

NATURAL ATTENUATION AND RISK BASED CORRECTIVE ACTION

12.1 INTRODUCTION

Natural attenuation is a remediation approach that relies on naturally occurring processes such as dispersion, sorption, and biodegradation to control the migration of contaminants dissolved in ground water. A related approach, Risk-Based Corrective Action (RBCA), involves determining the risks to human health and the environment associated with ground water plumes and remediating the plumes to that protective level. This chapter summarizes why these technologies are being used and how they are implemented.

12.1.1 Why Natural Attenuation Has Emerged

Two converging factors have prompted the increased use of natural attenuation as a plume management technique. First, our understanding of subsurface properties has increased tremendously over the past ten years, and we now realize that many active remediation technologies are not as effective as once thought. For example, studies of multiple operating pump-and-treat systems performed by the EPA in 1989 (U. S. EPA, 1989 and 1992a) and by the National Research Council (NRC) in 1994 indicated that most pump-and-treat systems were unable to achieve the remediation goals (most commonly, ground water restoration) that were established when the systems were installed.

The EPA studies concluded that three factors created the poor performance of pump-and-treat systems: (1) the presence of hydrogeologic controls, such as low permeability zones; (2) design problems, and most importantly, (3) the presence of NAPLs in the water-bearing units. Residual NAPLs were found to serve as continuing sources of constituents to ground water at most of the sites studied, undermining aquifer restoration efforts. In response to these findings, the EPA modified the guidelines for remedial actions at Superfund sites affected by NAPLs. In an EPA Directive issued in May 1992 (U. S. EPA, 1992b), the agency recognized that full remediation of ground water impacted by NAPLs, particularly DNAPLs, will be technically impracticable at many sites.

The NRC Committee on Ground Water Cleanup Alternatives also evaluated the effectiveness of ground water pump-and-treat systems (NRC, 1994). Out of 77 sites with active pump-and-treat systems, only eight had achieved their prescribed cleanup goals. A four-category site rating system characterized the relative practicability of ground water cleanup based on site hydrogeologic conditions, constituent type, and other factors (see Table 1). Only five of the 16 sites classified as Category 1 or 2 (easier to cleanup) had achieved their

TABLE 12.1 Relative Ease of Cleaning Up Contaminated Aquifers as a Function of Contaminant Chemistry and Hydrogeology (from National Research Council, 1994)

Hydrogeology	Mobile, Dissolved (degrades / volatilizes)	Mobile, Dissolved	Strongly Sorbed, dissolved (degrades / volatilizes)	Strongly Sorbed, dissolved	Separate Phase LNAPL	Separate Phase DNAPL
Homogeneous, single layer	1*	1-2	2	2-3	2-3	3
Heterogeneous, single layer	1	1-2	2	2-3	2-3	3
Homogeneous, multiple layers	2	2	3	3	3	4
Heterogeneous, multiple layers	2	2	3	3	3	4
Fractured	3	3	3	3	4	4

* Relative ease of cleanup, where 1 is the easiest and 4 is most difficult original cleanup goals, while none of the 42 sites categorized as Category 4 (hardest to cleanup) were successful. The presence of NAPLs, difficult hydrogeologic conditions, and nondegrading contaminants, were identified as key obstacles to restoring contaminated ground water. Overall, the NRC concluded that ground water pump-and-treat methods could require very long operating periods (in some cases, centuries) to restore ground water to drinking water standards at some sites (NRC, 1994).

The second reason for the emergence of natural attenuation as a viable remediation alternative is that our understanding of how natural processes impact plume migration has increased significantly over the past several years. For example, the U.S. Air Force initiated a Natural Attenuation Initiative in the mid-1990s that involved collecting natural attenuation data from over 30 different petroleum hydrocarbon sites (see discussion in Wiedemeier et al., 1999). The results showed that biodegradation processes at fuel sites were much more vigorous and widespread than once thought. In addition, "plume-a-thon" studies performed by several researchers (e.g., Rice et al., 1995; Mace et al., 1997; Newell and Connor, 1998) indicated that most dissolved hydrocarbon plumes from leaking underground storage tanks (primarily located at gas stations) were relatively short (see Figures 12.1 and 12.2), and that the majority of the plumes were either stable or shrinking. These studies, and other natural attenuation research efforts, showed that natural attenuation processes could contain many contaminant plumes without posing a risk to human health or the environment.

