Natural Attenuation Processes

API PUBLICATION 1628A FIRST EDITION, JULY 1996







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Natural Attenuation Processes

Manufacturing, Distribution and Marketing Department

API PUBLICATION 1628A FIRST EDITION, JULY 1996



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Natural Attenuation Processes

SECTION 1— INTRODUCTION

1.1 Purpose and Scope

This publication describes the physical, chemical, and biological processes that decrease the concentrations and ultimately limit the extent of the dissolved plume migrating from a hydrocarbon release. It is primarily focused on the more soluble hydrocarbon fraction that makes up the dissolved plume. Emphasis is given to the biological processes that can play a major role in the attenuation of a dissolved plume.

1.2 LNAPL Migration

After being released into the subsurface, petroleum hydrocarbons can be affected by the physical, chemical, and biological processes in the immediate vicinity. Initially, the hydrocarbons migrate through the vadose zone as a separate light non-aqueous phase liquid (LNAPL), moving downward in response to gravity, and laterally in response to changes in permeabilities encountered. This migration continues until (a) the migrating volume is immobilized by capillary forces and held within the pores of the soil in a residual state, (b) the liquid reaches an impermeable layer and perches upon it, or (c) the capillary fringe of the water table is encountered where the liquid begins to migrate laterally downgradient. When the hydrocarbons reach the capillary fringe, they can migrate laterally because they are lighter, and less dense than water. The fluctuations of the water table and capillary fringe cause this LNAPL layer to rise and fall accordingly. This coats the soils encountering the LNAPL and, in time, creates a smear zone marking the range in fluctuation of the LNAPL. The LNAPL eventually ceases movement when the lateral and vertical spreading has disseminated it to the extent that the forces driving its movement are overcome by capillary forces in both the vadose and saturated zones. These hydrocarbons are then trapped as a residual saturation of LNAPL in these soils and are a source for continued migration in the vapor phase or in the dissolved phase.

1.3 Vapor and Dissolved Phase Migration

Once immobilized, the hydrocarbon compounds can migrate further as vapors or dissolved in water. Those compounds that can transfer by volatilization into the air in the vadose zone can eventually migrate as a *vapor phase* through the land surface and discharge into the atmosphere. The compounds in contact with water transfer into the aqueous phase and are transported as a *dissolved phase*.

The transfer into the vapor and dissolved phases provides the means for the hydrocarbon compounds to potentially migrate away from the hydrocarbon source area. Once released from the source area, the concentrations of the hydrocarbon compounds are decreased by several physical, chemical, and biological processes. Given sufficient flow distances and times, these processes can ultimately result in the complete attenuation of the dissolved hydrocarbon compounds. These processes are described in this publication.

SECTION 2—PHYSICOCHEMICAL PROCESSES

2.1 General

The physicochemical processes in general decrease dissolved hydrocarbon concentrations by redistributing the hydrocarbon mass. In doing so, however, these processes can render the petroleum hydrocarbon compounds more bioavailable and hasten their attenuation by biodegradation. Several major physicochemical processes are discussed in this section. For further overview of these processes, refer to the book by Domenico and Schwartz [1].

2.2 Adsorption and Retardation

Because petroleum hydrocarbon molecules are to some degree nonpolar, there is a finite limit to their solubility in a more polar substance such as water. This results in low $(<10^{-3} \text{ mg/L})$ to moderate (10^3 mg/L) aqueous solubility limits for the petroleum hydrocarbon compounds, as well their tendency to partition to other forms of organic carbon in the subsurface. This characteristic can cause their migration in the dissolved plume as *micelles*, that is "packs" of organic molecules with the more hydrophilic compounds or the more hydrophilic portions of each molecule on the outer surface of the micelle. It also leads to adsorption of the petroleum hydrocarbon compounds to the organic coatings of the soil particles.

The tendency to adsorb to the subsurface material is different for each of the petroleum hydrocarbon compounds; the compounds that sorb strongly tend to migrate downgradient more slowly than those that sorb less strongly This leads to a "chromatographic" effect within a migrating dissolved plume, with the more mobile compounds arriving at

1

downgradient locations before the more retarded compounds.

This adsorption property is represented in transport equations by the *retardation factor* (R_f) which is defined as:

$$R_{\rm f} = 1 + (r_{\rm b} K_{\rm d})/r$$

Where:

n = porosity. $r_{\rm b} = \text{soil bulk density.}$

 $K_{\rm d}$ = distribution coefficient.

