

Natural Attenuation of Contaminated Soils

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ABSTRACT Natural attenuation is increasing in use as a low cost means of remediating contaminated soil and groundwater. Modelling of contaminant migration plays a key role in evaluating natural attenuation as a remediation option and in ensuring that there will be no adverse impact on humans and the environment. During natural attenuation, the contamination must be characterized thoroughly and monitored through the process. In this paper, attenuation mechanisms for both organic and inorganic contaminants, use of models and protocols, role of monitoring and field case studies will be discussed.

Introduction

According to the US EPA (1999), natural attenuation is the "use of natural processes to contain the spread of the contamination from chemical spills and reduce the concentration and amount of pollutants at contaminated sites". It can also be termed as intrinsic remediation, bioattenuation and intrinsic bioremediation. In this case, the contaminants are left on site and the naturally occurring processes are left to clean up the site. The natural processes include biological degradation, volatilization, dilution, dispersion, dilution of the contaminant and sorption of the contaminant onto the organic matter and clay minerals in the soil. It is mainly used for remediation of the aquifer when the contamination source has been removed but can also be used when the source is still present or if some hot spots are removed.

Although natural attenuation may be used at numerous sites, it rarely can be used as a sole treatment process since non-engineered biodegradation processes are very slow (Mulligan 2001). Long term monitoring is an absolute necessity since there must be no risk to the environment and to humans. Natural attenuation is subject to hydrological changes and can take substantial periods of time. The contaminant plume must not reach humans or aquatic wildlife habitats. Prior to 1994, natural attenuation was not acceptable remediation technique. However by 1996, most U.S. states had adapted policies concerning intrinsic bioremediation and by 1998 the Air Force evaluated it as an option for remediation at most of their petroleum- contaminated sites. The US EPA recognizes natural attenuation for remediation of Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA) and underground storage tank (UST) regulated sites. The site must be properly assessed with the identification of all potential receptors, fuel must be the main contaminants and the source should be removed or made harmless. Long term monitoring must be initiated to ensure protection of human and environmental health.

It has thus become almost routine as the sole remediation process but has also been used in combination with other processes (Brown et al., 1995). Guidelines have been issued by the National Research Council (NRC) for

metal and organic contaminated sites, in addition to others by the ASTM, U.S. Air Force, American Petroleum Institute (API), U.S. Navy, Environmental Protection Agency (EPA) and various states and provinces. Although many protocols exist, agreement on the requirements for evaluating and monitoring natural attenuation has not been achieved. Which parameters that must be monitored and the frequency and location of data collection are aspects of the protocols that need to be standardized.

Natural attenuation is mainly used for benzene, toluene, ethylbenzene and xylene (BTEX) and more recently for chlorinated hydrocarbons. Other contaminants that could potentially be remediated by natural attenuation include pesticides and inorganic compounds. The success of natural attenuation depends on the subsurface geology, hydrology and microbiology. In this paper we will examine the models and protocols used and case studies of natural attenuation of various pollutants at contaminated sites.

Transport and fate of contaminants

An important factor in successful development of transport prediction models (TPMs) is its ability to represent the many interacting relationships which govern transport of pollutants in the soil-water system. Fig. 1 illustrates the requirements for development and applications of TPMs. One of the most utilized groundwater flow models in the last 15 years is MODFLOW which has undergone many revisions and upgrades (McDonald and Harbaugh 1988).

The focus on TPMs is in the direction of the capability of the TPMs to fully accommodate or account for the phenomena (results) resulting from the various interactions between pollutants and soil fractions. It is not always clear whether: (a) the various processes contributing to the physical environment, such as those represented in Fig. 2 have been properly recognized, and (b) the various driving forces responsible have been incorporated in the models.