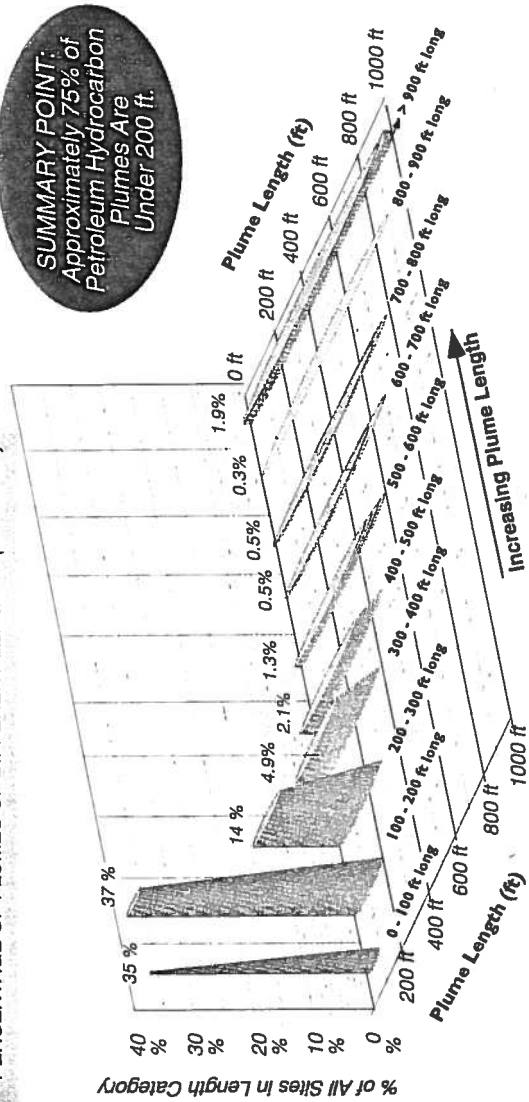
In summary, the limitations of ground water pump-and-treat technologies, combined with the realization that many plumes exhibited little or no risk, have led to increased application of natural attenuation as an approach to manage contaminated ground water.

12.1.2 Plume Life-Cycle

One of the most important studies supporting the concept of natural attenuation was a multiple site study performed by Rice et al., (1995), also referred to as the Lawrence Livermore National Laboratory (LLNL) Study. In this study, benzene plume lengths and trends over time were evaluated from 271 underground storage tank sites in California (primarily gas station tanks). After analyzing the trend data from sites with at least 8 sampling episodes, the authors defined a plume life cycle with four different stages:

- **Expanding:** Residual source present. Mass flux of contaminants exceeds assimilative capacity of aquifer.
- **Stable:** Insignificant changes. Active or passive remediation processes are controlling plume length.
- **Shrinking:** Residual source nearly exhausted and active or passive remediation processes significantly reducing plume mass.
- **Exhausted:** Average plume concentration very low (e.g., 1 ppb) and unchanging over time. Final stages of source zone dissolution over a relatively small area at a site.

COMBINED RESULTS FROM FOUR STUDIES:
PERCENTAGE OF PLUMES OF DIFFERENT LENGTHS (604 SITES)



SUMMARY POINT:
Approximately 75% of
Petroleum Hydrocarbon
Plumes Are
Under 200 ft.

Figure 12.1 Dissolved Hydrocarbon Plume Lengths from Four Studies. Source: Newell and Connor, 1998.

