP = reference application rate of metal (kg-metal/ha)

MS = assumed mass of dry soil in upper 30 cm (2×10^9 g-soil DW/ha)

10^{-9} = conversion factor (kg/µg)

MDC = maximum concentration of metal in dust (µg-metal/g-soil DW)

$$MDC = \frac{NIOSH}{TDA} \times 10^6$$

where:

NIOSH = NIOSH recommended health standard (mg dust/m^3 air)

TDA = ACGIH total dust standard (mg/m^3 soil) = 10

10^6 = conversion factor (μg/mg)/(g/mg-soil)

For pathway 11, the value of the MSC is equal to one-half the value of the reference application rate (RP). The values for each parameter used in the calculation of the MSC for barium, boron, and tin are listed in Table D3.

Table D3

Parameter Values for Pathway 11 Calculations

Metal	NIOSH Health Standard (mg/m^3)	Reference Application Rate (kg-metal/ha)	Maximum Soil Concentration (mg/kg)
Barium	10	2,000,000	1,000,000
Boron	10	2,000,000	1,000,000
Tin	2	400,000	200,000

These results indicate that there is no specific risk from barium or boron. As long as the total dust standard is met, a tractor operator is not exposed to any increased risk. Tin can be present in soil dust up to a total concentration of 20% without exposing the tractor operator to any increased risk. A soil containing 20% tin would be considered a high quality ore and mined for its economic benefit. It is improbable that E&P wastes containing such a large concentration of tin would exist or be managed by land application.

Pathway 12: Water quality criteria for receiving surface water for a person who consumes 0.04 kg fish per day and 2 liters of water per day.

This pathway is not relevant for barium, boron, or tin because it is based on a human cancer potency of which there is not one for any of these metals.

Pathway 13: Human breathing volatile pollutants from E&P waste-amended soils. This pathway is not relevant for these metals because none of these metals are a volatile pollutant.

Pathway 14: Human drinking water from wells contaminants with pollutants leaching from E&P waste-amended soils.

This pathway is not relevant for either boron or tin. The risk associated with this pathway is established by exceeding the maximum contaminant level (MCL) in drinking water and neither boron nor tin has a MCL.

The groundwater exposure pathway is also not relevant for barium in E&P wastes because there are several chemical processes that will prohibit barium from leaching from the treatment zone to the groundwater at a concentration level that will exceed the MCL (2 mg/L). The solubility of barium in E&P wastes and soils under typical environmental conditions is in the range of 1-2 mg/L, regardless of whether the total barium content of the soil is 1000 mg/kg, 100,000 mg/kg, or 100 %. Severely reducing conditions may increase solubilities somewhat, but studies have shown that leachates from drilling waste in severely reducing conditions do not exceed the MCL by more than a factor of three (Deuel and Freeman, 1989). Other soil chemical processes will attenuate barium before it migrates from the treatment zone to the groundwater table. Soluble barium is strongly retained by the cation exchange capacity of the soil and is strongly adsorbed to soil particles. Its lack of movement can be compared to that of lead and copper. The soil distribution coefficient for barium (2.8 m^3/kg; USHHS, 1992a) is greater than that of lead (0.621 m^3/kg; EPA, 1992) and copper (0.098 m^3/kg; EPA, 1992). In the EPA exposure modeling study, it was found that unlimited quantities of lead or copper could be placed in the soil without adversely affecting the groundwater (EPA, 1992). Therefore, by taking all of these factors into consideration, unlimited quantities of barium could be placed in the soil and the groundwater would not be adversely affected.

SUMMARY

The results of the risk evaluation for barium, boron, and tin are summarized in Table D4. Each metal has a different exposure pathway that is limiting. For barium, the soil ingestion by children exposure pathway limits total barium concentrations in soils to 180,000 ppm (18%). The phytotoxicity pathway limits soluble boron concentrations in soils to 2 mg/L, while total tin in soil is limited to 200,000 ppm (20%) by the tractor operator inhalation of dust pathway.

Table D4

Limiting Concentrations for Relevant Pathways for Barium, Boron, and Tin Reported as Maximum Soil Concentration (mg/kg)

	Pathway		
Pollutant	3	8	11
Barium	180,000	> 260,000 (NFR)	1,000,000
Boron	22,000	2 mg/L	1,000,000
Tin	940,000	---	200,000

Note: --- indicates that pathway was eliminated from consideration

NFR indicates that the pathway "needs further research"

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