The distribution coefficient, K_d , is derived from the relationship between aqueous concentration and degree of adsorption as defined by a linear Freundlich isotherm. Several studies have determined a relationship in turn between the distribution coefficient and the mass fraction of organic carbon:

$$K_{\rm d} = K_{\rm oc} f_{\rm oc}$$

Where:

 f_{oc} = mass fraction of organic carbon.

 K_{oc} = partition coefficient between soil organic carbon and water.

These studies have also found a good statistical correlation between the partition coefficient and the octanol/water partition coefficient, K_{ow} and between a compound's solubility and K_{ow} . Examples of these correlations are:

[2]

 $log(K_{oc}) = -0.21 + log(K_{ow})$ $log(K_{oc}) = 0.44 - 0.54 log(S_m)$

[3]

$$\log(K_{\rm oc}) = 0.49 + 0.72 \log(K_{\rm ow})$$

[4]

 $log(K_{oc}) = 0.088 + 0.909 log(K_{ow})$ $log(K_{oc}) = 3.95 - 0.62 log(S)$

Where:

 $S_{\rm m}$ = aqueous solubility (mole fraction).

S = aqueous solubility (mg/L).

Relationships between aqueous solubility and the octanol/water partition coefficient are well established. Examples of the relationship are shown in Figure 1. Consequently, the parameters that typically need to be obtained in order to assess the sorption and retardation of organic compounds are the soil bulk density (r_b) , the octanol/water partition coefficient (K_{ow}) , and the mass fraction of soil organic carbon (f_{oc}) .

2.3 Dispersion

The spreading and mixing of chemical compounds in groundwater caused by diffusion and mixing due to micro-

scopic variations in velocities within and between pores is defined as dispersion. Because dissolved hydrocarbon compounds typically migrate through subsurface materials that are not homogeneous, there are inherently different constituent migration rates in different portions of the plume. This process can result in an apparent lateral spreading from the plume's flanks and an apparent spreading of the plume's leading edge. This apparent spreading is represented by transverse and longitudinal dispersivity coefficients respectively. Empirical field studies of dispersion have found relationships with flow velocity and scale of plume. Figure 2 shows the relationship between longitudinal dispersivity and flow velocity; for greater flow velocities, the apparent longitudinal dispersivity determined in the field can be several orders of magnitude greater than the dispersivity measured in the laboratory.

Similarly, Figure 3 shows a compilation of observed relationships between longitudinal dispersivity and the magnitude of plume length. While these empirical relationships can be useful, these studies are known to be hampered by limitations in the field data (for example, large spacing between observation wells or poor definition of the initial volume occupied by injected tracer) and limited information on field conditions (for example, definition of the permeability distribution or temporal fluctuations in the flow system). Recent quantitative studies that take into account the stratigraphic heterogeneity of the test site have found dispersivity values more in line with laboratory values.

2.4 Diffusion

The migration of petroleum hydrocarbon compounds because of concentration gradients is known as *diffusion*. This is commonly described by Fick's Law:

$$J = -D \operatorname{grad}(C)$$

Where:

J = mass flux.

D = effective diffusion coefficient.

C =concentration.

This equation applies both to the dissolved petroleum hydrocarbon compounds in ground water and to the volatile petroleum hydrocarbon compounds in the soil air in the vadose zone. Order-of-magnitude values for diffusion coefficients for most compounds are 10^{-2} cm²/sec in air, and 10^{-5} cm²/sec in water. Equations for estimating air and water diffusion coefficients for petroleum hydrocarbon compounds can be found in the article by Tucker and Nelken [5].

While seemingly making only a modest contribution to the redistribution in permeable settings, diffusion can be a dominant transport mechanism in low-permeability settings in both the vadose and saturated zones [6, 7]. The diffusion process is also potentially important in the replenishment of dissolved oxygen in the near-water table portion of the saturated zone by influx from the vadose zone [8]. For these reasons, it can be important to determine diffusion coefficients for the petroleum hydrocarbon compounds of interest, and to monitor oxygen (O_2) , carbon dioxide (CO_2) , and methane (CH_4) in the soil air in the base of the vadose zone.