INDIVIDUAL STUDY RESULTS:	CALIFORNIA	TEXAS	FLORIDA	HGDB
	271 Sites	217 Sites	74 Sites	42 Sites
ALL SITES				
SUMMARY STATS- ALL	Summary Stats	Summary Stats	Summary Stats	Summary Stats
Maximum Length: 3020 ft	Max 1713 ft	Max 1619 ft	Max 600 ft	Max 3020 ft
90th Percentile: 319 ft	90th % 255 ft	90th % 382 ft	90th % 211 ft	90th % 945 ft
75th Percentile: 203 ft	75 % 146 ft	75 % 250 ft	75 % 158 ft	75 % 400 ft
MEDIAN LENGTH: 132 ft	MEDIAN 101 ft	MEDIAN 181 ft	MEDIAN 90 ft	MEDIAN 213 ft
25th Percentile: 80 ft	25th % 66 ft	25th % 137 ft	25th % 80 ft	25th % 85 ft
Minimum Length: 8 ft	Min 8 ft	Min 54 ft	Min 12 ft	Min 15 ft
• LOCATION OF SITES:	CALIFORNIA	TEXAS	FLORIDA	ENTIRE U.S.
• Plume constituent(s):	Benzene	Benzene	Benzene, BTEX	Mostly benzene, BTEX constituents
• Plume Delineation Limit:	10 ppb	10 ppb	1 - 50 ppb	Not reported; probably analytical detection limit.
• Types of Sites:	LUST sites with affected groundwater. No fractured rock sites.	LUST sites with affected groundwater. Includes limestone aquifers.	LUST sites with affected groundwater.	LUST sites at service stations located in various hydrogeologic settings.
• Method For Determining Plume Length:	Modeled: Length extrapolated from 2-D GW transport models fit to site monitoring data. Reported results for exponential and error-function equations (summary stats above from error function).	Modeled: Length extrapolated from 2-D GW transport model fit to site monitoring data. Used exponential equation only.	Measured: Length derived from site plume maps. Data analyzed as part of this bulletin.	Reported: Plume lengths reported by site consultants in survey questionnaires. Data analyzed as part of this bulletin.
• Sites w/ Soil Vapor Extract.	- Not reported	- 105 of 479 (22%)	- Not reported	- Not reported
• Sites w/ GW Pump & Treat	- 53 of 208 sites (26 %)	- 92 of 479 sites (19 %)	- 32 of 74 sites (43 %)	- Not reported
• Sites w/ GW Sparging	- Not reported	- 22 of 479 sites (5 %)	- 6 of 74 sites (8 %)	- Not reported
(note different #'s of sites reported)				
• Reference	Rice et al., 1995	Mace et al., 1997	Groundwater Services, Inc. 1997	Newell et al. 1989

Figure 12.2 Dissolved Hydrocarbon Plume Lengths Information from Four Studies. Source: Newell and Connor, 1998.

This type of plume life-cycle analysis was repeated by Mace et al. (1997) for 217 sites in Texas.

As shown in the conceptual plume lifecycle figures conceived by Rice and presented by Newell and Connor (1998) (see Figure 12.3), of the approximately 500 petroleum hydrocarbon sites addressed by this analysis, nearly 75% were found to be in either a stable or a shrinking condition, based on analyses of both plume length and concentration. Fewer than 10% of the plumes were found to be expanding in length (8% for the California study, only 3% for the Texas study). Plume lengths were frequently stable (42% to 61%), while average plume concentrations were predominantly shrinking (47% to 59%). These results suggest that dissolved hydrocarbon plumes tend to reduce more rapidly in concentration than in

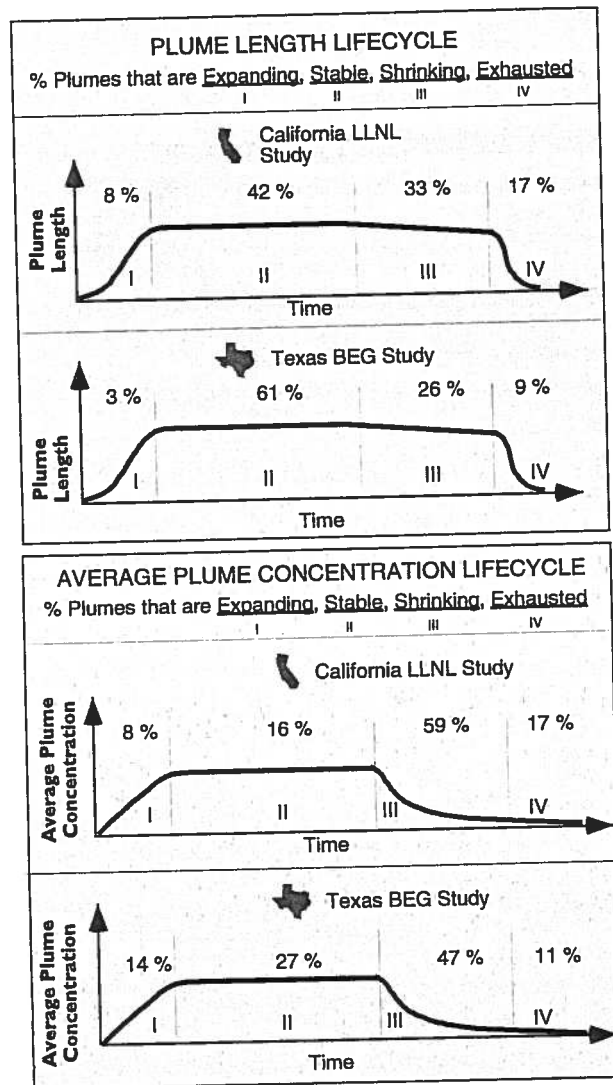


Figure 12.3 Summary of Trends for Plume Length and Plume Concentration from California and Texas. Source: Rice et al., 1995 and Mace et al., 1997.

length. Similar results were observed in a plume study performed by Buscheck et al. (1996), where 67% of 119 plumes in northern California were found to be stable/shrinking in length, and 91% had stable/diminishing concentrations.