Prediction of the transport of pollutants, represented for example by pollutant plumes such as those represented in Fig. 3, generally rely on analytical models of saturated transport, i.e., transport in fully saturated soil media. Without considering storage, the relationships are most

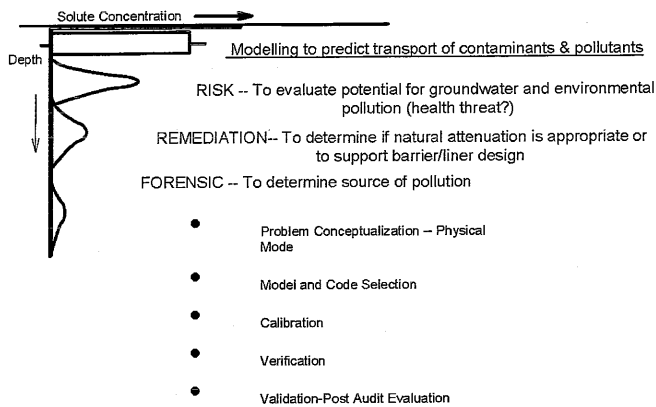


Fig. 1. Purpose and steps in modeling of contaminant transport as a function of distance from initial injection area

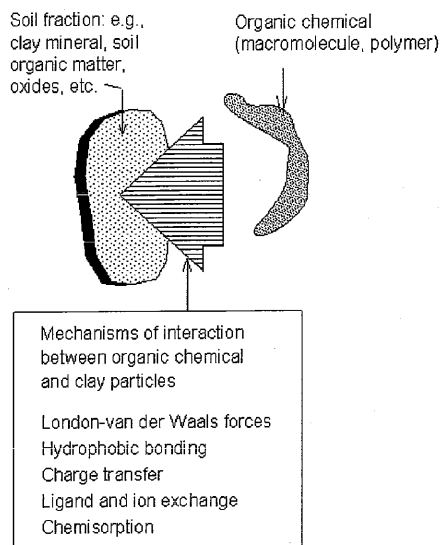


Fig. 2. Soil-contaminant interactions (adapted from Yong 2001)

often in terms of the "advection-diffusion" relationship as shown here:

$$[1] \quad \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\rho}{n\rho_w} \frac{\partial c^*}{\partial t}$$

where: c = concentration of contaminant of concern, t = time, D_L = diffusion-dispersion coefficient (most often called 'diffusion' coefficient), v = advective velocity, x = spatial coordinate, ρ = bulk density of soil media, ρ_w = density of water, n = porosity of soil media, and c^* = concentration of contaminants adsorbed by soil fractions. Note that for the purpose of discussion, we will use the more general term *contaminants* to include both non pollutants and pollutants. Also, note that this equation is sometimes erroneously called the advection-dispersion relationship. However, as the Peclet number becomes less than 1 (Perkins and Johnston (1963), diffusion of the contaminant dominates

over advective flow. The c^* term in eqn.1 is of particular interest since this is the parameter involved in the partitioning of contaminants between the soil fractions and pore fluid. Little information can be obtained about the transfer process of contaminants from the fluid phase onto the soil solids. Batch equilibrium isotherms do not provide information to distinguish between attenuation and retardation mechanisms responsible for partitioning but are used to determine k_d .

