United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

National Risk Management
Research Laboratory
Ada, OK 74820

EPA/600/F-98/022
May 1999

Monitored Natural Attenuation of Chlorinated Solvents

U.S. EPA REMEDIAL TECHNOLOGY FACT SHEET

Scope of this fact sheet:

This fact sheet explains what "monitored natural attenuation" means when the term is used to describe a potential strategy to remediate a contaminated site. It also describes the various physical, chemical and biological processes of natural attenuation that may occur at a site. This fact sheet is written for an audience with little or no scientific background and is meant to aid Federal, State, and local regulators in educating the public on complex environmental issues. Other informational materials are in preparation and will provide more specific details and scientific depth for the evaluation of monitored natural attenuation as a remedy at specific sites.

What Is Monitored Natural Attenuation?

The term "monitored natural attenuation," as used by the EPA, refers to the reliance on natural processes to achieve site-specific remedial objectives. Where found to be a viable remedy, monitored natural attenuation may be used within the context of a carefully controlled and monitored site cleanup approach. To be considered an acceptable alternative, monitored natural attenuation would be expected to achieve site remedial objectives within a time frame that is reasonable compared to that offered by other more active methods. Monitored natural attenuation is always used in combination with "source control;" that is, removal of the source of the contamination as far as practicable.

Natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water. These processes include biodegradation; dispersion; dilution; sorption; volatilization; and chemical or biological stabilization, transformation, or destruction of contaminants.

Spills and leaks of chlorinated solvents such as perchlorethylene (PCE), trichloroethylene (TCE) and trichloroethane (TCA) have caused widespread contamination in the environment. Generally these contaminants are present both in NAPL form (non-aqueous phase liquid; the bulk liquid chlorinated solvent) and also as dissolved contaminants in the ground water. Cleanup of both the NAPL and dissolved contamination in soils and ground water using many common remedial techniques is often expensive and slow. However, under the proper conditions at some sites, natural attenuation can contribute significantly to remediation of dissolved chlorinated solvent contamination and may accomplish site remediation goals at a lower cost than conventional remediation technologies, within a similar time frame. Natural attenuation is not expected to remediate NAPL.

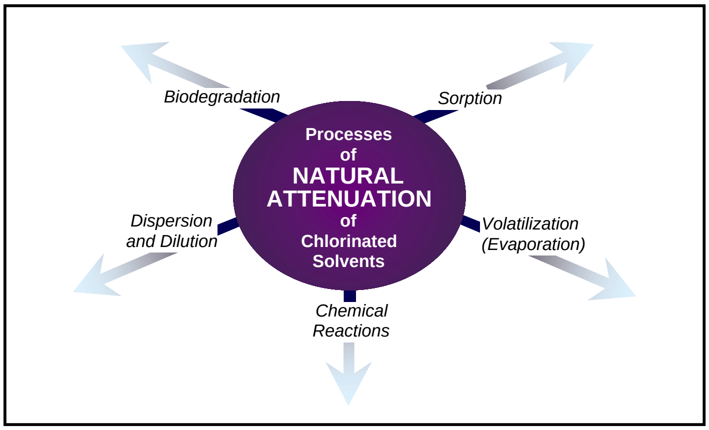

Figure 1. Processes of natural attenuation of chlorinated solvents.

How Does Natural Attenuation Work?

Biodegradation

One of the most important components of natural attenuation is biodegradation—the change in form of compounds carried out by living creatures such as microorganisms. Under the right conditions, microorganisms can cause or assist chemical reactions that change the form of the contaminants so that little or no health risk remains. Biodegradation is important because many chlorinated solvents can be destroyed by biodegradation, microorganisms that are capable of biodegrading contaminants are found almost everywhere, and biodegradation can be very safe and effective. However, most chlorinated solvents biodegrade only under very specific conditions, which are not present at all sites.

Microorganisms are most effective at degrading low to moderate concentrations of contaminants. High concentrations and very low concentrations of contaminants may not be biodegradable. Contaminants in the NAPL phase are not effectively degraded by microorganisms.

As chlorinated solvents biodegrade, the products of the degradation process may or may not be less harmful than the original contaminants. Sometimes chlorinated solvents may degrade to form more toxic compounds, and these toxic compounds may accumulate under certain conditions. Also, under some conditions, the microbial activity involved in degrading the contaminants could cause mobilization of certain materials such as manganese or arsenic which could cause environmental problems. Monitoring for these potential problems is necessary.

Sorption

The soil and sediment particles (sand, silt, clay, organic matter) through which the ground water and dissolved contaminants move can sorb the contaminant molecules onto the particle surfaces, and hold bulk liquids in the pores in and between the particles, thereby slowing or stopping the movement of the contaminants. This process can reduce the likelihood that the contaminants will reach a location (such as a drinking water well or stream) where they would directly affect human or environmental health.