McNab et al. (1999) applied a similar approach to chlorinated solvent sites. In this study, 29% percent of the 65 sites appeared to have expanding plumes, 55% of the plumes had no trends, and 16% of the plumes appeared to be shrinking.

These plume-a-thon studies have shown that most dissolved contaminant plumes are not expanding, and that natural attenuation processes have the potential to manage ground water contamination at many sites.

12.1.3 Advantages and Disadvantages

In 1997, the Environmental Protection Agency released a directive regarding Monitoring Natural Attenuation (see Section 12.3) that concluded that "Monitored natural attenuation has several potential advantages and disadvantages, and its use should be carefully considered during site characterization and evaluation of remediation alternatives." The policy memorandum listed several advantages and disadvantages (EPA, 1997):

Potential advantages of monitored natural attenuation include:

- As with any *in situ* process, generation of fewer remediation wastes, reduced potential for cross-media transfer of contaminants commonly associated with *ex situ* treatment, and reduced risk of human exposure to contaminated media
- Less intrusion as few surface structures are required
- Application to all or part of a given site, depending on site conditions and cleanup objectives
- Use in conjunction with, or as a follow-up to, other (active) remedial measures
- Lower overall remediation costs than those associated with active remediation

The potential disadvantages of monitored natural attenuation include:

- Longer time frames to achieve remediation objectives, compared to active remediation
- Complex and costly site characterization
- Toxicity of transformation products may exceed that of the parent compound;
- Need for long-term monitoring
- Need for institutional controls may be necessary to ensure long-term protectiveness
- Continued contamination migration, and/or cross-media transfer of contaminants

As with any remediation technology, natural attenuation is viable at some sites but not at others. Some of the key factors that determine whether natural attenuation is appropriate include:

1. plume stability
2. required remediation time frame
3. risk associated with contaminants and natural attenuation processes
4. economics of natural attenuation versus other technologies
5. off-site contamination issues
6. the degree of understanding regarding site processes

For example, a site with a stable or shrinking plume, no immediate need for restoration of ground water, no apparent risk from ground water contaminants, expensive active remediation alternatives, no off-site contamination, and well understood natural attenuation processes (i.e., BTEX biodegradation) is probably an excellent candidate for natural attenuation. On the other hand, a site with an expanding plume, a short remediation time frame (perhaps due to an impending property transaction), risks above state-mandated risk targets, relatively inexpensive active remediation alternatives (such as a very small plume), an off-site plume, or complicated natural attenuation processes might be a less suitable candidate.

12.2 GENERAL PRINCIPLES BEHIND NATURAL ATTENUATION

Natural attenuation controls contaminants released from source zones via dispersion, diffusion, sorption, degradation (either biodegradation or abiotic processes such as hydrolysis), volatilization, and dilution. Volatilization and diffusion are relatively unimportant in most non-clay ground water systems (Wiedemeier et al., 1999); therefore, the main attenuation processes are dispersion, sorption, degradation, and dilution. These key natural attenuation processes are discussed in Chapters 6, 7, and 8 and in more detail below.

12.2.1 Dispersion

Dispersion is subsurface mixing due to ground water movement and aquifer heterogeneities, and can occur in the longitudinal, transverse, and vertical directions (see Section 6.3). The amount of attenuation provided by dispersion can be estimated using computer models. As an example the BIOCHLOR model (Aziz et al., 1999; see Chapter 8) was used to predict the attenuation caused by longitudinal and transverse dispersion alone (no vertical dispersion or biodegradation or sorption) for a plume produced by a vertical plane source zone 200 ft wide with discharge into a water-bearing unit with 100 ft/yr seepage velocity. As shown in Table 12.2, longitudinal and transverse dispersion have only a minor effect in this typical example (11% reduction in concentration) over the first 1000 ft of plume length. For a 5000-ft long

plume, the reduction in concentration is more substantial (48%). Vertical dispersion, if included in the model, has a much more dramatic effect, but may not be present to this extent at many actual field sites.