Solubility in Water, log S_b (moles per liter)

Figure 1—Relationship Between Aqueous Solubility and Octanol-water Partition Coefficient for Several Groups of Organic Compounds (from Domenico and Schwartz, 1990)

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Figure 2—Relationship Between Longitudinal Dispersivity and Flow Velocity, After Pfannkuch (1962) (from Domenico and Schwartz, 1990)

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Figure 3—Compilation of Observed Relationships Between Longitudinal Dispersivity and Magnitude of Plume Length, After Gelhar et al, (1985) (from Domenico and Schwartz, 1990)

SECTION 3—BIOLOGICAL PROCESS

3.1 General

The biological processes are chiefly responsible for the transformation of the dissolved hydrocarbon compounds to simpler organic and inorganic compounds. These processes are almost entirely carried out by the microbiological, or *microbial*, populations inhabiting the subsurface. These microbial populations can mineralize the hydrocarbon compounds, transforming them into carbon dioxide (CO₂), water (H₂O), and salts. This microbial transformation process, known as *biodegradation*, is the major attenuation mechanism for petroleum hydrocarbons in the subsurface.

Note: While there has been little research on the other major removal mechanism, volatilization from the plume, this is thought to be minor in comparison to biodegradation for petroleum hydrocarbon compounds [9]. A dynamic equilibrium will be reached with the release rate of hydrocarbon compounds in the source area balanced by the biodegradation rates within the dissolved phase plume, with the rate of biodegradation determining the ultimate length of the plume. This equilibrium will result in a generally stabilized plume.

Biodegradation of hydrocarbons is, in essence, an oxidation-reduction reaction mediated by the subsurface micro-

bial populations, where the hydrocarbons are oxidized by giving up electrons (*electron donor*) and another compound is reduced, gaining electrons (*electron acceptor*) [9]. In the process, the microbial populations derive energy and/or organic carbon for building more cell material. When this process proceeds under natural conditions without artificial enhancements, it is termed *natural biodegradation*, *unenhanced biodegradation*, or *intrinsic bioremediation*. In contrast, when the biodegradation rates involved are increased by artificial enhancement or augmentation of environmental factors otherwise limiting these rates, the process is termed *enhanced biodegradation* or *bioremediation*.

There are several types of biodegradation processes that are mainly differentiated by the types of electron acceptors involved. The electron acceptors presently considered important for hydrocarbon biodegradation are oxygen (O₂), nitrate (NO₃), oxidized or ferric iron (Fe³⁺), oxidized manganese (Mn⁴⁺), sulfate (SO²₄), and bicarbonate (HCO₃). Of these, oxygen is generally considered the most important and results in the most rapid biodegradation rates. Consequently, these different types of biodegradation are commonly differentiated as aerobic biodegradation and anaerobic biodegradation. Both will be discussed further under these groupings. For further overviews on processes involved with natural biodegradation, the reader is referred to the books by Borden [10] and Wilson [11].

3.2 Aerobic Biodegradation

Almost all of the petroleum hydrocarbon compounds are biodegradable under aerobic conditions (that is, with free oxygen (O_2) present). Under favorable conditions (for example, fuels with low boiling point mixtures such as gasoline, diesel, or JP-4), aerobic biodegradation can proceed relatively rapidly. Consequently, the natural biodegradation process is commonly limited by the availability of oxygen, rather than by microbial capabilities.

The oxygen requirements for the complete mineralization by aerobic biodegradation varies, depending on the petroleum hydrocarbon compounds involved. As an example of the range in oxygen requirements, an aromatic constituent such as benzene and an aliphatic constituent such as hexane have the following reaction:

For benzene:

$$C_6H_6 + 7^{1/2}O_2 \xrightarrow{\text{microorganisms}} 6CO_2 + 3H_2O +$$

energy

6

For hexane:

 $C_6H_{14} + 9^{1/2}O_2 \xrightarrow{\text{microorganisms}} 6CO_2 + 7H_2O + energy$

By these reactions the mass requirement of oxygen is 3.1

to 3.5 kilograms per kilogram of hydrocarbon compound, respectively.

Within the vadose zone, the air in soil pores can contain up to 21 percent oxygen, which is the oxygen concentration in the atmosphere. Soils containing petroleum hydrocarbons or naturally high concentrations of organic carbon can have lower oxygen concentrations. Aerobic bioactivity is generally considered to become dormant where oxygen concentrations in the soil air are less than 2 percent, conditions that are commonly found within the zone of residual saturation of hydrocarbons. Under such conditions, aerobic biodegradation rates become limited to the natural rates of oxygen replenishment. This replenishment is largely due to the air exchange caused by barometric pressure and water table fluctuations. Oxygen replenished by this air exchange is redistributed within the vadose zone principally by diffusion.