Dispersion and Dilution

As the dissolved contaminants move farther away from the source area, the contaminants are dispersed and diluted to lower and lower concentrations over time. Eventually the contaminant concentrations may be reduced so low that the risk to human and environmental health will be minimal.

Chemical Reactions

Some chlorinated solvents such as TCA can undergo significant degradation by chemical reactions without microbial activity. However, most chlorinated solvents are not significantly degraded by chemical reactions in soil or ground water, though exposure to sunlight can break down many chlorinated solvents. Exposure to sunlight is significant only for chlorinated solvent vapors in the air, or possibly dissolved solvents in surface water or on the soil surface.

Volatilization (Evaporation)

Chlorinated solvents are volatile and readily evaporate into the atmosphere, where air currents disperse the contaminants, reducing the concentration. Also, the solvent vapors may be quickly broken down by sunlight. Vapors in contact with soil microorganisms may be biodegraded. Volatilization from NAPL or ground water to soil gas may be an important exposure pathway in a risk analysis.

Importance of Natural Attenuation Processes

The processes involved in natural attenuation are operating at all contaminated sites, but the contribution of natural attenuation to achieving remediation goals varies in different situations. At some sites natural attenuation may meet all the remedial goals, and at other sites natural attenuation may make little or no contribution. Therefore, before natural attenuation can be selected as a remedial alternative, it is necessary to study each contaminated site carefully to determine how effective natural attenuation is for attaining site remediation goals.

Bulk chlorinated solvents – in the NAPL form, rather than dissolved in water or sorbed on soil particles – are not readily degraded by microorganisms. Also, dispersion, dilution and sorption of the NAPL is slow. Therefore, it is important to determine where this NAPL may be at a polluted site, in order to remove or contain as much of it as possible, because the processes of natural attenuation would not effectively remediate most of this material in a reasonable time