TABLE 12.2 Reduction in Plume Concentration vs. Plume Length Due to Dispersion Only

DISPERSIVITY (FT)	BASE CASE	LOWER LONGITUDINAL TRANSVERSE DISPERSIVITY	HIGHER LONGITUDINAL TRANSVERSE DISPERSIVITY	BASE CASE WITH LOWER TRANSVERSE DISPERSIVITY	BASE CASE WITH VERTICAL DISPERSIVITY
Longitudinal	20	10	50	20	20
Transverse	2	1	5	0.2	2
Vertical	none	none	none	none	0.2

DISTANCE FROM SOURCE (ft)	REDUCTION IN CENTERLINE CONCENTRATION DUE TO DISPERSION ONLY (%)				
500	2.5 %	0.2 %	16 %	0 %	48 %
1000	11 %	2.5 %	32 %	0 %	66 %
2000	26 %	11 %	48 %	0 %	80 %
5000	48 %	32 %	65 %	2.5 %	91 %

12.2.2 Sorption

Sorption is a nondestructive process in which organic compounds and metals are sorbed to the aquifer matrix, and it is represented by a retardation factor (see Chapter 7). The retardation factor indicates two processes: (1) the degree to which a particular constituent moves slower than ground water seepage velocity, and (2) the ratio of total constituent mass per volume of aquifer matrix to the volume of dissolved constituents.

Sorption serves as an attenuation process by effectively reducing the mass available to the dissolved phase. Assuming a linear isotherm (a conservative assumption; see Chapter 7), a retardation factor of 3 means that only one-third of the released material will ever be dissolved in ground water. Therefore, for finite releases of contaminants to ground water (i.e., a pulse source), the resulting plume for the sorbed contaminants will have lower concentrations than a plume for contaminants that do not sorb.

12.2.3 Degradation

Biodegradation and abiotic degradation involve chemical transformation of the constituent (see Chapter 7). Biodegradation is a biochemical reaction that occurs in two different ways (McCarty, 1996): (1) use of the organic compound as a primary growth substrate, and (2) co-metabolism. The use of the organic constituent as a primary growth substrate is the dominant mechanism resulting in the degradation of contaminants and occurs when microorganisms gain energy by transferring electrons from an electron donor to an electron acceptor. Co-metabolism is typically not important under naturally-occurring conditions.

Depending on the geochemical characteristics of the ground water (such as redox conditions) and the type of microorganisms present, organic compounds can be either the electron donor or acceptor. If the redox conditions are appropriate, biodegradation is expected, but it can be fast or slow depending on the reaction rate. One way to determine whether biodegradation is occurring is to evaluate site data to demonstrate the consumption of electron acceptors, the presence of metabolic by-products, and that the geochemical conditions (primarily redox conditions) are appropriate for biodegradation reactions (see Section 12.2 and Chapter 7).

Hydrolysis is a naturally-occurring chemical process where dissolved constituents will degrade and form other compounds. It is important for a handful of compounds, primarily chlorinated solvents such as 1,1,1-TCA (half-life of 1-2 years) and chloroethane (half-life of 0.12 years). Other compounds such as the chlorinated ethenes (PCE, TCE, DCE) have hydrolysis half-lives greater than 10^6 years.

12.2.4 Dilution

Dilution can be an important attenuation process under several different circumstances, such as a slowly moving ground water plume that flows into a zone where significant surface recharge enters the water-bearing unit. Note that because mixing is limited in the subsurface, high concentration zones will probably still be present even with this influx of clean water, as the plume will be driven downwards by the recharge. Another example of dilution is when contaminants migrate vertically through a low-permeability layer, and then mix with faster moving ground water traveling horizontally through a more permeable, underlying water-bearing unit. Finally, many ground water plumes are diluted when they discharge to surface water, and the surface water mixes with ground water to reduce overall concentrations. If the surface water system has a high flowrate relative to the ground water discharge (a common occurrence) then considerable attenuation occurs. The BIOSCREEN and BIOCHLOR models contain mass flux calculators to facilitate surface water dilution calculations (Newell et al., 1997; Aziz et al., 1999).

12.2.5 Summary

Natural attenuation processes, primarily dispersion, sorption, degradation, and dilution, can reduce contaminant concentrations that leave plume source zones. A useful classification system described by Rice et al. (1995) defines contaminant plumes as either being expanding (source loading exceeds attenuation capacity), stable (source loading equal to attenuation capacity), shrinking (source loading smaller than attenuation capacity), or exhausted (only small zones of dissolved contaminants present in depleted source zones). Geochemical indicators can be used to indicate the presence of degradation processes that are destroying chemical mass. The goal of a natural attenuation study is to demonstrate that natural attenuation processes are ongoing, and that they can manage the dissolved contaminants leaving a source zone.

