NATURAL ATTENUATION
OF ORGANIC COMPOUNDS

The natural attenuation of organic compounds, particularly fuels and chlorinated solvents, has been subject to study for some time. The basic physical processes which, unaided by deliberate human intervention, reduce the concentration, toxicity, or mobility of such contaminants, are fairly well understood. However, techniques for predicting and monitoring natural attenuation are still in their infancy.

The mechanisms of natural attenuation can be classified as **destructive** and **non-destructive**. Destructive processes include **biodegradation** and **hydrolysis**. Biodegradation is by far the most prevalent destructive mechanism. Non-destructive attenuation mechanisms include **sorption, dispersion, dilution,** and **volatilization.** Dilution and dispersion are generally the most important non-destructive mechanisms.

Fuels and chlorinated solvents are organic compounds. That is, each molecule contains one or more carbon atom. Petroleum-based fuels not only contain molecules made up of hydrogen and carbon, but they generally contain benzene, toluene, ethyl benzene and xylene, known collectively as BTEX. These compounds, also made of carbon and hydrogen, are highly toxic. Chlorinated solvents, which are volatile organic compounds (VOCs), consist of molecules containing chlorine, carbon, and other elements, and they too are hazardous.

Degradation

Biodegradation, also called bioremediation, is a process in which naturally occurring microorganisms, such as yeast, fungi, and bacteria, break down target substances, such as fuels and chlorinated solvents, into less toxic or non-toxic substances. Like larger living things, these microbes must eat organic substances to survive. Certain microorganisms digest fuels or chlorinated solvents found in the subsurface environment.

The ability of microorganisms to metabolize, or use nutrients depends on the chemical composition of the environment, and different microorganisms have evolved to take advantage of varying conditions. In most organisms, including bacteria, the metabolic process requires the exchange of oxygen and carbon. Biodegradation can occur in the presence of oxygen (**aerobic** conditions) or without oxygen (**anaerobic** conditions).

In general, there are three biodegradation processes: 1) when the contaminant is used by the microbe as the primary food source; 2) when the contaminant is used to transfer energy; and 3) (called **cometabolism**) when biodegradation occurs in response to a chance reaction between the contaminant and an enzyme produced during an unrelated reaction. For fuel hydrocarbons containing BTEX, the first

process is dominant. The full degradation of chlorinated solvent plumes usually requires all three processes.

1. <u>The contaminant is used as the primary food source (or substrate).</u> In the presence of oxygen, bacteria are able to use the carbon found in contaminants as their primary food source. This relatively rapid process has greater potential for fuels and those chlorinated solvents with fewer chlorine atoms per molecule, such as vinyl chloride, which has just one. Substances with more chlorine, such as perchloroethene (PCE)-with four chlorine atoms-are less susceptible to this type of biodegradation.

   In addition, sometimes even in the absence of oxygen, microorganisms use contaminants as their primary food supply. This form of degradation, under anaerobic conditions, depends not only upon the compound, but the temperature, pH, and salinity of the subsurface. In breaking down chlorinated solvents, bacteria use nitrate, iron, sulfate, and carbon dioxide to help metabolize the carbon in the contaminant molecule. If degradation is complete, the byproducts are usually carbon dioxide, water, and chlorine.

   For fuels containing BTEX, as the oxygen is used up during degradation, other microorganisms use nitrate, manganese, iron, sulfate, and carbon dioxide to help complete the process. In this type of reaction, the byproducts are usually carbon dioxide and water.

2. <u>The compound is used as an electron acceptor to aid respiration.</u> All living things respire. That is, they use organic substances and other nutrients by breaking them down into simpler products. In the absence of oxygen, microorganisms often use chlorinated compounds to aid in respiration, not as a source of food. This is done through an electron transfer process. In the case where the carbon in the contaminant is the food source, the contaminant is an electron donor. In the case where food is obtained from another source, the contaminant sometimes aids this transfer by accepting electrons that are shed through respiration.

