

# TABS ON CONTAMINATED SITES

## Contaminated Sites Program - Federal Sites

This is one in a series of Technical Assistance Bulletins (TABs) prepared by Environment Canada-Ontario Region for Federal Facilities operating in Ontario.

### TAB #21



## Intrinsic Remediation - Attenuation Mechanism and Contaminant Transport

### DESCRIPTION:

A successful implementation of intrinsic bio-attenuation at a field site requires adequate site hydrogeological, chemical, and biological characterization; detailed data analysis to determine whether contaminants are being attenuated and/or removed from the aquifer; modeling of the fate and transport of the dissolved groundwater plume; and, finally, long-term monitoring to confirm and ensure protection of human health and the environment.

### 1. CONTAMINANT TRANSPORT AND ATTENUATION MECHANISMS

The environmental fate and transport of a contaminant is controlled by the compound's physical and chemical properties and the nature of the subsurface medium and geochemical conditions in the material through which the compound is migrating. Natural attenuation mechanisms include biological processes such as aerobic and anaerobic biodegradation, physical processes such as dispersion, diffusion and volatilization and the chemical process of sorption. The primary transport mechanism that does not directly cause a reduction of contaminant concentration is advection.

#### Advection

Advective transport is the process by which dissolved contaminants are transported by flowing groundwater at its average linear velocity. Flow rates are determined by the relationship:

$$V_x = -K i / n$$

where  $V$  is the average linear groundwater velocity (L/T),  $K$  is the hydraulic conductivity (L/T),  $i$  is the hydraulic gradient (L/L) and  $n$  is the porosity of the subsurface material. (*The symbols in brackets represent*

*dimensions e.g. L=length, T=time).*

#### Adsorption

Adsorption is a process that can remove potential contaminants from solution in groundwater and bind them temporarily to the surface of solid particles. This process is referred to as hydrophobic bonding and is an important factor in controlling the fate of many organic contaminants. Two components of an aquifer have the greatest effect on sorption: organic matter and clay minerals. In most aquifers, the organic fraction tends to control the sorption of petroleum hydrocarbons. This process results in the overall delay in contaminant movement with respect to the average velocity of groundwater and is referred to as "retardation". The amount of retardation that a dissolved chemical experiences depends on its characteristics and the properties and composition of the material through which it is migrating. For linear, reversible adsorption, the retardation factor can be expressed as:

$$R = 1 + K_d p_b / n \text{ (Freeze and Cherry, 1979)}$$

where  $p_b$  is the dry bulk density of the soil (M/L<sup>3</sup>),  $n$  is the porosity, and  $K_d$  is the distribution coefficient (L<sup>3</sup>/M) which describes the partitioning of a

dissolved solute between the aqueous and sorbed phases. The distribution coefficient is unique to individual contaminants and is dependent upon the chemical characteristics of the porous medium and groundwater.

The degree of adsorption of organic contaminants is directly related to the organic carbon content of the soil as described for example by Karickhoff *et al.* (1979). It has been found that an empirical relationship exists between the distribution coefficient ( $K_d$ ), the fractional mass of organic carbon in the soil ( $f_{oc}$ ) and the organic carbon distribution coefficient ( $K_{oc}$ ) ( $L^3/M$ ) as follows:

$$K_d = (f_{oc})(K_{oc})$$

This relationship is of importance because it is difficult to measure the distribution coefficient,  $K_d$ , directly, but  $f_{oc}$  can be measured or estimated and  $K_{oc}$  values are available in the literature for many compounds.  $K_{oc}$  data for the BTEX compounds are presented in the following table:

**TABLE 1:  $K_{oc}$  Data for BTEX Compounds.**

The retarded contaminant transport velocity is given by:

Compound	$\log K_{oc}$ (L/kg)
Benzene	1.58
Toluene	2.13
Ethylbenzene	1.93
Xylenes (mixed)	2.38

Source: ASTM, 1996 Draft

$$V_c = V_x/R$$

Where:  $V_c$  is the retarded contaminant transport velocity ( $L/T$ );  $V_x$  is the average linear groundwater velocity and  $R$  is the retardation factor.

### Dilution

Dilution results in a reduction in contaminant concentrations, but only in an apparent reduction in the total mass of contaminant in the groundwater system. The two most common causes of dilution are infiltration or recharge of precipitation to the aquifer and monitoring wells screened over large vertical intervals.

Infiltration of precipitation can cause an apparent reduction in contaminant mass by mixing with the contaminant plume thereby causing dilution. Monitoring wells screened over large vertical distances may dilute groundwater samples by mixing water from clean aquifer zones with contaminated water during sampling. This second source of dilution represents an artificial source of concentration reduction caused only by the sampling technique.