12.3 NATURAL ATTENUATION PROTOCOLS AND GUIDANCE

Several technical protocols have been developed to demonstrate natural attenuation of contaminants in ground water, with the most commonly used approaches being the ASTM Remediation by Natural Attenuation (RNA) standard and two air force protocols. In addition, the EPA has issued a directive for use of "monitored natural attenuation." These protocols are discussed in more detail below.

12.3.1 ASTM Standard for Petroleum Release Sites

The American Society for Testing and Materials (ASTM) has developed a standard for a systematic approach to evaluating the effectiveness of remediation by natural attenuation (RNA) at petroleum release sites (ASTM, 1998a), employing three lines of evidence (see Table 12.3). For the **primary line of evidence**, current and historical ground water monitoring data are analyzed to establish the relationship of constituent concentration over time. The ASTM Standard indicates that at some petroleum release sites, evaluation of historical data may be sufficient to indicate stable or diminishing plume area and constituent concentration.

TABLE 12.3 Lines of Evidence in ASTM RNA Standard for Petroleum Release Sites

<i>ASTM LINES OF EVIDENCE</i>	
<i>Primary</i>	<ul style="list-style-type: none"> Contaminant data to define plume as shrinking, stable, or expanding.
<i>Secondary</i>	<ul style="list-style-type: none"> Geochemical indicators of naturally-occurring biodegradation. Estimates of attenuation rates.
<i>Optional</i>	<ul style="list-style-type: none"> GW solute transport modeling. Microbiological studies. Estimates of assimilative capacity.

In other cases, the secondary and optional lines of evidence are developed to adequately demonstrate that natural attenuation is effectively controlling plume growth.

The **secondary line of evidence** consists of (1) an evaluation of geochemical indicators of biodegradation (e.g., the consumption of electron acceptors), and (2) calculation of lumped attenuation rate calculations. The **optional line of evidence** entails construction of comprehensive calibrated site models to quantify natural attenuation processes, including the combined effects of physical processes, (e.g., dispersion and dilution), chemical processes (e.g., sorption), and biological processes (including both aerobic and anaerobic processes).

Although developed for fuel sites, the basic approach of using historical data, geochemical/rate indicators, and modeling tools can be applied to other types of sites besides petroleum hydrocarbon sites. While analysis of concentration trend data should be similar for

all types of sites, different types of geochemical analysis and different types of solute transport models may be required for fuels versus solvents versus metals sites.

12.3.2 Air Force Fuel Contamination Protocol

The Air Force Center for Environmental Excellence (AFCEE) issued the first comprehensive natural attenuation protocol in 1995 (Wiedemeier, et al., 1995). This protocol, designed for fuel hydrocarbon sites, is based on a strategy where up to three lines of evidence are employed to demonstrate natural attenuation: (1) documented loss of contaminants at the field scale; (2) contaminant and geochemical analytical data, and (3) direct microbial evidence. The protocol emphasizes the first two lines of evidence, and states that direct microbial evidence can be used to "further document intrinsic remediation."

The document included a detailed discussion of the site characterization data needed to demonstrate natural attenuation. At that time, interest in anaerobic biodegradation of fuels was increasing (e.g., see Wilson, 1994). The protocol was based on the conclusion that anaerobic pathways could be a significant, or even the dominant, degradation mechanism at many petroleum fuel sites (Wilson, 1994). The AFCEE natural attenuation protocol was designed to illustrate how natural attenuation processes, particularly anaerobic biodegradation, could control the migration of plumes at petroleum release sites.

Besides emphasizing site characterization requirements, the protocol also discussed the development of conceptual models, required data analysis techniques, and the application of solute transport models such as BIOPLUME (see Chapter 10).

12.3.3 Air Force and EPA Chlorinated Solvents Protocols

In 1996, AFCEE issued a protocol for evaluating natural attenuation of chlorinated solvents in ground water (Wiedemeier et al., 1996). This document used the same three lines of evidence as the fuels protocol, but stressed that the third line (direct microbial evidence) should be used only "when absolutely necessary." The chlorinated protocol included a new discussion of geochemical indicators and a screening system to determine whether biodegradation of chlorinated solvents via reductive dechlorination (the most important biodegradation pathway for chlorinated solvents) was occurring at a particular site. In addition, a new classification system was introduced where chlorinated solvent plumes (or portions of plumes) are classified as one of three types of environments (Wiedemeier et al., 1999):