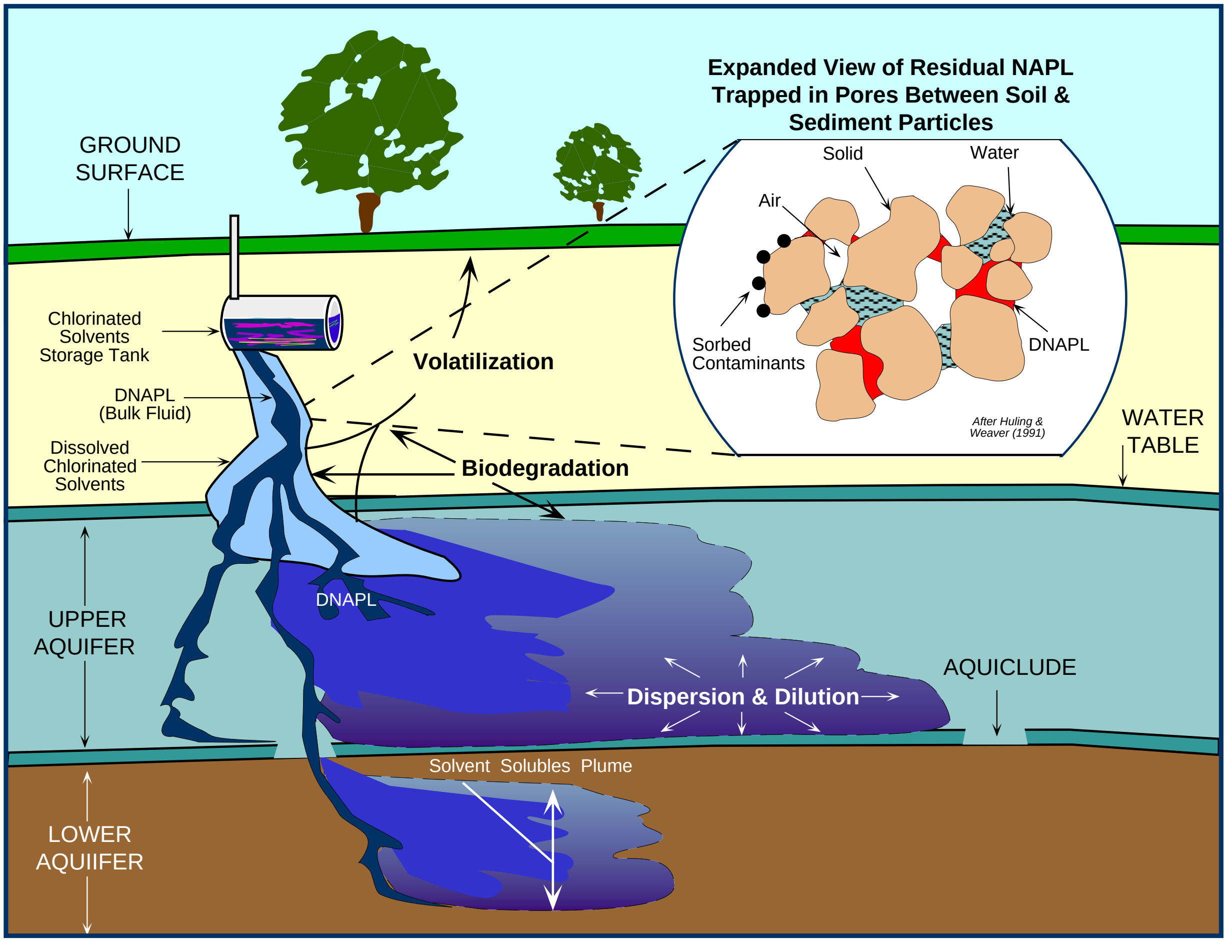

Figure 2. As the bulk chlorinated solvent moves through the subsurface, some of the liquid may be trapped in the soil or sediment pores (residual saturation); some may evaporate (volatilization); some may become sorbed to the surface of the soil particles (sorption) and some may dissolve in the ground water (dissolved plume). Since bulk chlorinated solvents are more dense than water, the liquid tends to move down below the water table. As the dissolved plume moves, the concentration of the dissolved solvents is lowered by dispersion and dilution effects. Microorganisms may degrade hydrocarbons that are dissolved, volatilized or sorbed.

frame. Natural attenuation processes are usually of most significance for the remediation of those contaminants dissolved in water, sorbed on soil particles, or in the vapor form.

How Is Natural Attenuation Evaluated?

In order to decide what contribution natural attenuation can make to meeting site remediation goals, very detailed site investigations must be carried out. Generally, the investment in site characterization for determining the applicability of natural attenuation is at least as expensive and time consuming, if not more so, than for any other site remediation technology. However, the long-term costs for natural attenuation (if natural attenuation is able to achieve most of the site remediation goals) may be less than for other remedial technologies.

In order to properly evaluate natural attenuation at a site, it is necessary to know the location and concentration of the contaminants, and how the contaminants move in the environment. Since contaminants commonly move dissolved in water, the movement of ground water at the site must be carefully investigated to determine how the water moves, when it moves and where it moves. The subsurface is often very complex in terms of water movement pathways, and determination of these pathways can be expensive.

Also, evaluation of natural attenuation processes may require a detailed understanding of the site geochemistry, especially where biodegradation processes are involved. The compounds that may be associated with microbial activity, such as oxygen, carbon dioxide, nitrate, sulfate, iron, etc., should be measured in order to gain understanding of what processes the microorganisms are using, how fast these processes are occurring, and what the results of these processes are likely to be. Biodegradation of many chlorinated solvents takes place under very specific conditions, which may not be present at many sites.

Evaluation of natural attenuation usually involves not only the determination of what processes of natural attenuation are occurring, but also the estimation of what the results of these processes will be in the future. Therefore, use of natural attenuation as part of the site remedial plan will necessarily require that a long-term monitoring plan be instituted. The monitoring plan should provide information to allow regulators to decide if natural attenuation is meeting site objectives, and to verify that there are no changes in conditions affecting natural attenuation. A detection system for early warning of impacts on sensitive receptors, such as drinking water wells, streams and wetlands should be provided. Also, plans must be developed for contingency remedial efforts that can be implemented if natural attenuation processes do not fulfill expectations.

Summary

Natural attenuation processes occur to varying degrees in all chlorinated solvent contamination sites, and may contribute significantly to site remedial goals. Biodegradation processes can be particularly important for natural attenuation of some chlorinated solvents, under specific environmental conditions. Chlorinated solvents dissolved in water, sorbed on soil particles or in vapor form are the most readily subject to natural attenuation processes, but bulk chlorinated solvents (NAPLs) are not readily subject to natural attenuation in the short term. The significance of natural attenuation processes at a given site for achieving site remedial goals must be carefully evaluated, and extensive site characterization and monitoring is usually necessary.

Additional Information:

U.S. EPA. *A Citizen's Guide to Natural Attenuation.* EPA 542-F-96-015. October 1996. http://www.epa.gov/swertio1/download/remed/citguide/natural.html.

U.S. EPA. *Commonly Asked Questions Regarding the Use of Natural Attenuation for Chlorinated Solvent Spills at Federal Facilities.* http://www.epa.gov/swerffrr/chlorine.htm (20 May 1999).

U.S. EPA. *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water.* EPA/540/R-97/504. May 1997. http://www.epa.gov:80/ordntrnt/ORD/WebPubs/natural/natural.pdf.

U.S. EPA. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water.* EPA/600/R-98/128. September 1998. http://www.epa.gov/ada/reports.html.

U.S. EPA. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.* OSWER Directive 9200.4-17P, April 21, 1999. http://www.epa.gov:80/ordntrnt/ORD/WebPubs/biorem/D9200417.pdf.

For more information, contact:

Jerry N. Jones or John T. Wilson
R.S. Kerr Environmental Research Center
Subsurface Protection and Remediation Division
National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
P.O. Box 1198
Ada, OK 74820

Authors:

Daniel F. Pope, Dynamac Corporation
Jerry N. Jones, RSKERC/SPRD/NRMRL/ORD