Within the saturated zone there are important oxygen limitations. The oxygen solubility limit for groundwater saturated with air ranges from approximately 6 to 15 mg/L and is 8 mg/L at 20°C. By these ranges, the dissolved oxygen (DO) in aerated ground water would result in the mineralization of up to 1.7 to 4.8 mg/L of dissolved hydrocarbons. Biodegradation is active in the saturated zone in both low DO (<2 mg/L) and high DO (2-8 mg/L) conditions. However, as oxygen concentrations drop below 2 mg/L, there may be a distinct decrease in aerobic bioactivity. Chiang et al. [12] found in laboratory studies that microcosms with ground water DO levels (2 mg/L degraded 80 to 100 percent of BTX (120-16,000 ppb) with $t_{1/2}$ of 5-20 days. When DO levels were 1 and 2 mg/L, aromatic hydrocarbon concentrations of 120-1,300 ppb were degraded 20 to 60 percent within 20 to 30 days. Studies by Kemblowski et al. [13] also showed that biodegradation rates decrease as DO concentrations declined to less than 2 mg/L.

Dissolved oxygen is replenished by hydrodynamic dispersion, diffusion, and reaeration. This last process occurs at the capillary fringe interface with the vadose zone. Because the petroleum hydrocarbon compounds dissolved in ground water are commonly located in the immediate vicinity of the water table, reaeration is a major source of oxygen. Caldwell et al. [14] found that this reaeration process provided 85 to 90 percent of the oxygen consumed by aerobic biodegradation.

3.3 Anaerobic Biodegradation

Anaerobic biodegradation occurs in the absence of or without the use of free O_2 using other electron acceptors. Because facultative microorganisms can be involved, anaerobic biodegradation usually commences after the oxygen supply has been depleted. However, the conditions under which the different anoxic electron acceptors are being used can be overlapping, and several of these anaerobic biodegradation processes can occur simultaneously.

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Anaerobic biodegradation rates are distinctly slower than aerobic rates. They are usually limited by the reaction rates of the microorganisms involved and the substrate (that is, petroleum hydrocarbon compounds) concentration, rather than the availability of the electron acceptor. They are typically not inhibited by high concentrations of petroleum hydrocarbon compounds.

When nitrate is used as an electron acceptor, it is reduced ultimately to nitrogen gas following the denitrification pathway:

$$NO_3 \rightarrow NO_2 \rightarrow N_2O \rightarrow N_2$$

Using toluene as an example of denitrification-based bioremediation ([10]):

 $C_6H_5CH_3 + 6NO_3 \xrightarrow{\text{microorganisms}} 7CO_2 + 4H_2O + 3N_2 + energy$

By this reaction, the mass requirement of nitrate is 4.0 kilograms per kilogram of toluene.

Because nitrate has a higher solubility limit than oxygen, denitrification-based biodegradation can be a potentially important natural process. However, the petroleum hydrocarbon compounds biodegraded by the process can be selective and vary among the areas that have been studied. For example, Hutchins et al., [15] found that benzene was recalcitrant (that is, not biodegraded) under denitrifying conditions, while Major et al. [16] found that benzene was degraded. Because the investigations of denitrification-based biodegradation in the subsurface have been initiated within the last decade, better characterization of the processes and substrates involved will be forthcoming in the near future.

Other studies have found iron and manganese reduction to be the electron acceptors involved in the biodegradation of aromatic hydrocarbons [17, 18]. Because both are common mineralogical components of the porous media involved, they are a potentially large supply of electron acceptors in anoxic environments. They are chiefly found as solids and require microbial species that are able to use them as such. While this can result in a buildup of dissolved Fe^{2+} and Mn^{2+} , the simultaneous generation of sulfide by sulfate reduction can result in the precipitation of FeS from solution; the reduced manganese, however, would not be affected by sulfide buildup [19]. Because they can be involved with sulfate reduction, it has been difficult to differentiate direct biodegradation via metals reduction from indirect reduction because of direct microbial reduction of sulfate. More information on hydrocarbon biodegradation by iron and manganese reduction will undoubtedly be forthcoming in the near future.