### Hydrodynamic Dispersion

Hydrodynamic dispersion is the process whereby a contaminant plume spreads out in directions that are longitudinal and transverse to the groundwater flow path. Hydrodynamic dispersion is the result of two physical processes, namely: mechanical dispersion and molecular diffusion. Mechanical dispersion occurs only under ground water flow conditions, whereas, molecular diffusion occurs under both flowing and stagnant conditions.

Hydrodynamic dispersion  $D$  ( $L^2/T$ ), incorporates the effect of both dispersion and molecular diffusion and can be written as:

$$D = \alpha V_x + D_e$$

Where  $\alpha$  is the dispersivity of the porous medium,  $V_x$  is the average linear groundwater velocity and  $D_e$  is the diffusion coefficient ( $L^2/T$ ) (a property of the dissolved contaminant).

### Mechanical Dispersion

Mechanical dispersion occurs because of the tortuosity in flow paths within a porous medium. That is, when the particles in a porous medium prevent groundwater and any dissolved contaminants from flowing in a straight line. This typically results in longitudinal and transverse spreading of the contaminant plume. The component of hydrodynamic dispersion contributed by mechanical dispersion is given by the relationship:

$$\text{Mechanical Dispersion} = \alpha V_x$$

Mechanical dispersion is the dominant mechanism causing hydrodynamic dispersion at typical groundwater velocities.

### Diffusion

Molecular diffusion results in the movement of chemicals from zones of higher concentrations to zones of lower concentrations. Diffusion is

dependent only on concentration gradients and will occur even in materials of low hydraulic conductivities. Diffusion as a contaminant migration mechanism is most important when groundwater velocities are low, typically less than a few centimetres a year. The mass flux of a diffusing chemical is represented in the hydrodynamic dispersion equation as  $D_e$ . Diffusion is likely insignificant compared to dispersion in most settings.

### Volatilization

Volatilization is the process by which chemicals dissolved in groundwater are transferred from the aqueous phase into the vapour phase. The chemical then migrates through the capillary fringe and into the unsaturated or vadose zone. This process is dependent on the Henry's Law constant (a coefficient describing the partitioning of a chemical between the gas and aqueous phases), the concentration of the chemical, the depth to the water table, and the temperature. Generally, the higher the vapour pressure and Henry's Law constant, the more likely the chemical will be released from the soil or groundwater to the soil gas. The physico-chemical properties of the BTEX compounds give them relatively high Henry's Law constant compared to many other organic compounds. Data for these compounds are presented in the following table ( $H$  is the dimensionless Henry's law constant (air/water partition coefficient)):

**TABLE 2: Henry's Law Constants (Air/Water) for BTEX Compounds.**

Compound	H
Benzene	0.22
Toluene	0.26
Ethylbenzene	0.32
Xylenes (mixed)	0.29

Source: ASTM, 1996 *Draft*

### Aerobic and Anaerobic Biodegradation

Biodegradation of BTEX parameters by indigenous subsurface microbes appears to be the primary mechanism for intrinsic remediation at sites where natural attenuation has been documented. During biodegradation, microbes transform available nutrients, including hydrocarbons, into substances useful for energy and cell reproduction. Microbes

obtain this energy by facilitating the transfer of electrons from electron donors to electron acceptors. This results in the oxidation of electron donors and the reduction of electron acceptors. Electron donors include natural organic material and petroleum hydrocarbons. Electron acceptors in groundwater include dissolved oxygen, nitrate, Fe (III), sulphate and carbon dioxide.

The use of electron donors by microbes begins with dissolved oxygen (aerobic conditions) followed by anaerobic (absent or minimal dissolved oxygen). The natural bioattenuation for aromatic hydrocarbons can follow both aerobic and anaerobic pathways. These patterns are summarized in the following subsections based on Wiedemeier *et al.* (1995).

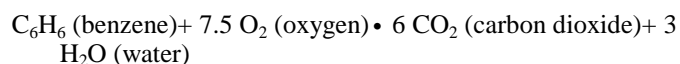
### Aerobic Biodegradation

Biodegradation of petroleum hydrocarbons is often an aerobic process that occurs when indigenous hydrocarbon-degrading micro-organisms are supplied with oxygen and nutrients necessary to utilize fuel hydrocarbons as an energy source. The supply of oxygen in a petroleum hydrocarbon-impacted aquifer is constantly renewed by the influx of oxygenated, upgradient flow and the vertical diffusion of oxygen from the unsaturated soil zone into the groundwater (Borden and Bedient, 1986). Aquifers consisting of sandy soil and characterized by moderate to high hydraulic conductivities typically support effective aerobic biodegradation.