- **Type 1: Anaerobic Systems Due to Anthropogenic Carbon.** Anaerobic conditions are typical at sites contaminated with fuel hydrocarbons, landfill leachate, or other anthropogenic carbon because these organics exert a electron-acceptor demand on the system (see Figure 12.4).
- **Type 2: Anaerobic Systems Due to Naturally-Occurring Carbon.** This environment occurs in hydrogeologic settings that have inherently high organic car-

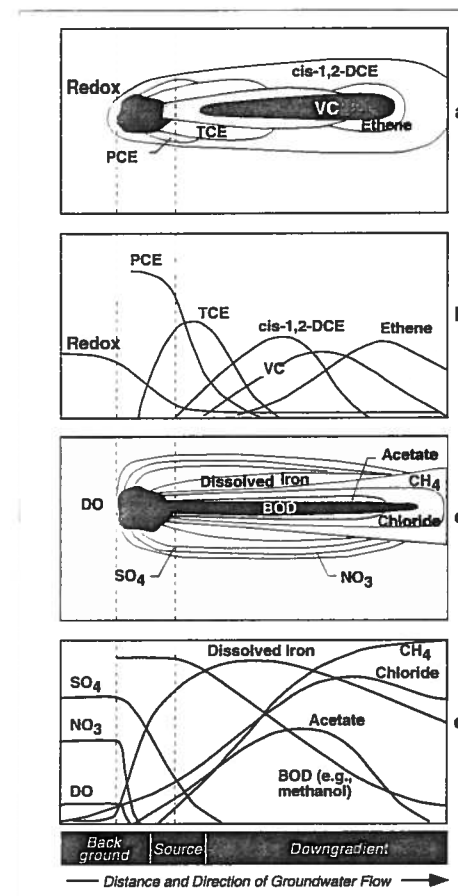


Figure 12.4 Conceptual Model of Type 1 Environment for Chlorinated Solvent Plumes. Source: Wiedemeier et al, 1999.

bon concentrations, such as coastal or stream/river deposits with high concentrations of organics, shallow aquifers with recharge zones in organic-rich environments (such as swamps), or zones impacted by natural oil seeps.

- **Type 3: Aerobic Systems Due to No Fermentation Substrate.** A Type 3 environment is characterized by a well-oxygenated ground water system with little or no organic matter (see Figure 12.5). Concentrations of dissolved oxygen typically are greater than 1.0 mg/L. In such an environment, halorespiration will

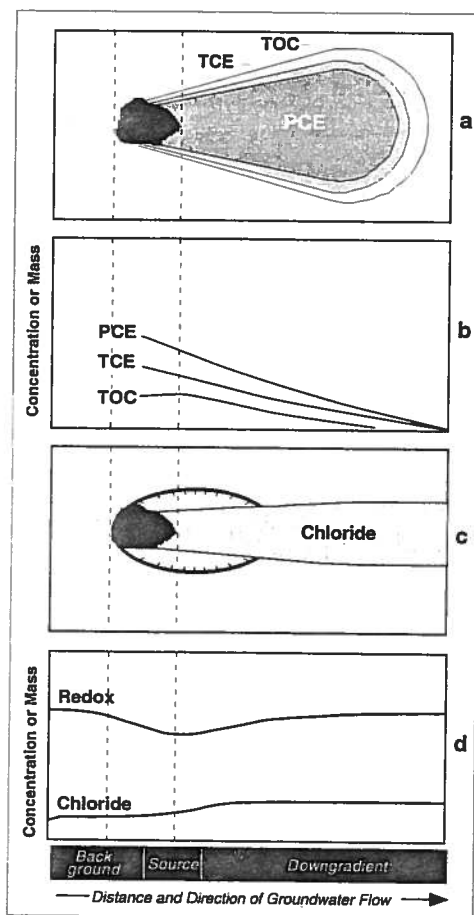


Figure 12.5 Conceptual Model of Type 3 Environment for Chlorinated Solvent Plume due to PCE and TCE Release. Source: Wiedemeier et al, 1999.

not occur and chlorinated solvents such as perchloroethene, trichloroethene, trichloroethane, and carbon tetrachloride will not biodegrade. In this environment, very long dissolved-phase plumes are likely to form.

In 1998, the EPA issued a technical protocol for chlorinated solvents based on the air force protocol (Wiedemeier et al., 1998). While much of the two documents are similar, the EPA document includes additional information on the use of natural attenuation from a regulatory perspective. Some technical information was also modified, such as the screening system to determine the presence of biodegradation processes at chlorinated solvent sites.