   The most common anaerobic process for degrading chlorinated compounds is an electron transfer process called **reductive dechlorination.** In this process, hydrogen atoms are sequentially substituted for a chlorine atom in the contaminant molecules. Perchloroethene (PCE) turns to trichloroethene (TCE), TCE to dichloroethene (DCE), DCE to vinyl chloride, and vinyl chloride to ethene. However, vinyl chloride resists reductive dechlorination. Once it is formed, the process may change, with vinyl chloride becoming the primary food source for different bacteria -- as in process 1 above. The major

requirement for reductive dechlorination is the presence of other organic compounds, such as fuels, that can serve as the food source.

3. <u>Cometabolism.</u> When a chlorinated solvent is biodegraded through cometabolism, it does not serve as a primary food source or an electron acceptor. Cometabolism is the process in which biodegradation takes place as a result of a secondary reaction, initiated, for example, by enzymes produced by the metabolism of methane. Cometabolism has only been documented under aerobic conditions.

   Chemical reactions, in which substances are broken down without the help of living organisms, are dwarfed by the effects of biological reactions. Still, contaminants may react directly with compounds in the soil or groundwater. The major chemical degradation process is **hydrolysis**. Hydrolysis is a chemical substitution reaction in which hydrogen ions in water react with organic molecules, replacing the chlorine atoms. However, unlike reductive chlorination (see above), living organisms play no part in the reactions. The amount of clay in the soil and its pH also influence these reactions. When trichloroethane (TCA) is present, it may be dechlorinated to dichloroethane (DCA) and then to vinyl chloride. The byproducts of hydrolysis are acids and alcohols. Because these byproducts biodegrade easily, hydrolysis is difficult to measure.

Non-Destructive Mechanisms

There are four principal non-destructive mechanisms that cause a decrease in measurable contaminant concentrations.

1. <u>Dispersion</u> is the spreading of a chemical in groundwater outward from its expected path. As groundwater moves through different soil types and geological features, it travels at different velocities. This creates mechanical mixing, so groundwater spreads away from source areas into wider plumes. Dispersion rates depend on differences in soil types as well as the size and shape of subsurface materials. This effect occurs naturally in most groundwater flow systems.
2. <u>Dilution</u> is simply a decrease in the chemical concentration in a fluid caused by mixing with a fluid containing a lower concentration. Dilution is an effect of dispersion, and it also takes place in most groundwater flow systems.
3. <u>Sorption</u> occurs when contaminants attach to soil particles. This occurs in large part because they either dissolve into the organic matter in the soil or are attracted by electrical charge. Sorption may also occur in groundwater, as dissolved chemicals are removed from the solution. Sorption capacity is determined by factors such as soil particle size, the amount of organic material in the soil, and the pH and temperature of the soil. However, chemicals can also desorb from the soil and enter the groundwater or volatilize. Environmental conditions that may cause desorption include changes in

temperature or pH; changes in the concentration of contaminants coming into contact with the sorbed material; and changes in the chemical make-up of the groundwater.

4. <u>Volatilization</u> occurs when dissolved chemicals change from a liquid phase to the gaseous phase. For example, when water evaporates, it changes from a liquid to a vapor. In general, factors affecting volatilization from groundwater include concentration, change in concentration with depth, and temperature. Different chemicals have different propensities to volatilize. Volatilization is usually a minor element in natural attenuation.

Predicting Natural Attenuation

By definition, natural attenuation processes occur without intervention. The key question, for responsible parties, regulators, and the public, is to what degree those processes are likely to contribute to the achievement of remedial action goals. In considering monitored natural attenuation as a remedy, it's necessary to evaluate the potential for biodegradation, chemical degradation, dispersion, dilution, sorption, and volatilization.