Aerobic biodegradation is typically found within aquifers with dissolved oxygen (DO) concentrations greater than 1 to 2 mg/L. Dissolved oxygen concentrations are used to estimate the mass of contaminant that can be biodegraded aerobically. In this process, the microbes utilize dissolved oxygen as an electron acceptor to degrade the hydrocarbon substrate. Under aerobic conditions, dissolved oxygen levels are reduced as aerobic respiration occurs.

Anaerobic bacteria generally cannot function at DO levels greater than 1 mg/L. As documented by Chiang *et al.* (1989), an inverse correlation between DO and aromatic hydrocarbon concentrations has been observed suggesting that aerobic biodegradation is the most significant mechanism for natural attenuation of BTEX. In general, dissolved oxygen concentrations will be lower than background conditions in groundwater impacted by BTEX compounds. Thus a reduction in DO

concentrations within an existing BTEX groundwater plume provides strong indication that microbes are already established and actively biodegrading petroleum hydrocarbons by aerobic respiration. The equation that describes the overall stoichiometry of the oxidation of aromatic hydrocarbon compounds to carbon dioxide and water under aerobic conditions is given below, using benzene as an example:



The balanced reaction indicates that 7.5 moles of oxygen are required to metabolize one mole of benzene. Similar calculations can be made for toluene, ethylbenzene and xylenes. Thus in the absence of microbial cell production, each 1.0 mg/L of D.O. consumed by microbes will mineralize (convert completely to carbon dioxide and water) approximately 0.32 mg/L of benzene or BTEX compounds.

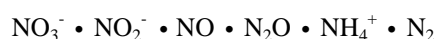
### Anaerobic Biodegradation

Typically, depletion of dissolved oxygen is observed in the impacted groundwater plume as a result of increased levels of microbial respiration. This depletion of DO results in the development of anaerobic conditions within and near the margins of the groundwater plume.

When oxygen is absent or exists at low levels, then nitrate, iron (III), sulphate, and carbonate can serve as terminal electron acceptors in the following order of reduction:

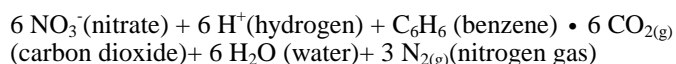
### Denitrification

Nitrate can be used as an electron acceptor by anaerobic microbes to mineralize the BTEX compounds via denitrification, after almost all of the dissolved oxygen has been consumed and anaerobic conditions have developed. Nitrate concentrations are used to estimate the mass of contaminant that can be biodegraded by denitrification processes. The de-nitrification occurs in the following sequence:



In areas where denitrification is occurring, there will be a strong correlation between areas of high BTEX concentrations and areas depleted of nitrate relative to measured background concentrations. The following equation describes the overall stoichiometry of aromatic hydrocarbon

transformation (example of benzene) to carbon dioxide and water under denitrifying conditions caused by anaerobic biodegradation:



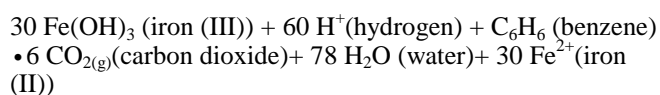
The balanced equation indicates that six moles of nitrate are required to metabolize one mole of benzene. Thus in the absence of microbial cell production, each 1.0 mg/L of ionic nitrate consumed by microbes will mineralize approximately 0.21 mg/L of benzene or BTEX compounds.

### Iron (III) Reduction

Once the available dissolved oxygen and nitrate in the aquifer have been depleted, iron (III) can be used as an electron acceptor. During this process, iron (III) is reduced to iron (II), which is relatively soluble in water. Iron (II) concentrations are used as an indicator of anaerobic degradation of hydrocarbon compounds. By knowing the volume of contaminated groundwater, the background iron (II) concentration and the iron (II) measured in the contaminated area, it is possible to estimate the mass of BTEX lost to biodegradation through iron (III) reduction.

The oxidation of the BTEX compounds coupled with the reduction of iron (II) may result in the high concentrations of iron (II) in groundwater within and near the contaminated plume. Most of the iron (III) that is reduced to iron (II) is subsequently precipitated when the groundwater mixes with oxygenated groundwater downgradient of the plume.

The following equation describes the overall stoichiometry of benzene oxidation by iron reduction to carbon dioxide, iron (II) and water under anaerobic biodegradation:



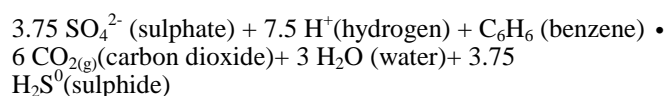
The balanced reaction indicated that thirty (30) moles of iron (III) are required to metabolize one mole of benzene. Thus in the absence of microbial cell production, 1.0 mg/L of benzene or BTEX results in the production of 21.8 mg/L of iron (II) during the iron (III) reduction.