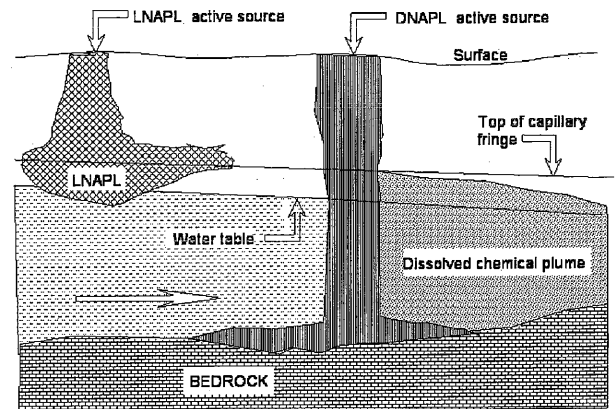


Fig. 3. Representation of contaminant plumes by LNAPL and DNAPL contamination

Processes involved in natural attenuation

Abiotic processes

Adsorption reactions or processes involving organic chemicals and soil fractions are governed by: (a) the surface properties of the soil fractions, (b) the chemistry of the porewater, and (c) the chemical and physical-chemical properties of the pollutants. In general, organic chemical compounds develop mechanisms of interactions which are somewhat different from those given previously for inorganic contaminants. If the transport of organic chemicals in soils is considered, interactions between the contaminant and soil surfaces are important in predicting the retention capacity of the soil and the bioavailability of the contaminant. (We define *bioavailability* as the degree to which a pollutant is available for biologically mediated transformations.) The interaction mechanisms are influenced by soil fractions, the type of and size of the organic molecule, and the presence of water. As in the case of inorganic contaminant-soil interaction, the existence of surface active fractions in the soil such as soil organic matter (SOM), amorphous non-crystalline materials and clays, can significantly enhance oil retention in soils significantly because of large surface areas, high surface charges and surface characteristics.

Interactions at the intermolecular level contribute directly to the mechanisms for "binding" organic chemicals to soil fractions (Yong 2001). They can be physically, chemically, or exchange-motivated. The basic sets of forces, reactions and processes which constitute the major sets of interactions include:

- London-van der Waals forces
- Hydrophobic reactions

- Hydrogen bonding and charge transfer
- Ligand and ion exchanges
- Chemisorption

Volatilization may be an important attenuation for volatile organic contaminants in subsurface as a free product, in the groundwater and in the vadose zone as seen in the later case studies. Freshly spilled petroleum products such as gasoline can exhibit high rates of volatilization. Volatilization can occur from the free phase or dissolved phase. Henry's constant law describes volatilization from the dissolved phase. The rate of volatilization slows as the age of the spill increases. As a general guideline, a dimensionless Henry's constant greater than 0.05 means that volatilization or off-gassing is likely while if it is less than 0.05, volatilization would be negligible.

The distribution of organic chemical pollutants between soil fractions and porewater is generally known as *partitioning*. By this, we mean that the chemical pollutants are partitioned such that a portion of the pollutants in the porewater (aqueous phase) is removed from the aqueous phase. We have seen from the study of partitioning of heavy metals, that this assumption of sorption by the soil fractions may not be totally valid. This is because precipitation of the heavy metals will also serve to remove the heavy metals from solution. Since we do not have equivalent precipitation mechanisms for organic chemical pollutants, it is generally assumed that the total "partitioned" organic chemicals are sorbed or attached to the soil solids. The partitioning or distribution of the organic chemical pollutants is described by a coefficient identified as k_d . As defined previously, this coefficient refers to the ratio of the concentration of pollutants "held" by the soil fractions to the concentration of pollutants "remaining" in the porewater (aqueous phase), i.e. $C_s = k_d C_w$, where C_s refers to concentration of the organic pollutants sorbed by the soil fractions and C_w refers to the concentration remaining in the aqueous phase (porewater) respectively.

The abiotic reactions and transformations are sensitive to at least two factors: (a) the physico-chemical properties of the pollutant itself, and (b) the physico-chemical properties of the soil (i.e. soil fractions comprising the soil). Similar to inorganic contaminants, abiotic chemical reactions with organic compounds occur and include (a) hydrolysis, (b) formation of a double bond by removal of adjacent groups and (c) oxidation/reduction, dehydrohalogenation or hydrolysis reactions.

Chemical mass transfer is responsible for partitioning of contaminants in the fate and transport of contaminants. Reduction-oxidation reactions can also play an important role in the fate of the contaminants. Assessment of retention or retardation processes are responsible for partitioning and the attenuation of contaminants within the soil. If potential pollution hazards and threats to public health and the environment are to be minimized or avoided, we must ensure that the processes for contaminant attenuation are irreversible or below the levels of contaminants are below allowable limits or levels.