The evaluation of natural attenuation requires expertise in several technical areas including microbiology/bioremediation, hydrogeology, and geochemistry. The extent of contaminant degradation depends on a variety of parameters, such as contaminant types and concentrations, temperature, moisture, and the availability of nutrients and other compounds that influence the metabolism of microorganisms. Some studies suggest that high contaminant concentrations are lethal to microbes, and thus source removal of any free product is recommended. According to those studies, natural attenuation is not effective for fuel plumes when levels in soil exceed 20,000 parts per million. Information to be obtained during data review includes:

1. Distribution, as well as chemical and physical characteristics, of the contaminants.
2. Geochemical data, including pH, temperature, dissolved oxygen, nitrate, sulfate, methane, total organic carbon, iron, and degradation byproducts.
3. Hydrogeological data, including stratigraphy (i.e., the composition and sequence of rock strata), grain-size distribution (e.g., sand vs. silt vs. clay), groundwater flow gradients, preferential flow paths, and data on the interaction between groundwater and surface water.
4. Location of potential receptors (e.g., humans and animals), groundwater wells, and surface water discharge points.

There are generally three lines of evidence that are used to support natural attenuation as a remedy. The first attempts to demonstrate attenuation through historical documentation of decreasing contaminant concentrations, in conjunction with hydrogeological information. The second uses chemical analysis to determine not only to what degree degradation is responsible for those decreased contaminant concentrations, but whether there is a sufficient supply of nutrients and other

compounds to continue the process. This line of evidence can be used to show that conditions are sufficient for natural attenuation to occur. The third line of evidence requires the extraction of bacteria from the soil to demonstrate, in a laboratory, that the bacteria at the site do indeed destroy the contaminants.

Long-Term Monitoring

Long-term monitoring is necessary to demonstrate that contaminant concentrations continue to decrease at a rate sufficient to ensure that they will not become a health threat or violate regulatory criteria. EPA recommends that monitoring be designed to accomplish the following:

- Identify potentially toxic transformation products.
- Determine if the plume is expanding either laterally and vertically.
- Ensure that there is no effect on downstream receptors.
- Detect any new releases that could effect the remedy.
- Detect changes in hydrogeological, geochemical, or microbiological parameters that might reduce the effectiveness of natural attenuation.

EPA also recommends that monitoring continue as long as contamination remains above required cleanup levels, and for two to three years after attainment of cleanup levels to ensure that the plume is stable.

While the number of sampling points -- monitoring wells, for example -- required for any particular purpose is site-specific, greater certainty is generally achieved with the installation of more wells over larger areas, with samples taken at a greater variety of depths. More frequent sampling, as well as monitoring over longer time periods, also leads to more reliable conclusions. However, since additional monitoring costs money, natural attenuation becomes less attractive as a remedial option when regulators or others insist on more certain measurement of the results.

Hazardous Transformation Products

Sometimes compounds degrade into byproducts that are as toxic, or even more hazardous, then the original contaminants. For example, the reductive chlorination of PCE and TCE creates vinyl chloride, a confirmed carcinogen for which drinking water standards are typically ten times as stringent as the parent compounds. Though benzene, toluene, ethyl benzene and xylene are initially considered the most toxic compounds in petroleum-based fuels, a residue of heavier, potentially hazardous petroleum hydrocarbons may remain following BTEX degradation.

Other Contaminants

Though cleanup documents often focus on a "contaminant of concern," most subsurface contamination plumes contain a mix of chemicals resulting from a variety of operations and disposal activities. Even if BTEX or chlorinated solvents attenuate naturally, other contaminants may be resistant to natural processes.

For example, the gasoline additive methyl tertiary butyl ether (MTBE), which has been found in a large number of fuel-contamination plumes, is both resistant to biodegradation and more mobile than BTEX. A study of thirty MTBE sites indicated that on average the MTBE plume was 1.5 to 2.0 times further out than the leading edge of the benzene plume. MTBE is classified by U.S. EPA as suspected to cause cancer, and even at low levels it affects the taste and smell of drinking water. Similarly glycol ethers, a family of toxic industrial chemicals, are present in many plumes, but they are rarely named as chemicals of concern. These compounds are difficult to detect; they do not degrade well in anaerobic environments; and they are known to cause reproductive disorders.

Science now gives us a fundamental understanding of the mechanisms of natural attenuation, but we -- hopefully all stakeholders -- still must develop the policies and tools to evaluate when monitored natural attenuation is an acceptable remedy.

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