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Sulfate reduction (converting sulfate to sulfide) and methanogenesis (methane production) can be important for biodegradation under strongly reducing conditions. This is especially significant where sulfate is a significant constituent in the ambient ground water chemistry or in the subsurface mineralogy. The mechanisms for these processes are also poorly understood, but there is empirical evidence accumulating that these processes do contribute to the biodegradation of petroleum hydrocarbon compounds. For example, Beller et al. [20] and Acton and Barker [21] monitored the attenuation of monoaromatic hydrocarbons by sulfate reduction, and Grbi-Gali and Vogel [22] documented biodegradation of aromatic hydrocarbons by methanogenesis.

Taken together, the anaerobic biodegradation processes can be important in the attenuation of a hydrocarbon plume. Cozzarelli et al. [25] investigated the anaerobic biodegradation occurring within the dissolved plume migrating from a crude oil spill in northern Minnesota. They found reducing, methanogenic conditions prevailing up to 80 meters downgradient of the source area; within ten meters of the source, most of the alkylbenzenes had been degraded to very low concentrations with an accompanying buildup of organic acids. Further downgradient these organic acids were also being degraded. Benzene and ethylbenzene were the most persistent monoaromatics in the anaerobic zone, with their concentrations attenuated within a short distance of encountering trace concentrations of dissolved oxygen. A number of anaerobic metabolic intermediates of various alkylbenzenes were identified. These findings are summarized in Figure 4.

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SECTION 4—SUGGESTED PARAMETERS TO BE MONITORED

4.1 General

There are several parameters that can be monitored to determine the extent to which these physiochemical and biodegradation processes are attenuating the migrating dissolved hydrocarbon compounds. The parameters listed in this section are intended to be practical, inexpensive parameters that could be included in typical hydrocarbons investigations.

4.2 Relative Plume Lengths

A comparison of theoretical and actual plume lengths will give an approximation of attenuation rates. For dissolved plumes that have existed for at least several years, the comparison of the downgradient extent of different compounds of the dissolved plume can often reveal significant differences, especially if there are conservative compounds (that is, compounds that move at the same rate as the groundwater, such as chloride) associated with the plume. MTBE is considered by some to be a conservative constituent, although that has not been conclusively determined. This approach can also be used by comparing the actual extent of a constituent with its theoretical extent based upon its calculated transport rate. Parameters for this approach include:

a. BTEX, or other hydrocarbon chemical(s) of conce.

b. Conservative compound, if any, (for example, Cl, MTBE(?)).

- c. Hydraulic conductivity (K).
- d. Hydraulic head gradients.
- e. Porosity.
- f. Retardation factor.

Actual plume length and stability can be determined by evaluating time trends in monitoring data. The dimensions of the hydrocarbon plume can be plotted for a series of sampling events, and the relative stability of the plume can be observed. Fluctuations in the plume dimensions, if they occur, may also be correlated to changes in site variables such as water levels, infiltration areas, and source removal.

Several methods can be used to calculate theoretical plume lengths. Analytical solutions or numerical modeling can be used to estimate theoretical plume lengths. Input parameters are dependent on the method used. An expected attenuation rate can be applied to the theoretical solutions to approximate the expected actual plume length. Field data points can then be located to calibrate the analytical solution. Once the actual steady state plume conditions are determined, a comparison of the two plume lengths will allow for the adjustment of the attenuation rate for the plume.

4.3 Water Quality Changes

The transformations in water quality as groundwater flows through the source area can often indicate the presence of anaerobic and/or aerobic biodegradation activity. This can best be assessed by collecting groundwater samples upgradient and downgradient of the dissolved plume, within the source area, and in some location(s) within the dissolved plume. Groundwater parameters for this approach include:

- a. BTEX, other chemical(s) of concern.
- b. Dissolved oxygen (O_2) .
- c. Reduction-oxidation potential (redox).
- d Chemical oxygen demand (COD).
- e. Biochemical oxygen demand (BOD).
- f. Nitrate (NO₃).
- g. Nitrite (NO₂).
- n. Ammonium (NH₄+).
- i. Sulfate (SO₄).
- j. Methane (CH₄).
- k. Iron (Fe^{2+} and Fe^{3+}).
- 1. Manganese (Mn^{4+} and Mn^{2+}).
- m. Organic acids.

4.4 Vadose Zone Air Quality Changes

The transformations in the volatile compounds with migration in the vadose zone from the source area can be assessed in two ways. A soil gas survey can be conducted in the vicinity of the source area. Parameters to be monitored include:

a. BTEX, total volatile organic compounds, or other chemical(s) of concern.