The linear constant k_d , partition coefficient, used in the retardation coefficient R implies that adsorption by the soil fractions is infinite. As the concentration of contaminants increases, the sorption also increases. The relationship cannot be linear since a maximum level must be defined. Non-linear adsorption isotherms are more representative of field situations and should be used (Fig. 4).

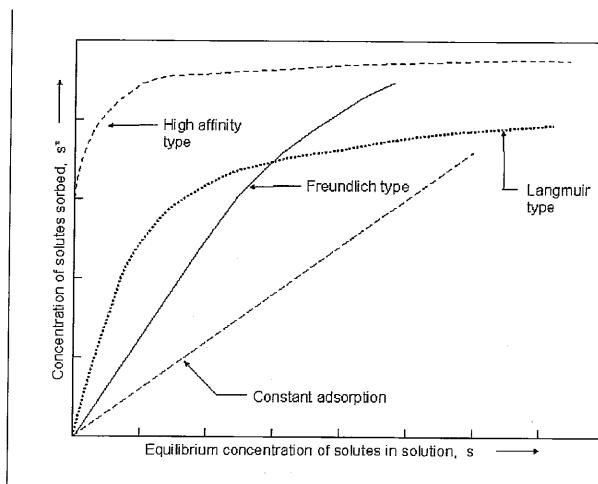


Fig. 4. Types of adsorption isotherms

Biotic processes

Understanding the types of chemicals that can be biodegraded or transformed, and the pathways of conversion is important and will be discussed, as well as the toxicity and availability of several chemicals since this will serve as the foundation of knowledge required for determining the potential for natural attenuation. These concepts are described in further detail in Yong and Mulligan (2003).

Microorganisms, the key to the biological treatment of contaminants, include bacteria, protozoa, fungi, algae and viruses (Mulligan 2002). Microbes are smaller than plant and animal cells and are divided into two groups depending on their cell structures: prokaryotes (simple, single cells less than 5 microns) and eukaryotes (single or more complex multi-cells which are greater than 20 microns). Prokaryotes have a nuclear region not encompassed in a membrane with only a single strand of deoxyribonucleic acid (DNA), whereas eukaryotes have a nucleus surrounded by a membrane containing DNA molecules. Eukaryotes are subdivided into unicellular organisms that have multipurpose cells and multicellular organisms (plants and animals) with special-purpose cells.

A wide variety of hydrocarbons can be degraded by microorganisms through electron transfer by various mechanisms. Most of the knowledge related to natural attenuation is related to the degradation of BTEX compounds. Table 1 indicates the likelihood and understanding of the natural attenuation of various inorganic contaminants. The availability of oxygen and other electron acceptors such as nitrate, sulfate and iron (III) determine the rate of biodegradation. Other factors include the presence of water, and mineral nutrients. Although the rate of aerobic biodegradation is higher than anaerobic, the latter type may be more dominant. Products of aerobic degradation are carbon dioxide and water while the products of anaerobic degradation include carbon dioxide, water, methane, hydrogen, nitrogen and others.

A variety of other products from bacteria can also influence the desorption of hydrocarbons and metals from the soil. Due to their anionic and hydrophilic/hydrophobic nature, biodegradable surfactants including rhamnolipids, surfactin, and sophorolipids, by-products of bacteria or yeast, have been able to remove metals and hydrocarbons

from an oil-contaminated soil by disruption of the pollutant/soil bonds (Mulligan et al. 1999). Other biological products such as organic acids produced by fungi can also chelate and remove metals from soils or mining residues (Mulligan and Galvez-Cloutier 2000).