### Sulphate Reduction

Following nitrate and iron (III) reduction, sulphate

may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulphate reduction and results in the production of sulphide. The presence of decreased concentrations of sulphate and increased concentrations of sulphide relative to background concentrations indicates that hydrocarbon biodegradation may be a result of sulphate reduction. By knowing the volume of contaminated groundwater, the background sulphate concentration and the concentration of sulphate measured in the contaminated area, the mass of BTEX lost to biodegradation through sulphate reduction can be calculated.

The following equation describes the overall stoichiometry of benzene oxidation by sulphate reduction to carbon dioxide, sulphide and water under anaerobic biodegradation:



The balanced equation indicates that 3.75 moles of sulphate are required to metabolize one mole of benzene. Thus in the absence of microbial cell production, 1.0 mg/L of sulphate consumed by microbes results in the destruction of approximately 0.21 mg/L of benzene or BTEX compounds.

### Carbon Dioxide

As noted in the above reaction equations, metabolic processes operating during biodegradation lead to the production of carbon dioxide. The electron acceptor (e.g. nitrate) plus hydrogen and carbon source (e.g. benzene) results in the production of an oxidized chemical (nitrite) plus carbon dioxide and water. Carbon dioxide is typically measured in the field. However, accurate measurements of carbon dioxide are difficult because carbonate in the groundwater (measured as alkalinity) serves as both a source of and sink for carbon dioxide. In the absence of carbon dioxide data, the spatial distribution of alkalinity can serve as an indicator of biodegradation. With the production of carbon dioxide in the impacted area, alkalinity levels should increase based on the production of carbon dioxide gas (which acts as a mild acid) followed by a decrease due to carbonate buffering.

### Methanogenesis

During methanogenesis, carbon dioxide is used as an electron acceptor, and methane is produced. The presence of methane in groundwater is indicative of

strongly reducing conditions and occurs after oxygen, nitrate, iron and sulphate have been depleted in the treatment zone. The degradation of 1 mg/L of BTEX results in the production of approximately 0.78 mg/L of methane. Methanogenesis is not a favoured reaction in the anaerobic environment, because its spatial distribution in the treatment zone of the groundwater plume is somewhat limited and it will proceed only when all other electron acceptors have been depleted.

### SUMMARY

Intrinsic bioremediation is the degradation of organic compounds by indigenous microbes without artificial enhancement. Advection, dispersion, sorption, and decay contribute to the overall attenuation and can affect the configuration of dissolved hydrocarbon plumes.

Overall attenuation can cause a plume to shrink over time, create a stable plume, or reduce the rate of plume migration (Buscheck and Alcantar, 1995). Two of the conditions for which intrinsic bioremediation is likely to contribute to the configuration of a contaminant plume are a shrinking plume and a stable plume. The configuration of a migrating plume can also be affected by intrinsic bioremediation. Under the conditions of a shrinking plume, degradation mechanisms are necessarily present. Intrinsic bioremediation is also likely to contribute to a stable plume, particularly if the source persists in residually contaminated soils at the water table.

### SOURCES

Buschek, T.E. and C.M. Alcantar (1995). *Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation..* In R.E. Hinchee, J.T. Wilson and D.C. Downey (Eds.), *Intrinsic Bioremediation*, pp. 109-116. Batelle Press, Columbia, Ohio.

Chiang, C.Y., Salanitro, J.P., Chai, E.Y., Colthart, J.D. and C.L. Klein (1989). *Aerobic biodegradation of benzene, toluene and xylenes in a sandy aquifer - data analysis and computer modelling*. Groundwater, Vol. 27, No. 6, pp. 823-834.

Freeze, R.A. and J.A. Cherry (1979). *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NY, p. 604.

Karickhoff, S.W., Brown, D.S. and T.A. Scott

(1979). *Sorption of hydrophobic pollutants on natural sediments and soils*. Water Resources Research, Vol. 13, pp. 241-248.

Wiedemeier, T., Wilson, J.T., Kampbell, D.H., Miller, R.N. and J.E. Hansen (1995). *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring of Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Volume 1)*, U.S. Air Force Centre for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, TX.

For further information please contact:

Environment Canada  
Ontario Region - Environmental Protection Branch  
Environmental Contaminants &  
Nuclear Programs Division  
4905 Dufferin Street  
Downsview, ON M3H 5T4  
Telephone: (416) 739-4826  
Fax: (416) 739-4405

Our TABs can be found on the Internet at:

<http://www.on.ec.gc.ca/pollution/ecnpd/>