- b. Oxygen (O_2) .
- c. Carbon dioxide CO₂).
- d. Methane (CH₄).

Another method that can be used to supplement the soil gas survey is the in situ respiration test. This test can be carried out in monitoring wells where oxygen levels are found to be less than two percent. The method is best described in the article by Hinchee and Ong [24].

SECTION 5—CASE STUDY

To evaluate the effectiveness of the natural attenuation processes in controlling the extent of a dissolved plume of petroleum hydrocarbon compounds, a study was undertaken of several service station sites in southeastern Florida. A series of field and laboratory activities was performed to assess the presence of ongoing anaerobic and aerobic biodegradation activity. The results for one of the sites are summarized below. The study is described more fully by Caldwell et al. [14].

The study characterized the chemical quality in three zones: (a) upgradient of the hydrocarbons source area, (b) downgradient of the petroleum hydrocarbons source area, and (c) within the source area. The ground water and soil air quality in the three zones is summarized in Tables 1 and 2. These results indicated that the upgradient area was aerobic and unaffected by petroleum hydrocarbon compounds. Dissolved oxygen was detected, redox potential was strongly oxidizing, and the pH was neutral.

In contrast, the source area had elevated petroleum hydrocarbon concentrations and was anaerobic. The dissolved oxygen was below the method detection limit of 0.2 mg/L, the redox potential was strongly reducing, and the pH was depressed by 0.7 units. The concentrations of metals and other cations were higher than the upgradient values.

Downgradient of the source area, petroleum hydrocarbon concentrations were decreased, but the area was still anaerobic. The dissolved oxygen was nondetectable, the redox potential was moderately reducing, and the pH was still slightly depressed. These results are consistent with the typical profile through a dissolved plume of petroleum hydrocarbons.

Laboratory screening of soil samples from each of the three zones was carried out to assess the presence of aerobic microbial populations using plating tests and respirometry tests. The results are summarized in Figure 5. The plating tests for all three zones indicated that total heterotrophic populations and microbial populations specifically capable of degrading gasoline were ample, with population densities generally ranging from 10^5 to 10^6 colony-forming units per gram dry weight of soil (cfu/gdw). The ratios of specific degraders to total heterotrophs were also favorable, ranging from 12 to 36 percent.

Respirometry tests were also carried out to determine the respiration rate (that is, the rate of oxygen consumption and

| | | Upgradient | Impacted Zones | Downgradient | |
|---------------------------------------|--------|------------|-------------------|----------------|--|
| Parameter | Units | MW-7 | MW-6 | MW-16 | |
| Water 10/30/91 | | | | | |
| DO (Winkler) | mg/L | 2.2/2.2 | ND/ND | ND/ND | |
| DO (Probe) | mg/L | 3.2 | 1.35 | 0.75 | |
| Eh | mv | +279.4 | -175/-204 | -46.5 | |
| pH | SU | 7.25 | 6.54 | 6.66 | |
| Conductivity | mmh/cm | 290 | 820 | 670 | |
| Т | °C | 28 | 30 | 26 | |
| Soil Vapor | | | | | |
| DTŴ (4/3/92) | ft bls | NM | 8.20 | NM | |
| Probe Depth | ft bls | 7.0 | 7.0 | 7.0 | |
| O ₂ (Probe) | % | 15 | 6 | 19.5 | |
| CO ₂ (Probe) | % | 5 | 12 | 1 | |
| OVA (Probe) Total/Methane | ррт | ND/ND | ND/ND | ND/ND | |
| DTW (10/30/91) | ft bls | 7.4 | 7.02 | 6.02 | |
| O ₂ (Well) | % | 16 | 15 | 19.5 | |
| CO ₂ (Well) | % | 2 | 1 | 1 | |
| OVA (Well) Total/Methane | ppm | ND/ND | 3/3 | 95/94 | |
| Relative Humidity (Well) (Ambient) |) % | 54.3 | 51.3 (54.9) | 46.5 (45.3) | |
| T (Well) (Ambient) | °C | 28.8 | 26.5 (25.8) | 32 (31.2) | |

Table 1—Field-Measured Groundwater and Soil Air Quality Parameters (from Caldwell et al., 1992)