Table 1. Likelihood of inorganic contaminant bioconversion (adapted from Yong and Mulligan 2003)

Contaminant	Transformation	Level of understanding
Copper, nickel, zinc	Immobilization by sorption	Moderate
Cadmium, lead	Immobilization, possible methylation	Moderate
Iron, manganese	Increase in mobility by reduction, immobilization by precipitation and sorption	Moderate
Chromium	Immobilization by precipitation	Moderate
Mercury	Volatilization, immobilization by precipitation and sorption	Low
Arsenic	Volatilization or immobilization by precipitation or sorption	Low
Selenium	Volatilization or immobilization by precipitation or sorption	Low
Nitrate	Conversion to nitrogen	Low
Perchlorate	Reduction to chloride	Low
Uranium	Immobilization by precipitation	Low
Plutonium	Increased mobility by reduction, immobilization by precipitation and sorption	Low
Technetium	Immobilization by precipitation	Low

Modeling of natural attenuation

Models are used to predict the fate and transport of contaminants for evaluating natural attenuation and determining if and when receptors will be impacted. Models can also be used to determine the effects of source removal or reduction, pump and treat and the use of barriers and their effect on natural attenuation. Models can

either predict plume length without calibration or for fitting the observed data to the model by calibration by inputting data. Risk based corrective action programs used models without calibration whereas the Air Force Natural Attenuation Initiative is based on the second approach and the modeling results are used as lines of evidence.

Both analytical and numerical models are used to simulate the conditions at a contaminated site. Analytical models provide exact solutions, while numerical models provide approximate solutions and are more applicable of a wide range on hydrogeological conditions. Many processes must be approximated for analytical models. The heterogeneity of the subsurface can lead to over or underestimation of contaminant movement. Decisions concerning which model to use should be based on available data, the complexity of the site and the accuracy of the information required. Assumptions within each of the models must be known to understand their limitations.

Analytical models are used to simulate advection, biodegradation, dispersion and sorption in one, two or three dimensions as shown in Table 2.

Table 2. Common analytical models for fate and transport

Processes simulated	Description	References
Advection, dispersion, linear sorption	Semi-infinite solute transport with continuous or decaying source, first order biodegradation	Bear 1972, van Genuchten and Alves 1982, Wexler 1992, Wilson and Miller 1978
with constant or decaying source	decay, concentration over time and distance in one, two or three dimensions	Domenico 1987

Various packages are available for predictive modeling of natural attenuation. Bioscreen was developed for the Air Forces Centre for Environmental Excellence by Groundwater Services Inc. (Houston, TX) is used to simulate the natural attenuation from petroleum fuel releases. The Domenico analytical transport model is the basis for the model which is in a Microsoft Excel format. Attenuation processes for the soluble hydrocarbons include advection, dispersion, adsorption, in addition aerobic and anaerobic degradation.

Biochlor is a model that simulates the natural attenuation of chlorinated solvents. Reductive dechlorination of chlorinated ethenes to ethenes and chlorinated ethanes to ethanes is included in sequential steps. Like Bioscreen, advection, dispersion and adsorption are incorporated. Both this software and Bioscreen are available from the USEPA's Centre for Subsurface Modeling Support Internet Site and is found at www.gis-net.com.

One of the major drawbacks of using models such as Bioscreen is that a first order decay coefficient is used to calibrate the models (Odenratz et al. 2002). coefficient is adjusted until it coincides with field analyses. All information regarding dispersion, sorption and biodegradation are all represented as one parameter. This can lead to tremendous inaccuracies if calibrations and validation are not done properly. The model can be found at www.epa.gov/ada/bioscreen.html.

The BIOPLUME III model (Rifai et al. 1997) is two-dimensional and simulates the natural attenuation by taking into account advection, dispersion, ion exchange and biodegradation. Both aerobic and anaerobic electron acceptors are included. The U.S Geological Survey (USGS) formed the basis of the model in 1989. (Konikow and Bredehoeft 1989). It is mainly for groundwater flow and transport. Biodegradation reactions can be simulated by instantaneous degradation, first-order decay, and Monod kinetics. Electron acceptors include oxygen, nitrate, iron, sulfate and carbon dioxide. One of the main limitations is that components such as BTEX are treated as one component not as individual ones. This is particularly problematic since benzene and toluene are more biodegradable than xylene. Other models are described and analysed in Yong and Mulligan (2003).