DTW = Depth to Water ND = Not detected

NM = Not measured

NATURAL ATTENUATION PROCESSES

| | Det Limit | | Impact | | USEPA |
|---------------|-----------|------------|---------|--------------|--------|
| Parameter | Units | Upgradient | Zones | Downgradient | Method |
| Water | | | | | |
| Benzene | ìμg/L | BDL | < 50 | < 50 | 602 |
| Toluene | 1μg/L | BDL | < 50 | < 50 | 602 |
| Ethyl Benzene | 1 μg/L | BDL | 950 | 190 | 602 |
| Xylenes | 1 μg/L | BDL | 320 | 520 | 602 |
| Total BTEX | | | 1270 | 710 | |
| MTBE | 1 μg/L | BDL | < 50 | < 50 | 602 |
| TRPH | l mg/L | BDL | 5 | 3 | 418.1 |
| TOC | 1 mg/L | 3 | 16 | 8 | 415.1 |
| BOD | 2 mg/L | BDL | 10 | 4 | 405.1 |
| COD | 5 mg/L | BDL | 34 | 34 | SM508B |
| NO2 | 0.05 mg/L | BDL | 0.22 | BDL | 353.3 |
| NO3 | 0.05 mg/L | 0.34 | 0.42 | 0.05 | 353.3 |
| PO4 | 0.2 mg/L | BDL | BDL | BDL | 365.2 |
| NH4 | 0.2 mg/L | BDL | 2.9 | 1.8 | 350.3 |
| SO4 | 5 mg/L | BDL | 75 | - | 375.4 |
| C1 | 5 mg/L | 7 | 16 | | 325.2 |
| CO2 | 5 mg/L | 130 | 370 | - | Calc. |
| ALK | 5 mg/L | 140 | 340 | - | 310.1 |
| TDS | 5 mg/L | 160 | 510 | - | 160.1 |
| Ca | 50 µg/L | 47,000 | 150,000 | - | 200.7 |
| Fe | 100 µg/L | BDL | 1,800 | - | 200.7 |
| Mg | 50 µg/L | 790 | 5,900 | | 200.7 |
| Mn | 50 µg/L | BDL | BDL | - | 200.7 |
| Na | 100 µg/l | 3,400 | 13,000 | - | 200.7 |

Table 2-Groundwater Analytical Results (from Caldwell, et al., 1992)

carbon dioxide production) attainable by the soil microbial populations. The respirometry results indicated oxygen consumption rates ranging from 7 to 100 microliters per gram of soil per hour (mL/g/hr), and carbon dioxide production rates ranging from 7 to 90 mL/g/hr. Rates were highest for the soil samples from the source area, indicating higher aerobic biodegradation rates attainable in these affected soils.

These results, along with the results of previous site investigations, were used to develop and calibrate a computer model of the transport and fate processes ongoing at the site, including biodegradation. Results of this biodegradation model are summarized in Figures 6 and 7. The simulated 1989 historical distributions and the predicted 1994 distribution of the monoaromatic compounds (BTEX) collectively are shown in Figure 6. The BTEX plume was predicted to retreat with the concentrations in the source area decreasing.

The effects of biodegradation can be assessed with a biodegradation model. The biodegradation parameters can be inactivated to evaluate what the extent and concentrations of a dissolved plume would be without the ongoing bioactivity. Figure 7 shows the predicted distribution of the dissolved BTEX plume with and without biodegradation. As can be seen, without biodegradation the dissolved plume extends significantly beyond the extent of the actual plume and out of the modeled area at concentrations over 3,000 mg/L. These results suggest that biodegradation processes naturally occurring at petroleum hydrocarbons sites are important in limiting the extent of the plume and determining the ultimate extent of the dissolved plume migrating from the site.

The role of natural attenuation in the regulatory process is coming to the forefront. Many states have approved closure of sites where natural attenuation was demonstrated to be effective. The State of California Regional Water Quality Boards have formed a University of California LUFT Team to support revisions of the LUFT manual. Recommendations are being made by the LUFT Team regarding fate and transport, natural attenuation, and other topics related to corrective action for petroleum hydrocarbons. A random sample of 1,500 cases in 13 counties within California is being used for the study. Recommendations are being made regarding analytical procedures that measure the natural attenuation capacity of LUFT sites for bioremediation of fuel hydrocarbons. 12

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Time (hr)



NATURAL ATTENUATION PROCESSES



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Not for Resale

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BTEX Constituents (from Caldwell, et al., 1992)

API PUBL*1628A 96 🎟 0732290 0559126 477 📟

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