Evidence of natural attenuation

To prove that natural attenuation is taking place, lines of evidence are established to indicate decreases in contaminant concentrations. They include:

- Decreases in contaminant concentration and/or plume size over time. This is used to indicate that biodegradation is occurring faster than the increase plume size.
- Chemical indicators of microbiological activity in the groundwater chemistry such as consumption of oxygen, nitrate, and sulfate and production of Fe(II), Mn(II) and methane.
- Laboratory microcosm studies are used to simulate aquifer conditions to determine if bacteria at the site can biodegrade the contaminants and at what rate. This step is mainly used if neither of the first two clearly indicate significant trends.

Various technical protocols have been established such as the Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater by the Air Force Centre for Environmental Excellence (Weidemeier et al. 1995).

Case studies

Although many case studies of natural attenuation in groundwater have been performed, there are considerably fewer that have taken place in the soil. In this section, some applications of natural attenuation in the soil will be described.

After contamination of the groundwater by trichloroethylene (TCE) at the U.S. Department of Energy Savannah River Site, SC, a study was performed to determine if natural attenuation of TCE in rhizosphere soils was occurring (Brigmon et al. 1998). Microcosms tests were designed for the evaluation of abiotic and biotic attenuation. Sorption of the TCE from the water onto the soil was a major mechanism, removing up to 90% of the TCE from the water. Linear partitioning coefficients, K_d , were determined to be from 0.83 to 7.4 mL/g and organic carbon partitioning (K_{oc}) were from 72 to 180 mL/g of

carbon. Diffusion also played a significant role in the attenuation process. Only small amounts of TCE was biodegraded (less than 5%). The main biological mechanism was anaerobic reductive dechlorination as indicated by the presence of the by-products, cis-1,2-dichloroethylene (c-DCE) and trans-1,2-dichloroethylene (t-DCE). Addition of methane, oxygen and methanol did not enhance biodegradation. Therefore, sorption was the principal attenuating mechanism in this case.

The natural attenuation of polychlorinated biphenyls and chlorinated ethenes was investigated at three sites (Katanek et al. 1999). The individual PCB congeners composition seemed to vary over the period of 20 years which indicated that some biodegradation of the lighter congeners occurred in the oxygenated surficial soil layers. Anaerobic dechlorination could also have occurred. Abiotic mechanisms such as volatilization or solubilization in to the groundwater can also contribute to the natural attenuation of the lighter PCBs. In the field, it is quite difficult to demonstrate PCB natural attenuation. PCBs with fewer chlorines can completely biodegrade. In this study PCBs with low number of chlorines decreased more than the PCBs with a high content of chlorines. In sediments, reductive dechlorination of PCBs has been shown to occur (Sokol et al. 1994). Mechanisms for natural attenuation must be further investigated for PCBs.

A study was also performed at an alpine skiing area (2,875 m above sea level) for the natural attenuation and biostimulation of diesel-contaminated soil (2,600 mg diesel fuel/kg) by field incubated lysometers (Margesin and Schinner 2001). Hydrocarbon contents were followed in both the soil and leachate for three summers (July to September). After three summers, hydrocarbon levels decreased by 50% and 70%, in the non-fertilized and fertilized soils, respectively. Levels were still 1,296 mg/kg and 774 mg/kg after this time. Therefore, significant reduction in diesel fuel concentrations could be achieved even at extreme conditions. Rates slowed significantly in the third summer. Abiotic processes such as volatilization could have played a significant role in the non-fertilized soil.

The leaching and natural attenuation of irrigation water and kerosene has been examined in field experiments by Dror et al. (2001) over a 39 day period. Volatilization of many components was immediate, while transport was minimal. When the soil moisture was high, volatilization of low vapor pressure compounds was substantial since infiltration to deeper soil layers was delayed. The heavier compounds remained in the upper layers of the soil.

Few studies have been performed on the natural attenuation in clays. Berry and Burton (1997) examined the natural attenuation of diesel fuel (5,000 mg/kg) in a heavy clay soil. The postulated that since the hydraulic conductivity is low, this would lead to anaerobic conditions, even near the soil surface which could inhibit biodegradation. On the other hand, migration of the diesel to the groundwater would be slowed, particularly due to clay soil swelling. The field test was carried out 10 km south of Winnipeg, MB. The clay mineral was mainly montmorillonite. Using the extractable organic method (EPA 3520B and EPA 8000A) they determined that complete attenuation occurred with 74 days. Another method called the enzyme-linked immunosorbent assay (ELISA) was used and showed that the hydrocarbon degradation was near complete. The mechanism of attenuation cannot be determined, however, since only disappearance is indicated not biological transformation to

other by-products. Levels of hydrocarbons were also low, indicating insignificant amounts of contaminant migration.

Some investigations were performed concerning the natural attenuation of uranium in a tailings disposal site by Abdelous et al. (1998 and 2000). Chemical investigations indicated that the uranium did not significantly adsorb on the surface of the sandstone minerals due to the negative charge of Abdelous et al. (1998). The carbonate formed was the dominant form. Biological reactions to precipitate U(VI) by conversion to U(IV) are also possible by sulfate-reducing bacteria and warrant further investigations (Abdelous et al. (2000).

Combination of natural attenuation and other processes

Natural attenuation alone may not be sufficient for the remediation of contaminated sites in a reasonable time frame. In this case, natural attenuation can be combined with engineered processes to reduce risk and enhance remediation rates. Source reduction or oxygen addition are methods of enhancing natural attenuation. Source reduction technologies include free product removal, soil vapor extraction, bioventing, and bioslurping. Oxygen can be achieved by biosparging, and the addition of oxygen releasing compounds. These processes are described in more detail in Mulligan (2002).

Recently, a field test was conducted where sodium lactate, an electron donor in many biochemical reactions, was injected into the groundwater to enhance biodegradation of trichloroethene (TCE). Initially, 1135 L of lactate were injected weekly. After 5 weeks concentrations of 3800 µg/L of TCE dropped to 10 µg/L. The injection program began in 1998 and currently 5000 L of lactate are injected every two months (Strzelecki 2002).

A similar approach is utilized by using hydrogen release compound (HRC, Regenesis, San Clemente, CA) addition. After injection into the groundwater, lactic acid is slow released and hydrogen gas is produced by the bacteria. The hydrogen serves as an electron donor for chlorinated hydrocarbon and nitroaromatic compounds. At an Army Chemical Depot in Texas, heavy metal, and VOC contamination of groundwater and soil occurred from the 1940s to 1974 (Koenigsberg and Vigue 2002). Explosives were discharged and contaminated the upper aquifer with 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), hexahydro-1,3,5-triazine (RDX), 1,3,5 trinitrobenzene (1,3,5-TNB) and nitrate. As the TNT naturally degraded but the other products did not, HRC addition at 30 places was chosen to enhance the biodegradation. Monitoring was done at 15 wells. 2,4-DNT and 1,3,5 TNB are by-products of TNT. 105 days after injection showed significant reduction of all by-products: 72 to 98% for 2,4-DNT, 45 to 99% for RDX, 86 to 100% for 1,3,5-TNB and 52 to 94% for nitrate.

Conclusions

There are various advantages to natural attenuation including:

- Possibility of destroying the contaminant completely

- Remediation method that is potentially more acceptable to the public than other remediation technologies
- Can be used with other methods as a pre- or post treatment at a site.
- Can potentially reduce remediation costs significantly.

Potential disadvantages are:

- Longer remediation times compared to other technologies
- Lack of knowledge concerning mechanisms for remediation particularly with regard to inorganic contaminants
- Substantial requirements for monitoring
- By-products can be more environmental hazardous than the parent compounds.
- Desorption or resolubilization of contaminants can occur
- Public acceptance is slow
- Modeling data has to be evaluated with caution and may be subject to significant uncertainty.

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