12.3.4 EPA Monitored Natural Attenuation Directive

In 1997, the EPA issued a directive to clarify the use of "monitored natural attenuation" (MNA) at Superfund, RCRA, UST, and other contaminated sites (EPA, 1997). While natural attenuation had been used occasionally for ground water remediation, it was not widely applied until the late 1990s. The 1997 directive stated that MNA will serve as only one component of the total remedy for the majority of cases, and it should be "used very cautiously as the sole remedy at contaminated sites." In addition, EPA reiterated that it did not change EPA's remediation directive related to source control and ground water restoration, and any application of MNA must be supported by a careful technical demonstration and subsequent performance monitoring.

Some key directives in the memorandum are:

- "Monitored natural attenuation is an appropriate remediation method only where its use will be protective of human health and the environment and it will be capable of achieving site-specific remediation objectives within a reasonable timeframe."
- "Decisions to employ natural attenuation as a remedy or remedy component should be thoroughly and adequately supported with site-specific characterization data and analysis."
- "Three types of site-specific information or 'evidence' should be used in such an evaluation: These are (1) Historical ground water and/or soil chemistry data that demonstrate a clear and meaningful trend of declining contaminant mass and/or concentrations at appropriate monitoring or sampling points; (2) Hydrogeologic or geochemical data that can be used to indirectly demonstrate the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels; and (3) Data from field or microcosm studies that directly demonstrate the occurrence of a particular natural attenuation process at a site."
- "Unless EPA or the implementing State agency determines that historical data (number 1 above) are of sufficient quality and duration to support a decision to use monitored natural attenuation, EPA expects that data characterizing the na-

ture and rates of natural attenuation processes at the site (number 2 above) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (number 3 above) may also be necessary."

12.3.5 Modeling Tools

Software products have recently been introduced to help people perform natural attenuation studies. For example, the RNA Tool Kit (Groundwater Services, 1999) provides statistical, graphing, and geochemical tools to help analyze and present natural attenuation data. Key modeling tools include the BIOSCREEN, BIOCHLOR, and BIOPLUME III models (see Chapter 8). Another useful web source, The Natural Attenuation Tool Kit web page (<http://members.aol.com/jacrosby1/home.htm>), provides key links to natural attenuation resources.

12.4 DEMONSTRATING NATURAL ATTENUATION

While the different protocols all place a different emphasis on how to demonstrate natural attenuation, three key elements are:

- **plume history** (to demonstrate loss of contaminant mass that leaves the source)
- **geochemical indicators and rates** (to demonstrate conditions are favorable for mass loss)
- **computer modeling** (to demonstrate that site data are consistent with loss via natural attenuation)

These three components of a natural attenuation demonstration are discussed in more detail below.

12.4.1 Plume History

Analysis of plume history is intended to define a ground water plume as stable, shrinking, or expanding. RNA is appropriate at sites with shrinking or stable plumes if the remediation goals and timeframe are constant with the expected performance of RNA at the site.

Guidelines developed as part of the ASTM RNA Standard (ASTM, 1998a; Nevin et al., 1998) suggest that at least one upgradient well, one downgradient well, and at minimum two wells located within the ground water plume, and that data must be available from at least four independent sampling events. (Note that the requirements were developed for small fuel sites such as gas stations, and may not be appropriate for larger, more complex sites).

Methods for analysis plume history are shown in Table 12.4. At some sites, the plume status may be apparent from a visual inspection of the contour maps or concentration and plume length graphs (see Figure 12.6 for an example). However, at many sites a statistical evaluation of the historical monitoring data may be desired to provide an objective measure of plume status or to resolve differences in interpretation of the data between site stakeholders.

TABLE 12.4 Methods to Analyze Plume History Data to Determine Plume Stability

SCOPE and DATA REQUIREMENTS: Involves graphical analysis of historical plume concentration measurements to define plume status as either stable, shrinking, or expanding. Requires data from multiple well locations, 4 or more sampling episodes. Methods include:

• <i>Plume contour maps</i>	Plot plume contours over time to illustrate stable, shrinking, or expanding condition .
• <i>Centerline concentration plots</i>	Plot centerline plume concentration data for multiple time periods, showing concentration trends from plume source to plume edge.
• <i>Well concentration plots</i>	Plot concentration vs. time data for individual monitoring wells, and provide linear regression to define concentration trend. When performed in source areas, an estimate of the lifetime of the source can be derived.
• <i>Average plume concentration plots</i>	Define average plume concentration vs. time based on data collected from several monitoring wells.
• <i>Statistical trend analysis</i>	Quantify groundwater concentrations trends using Mann-Whitney or Mann-Kendall statistical methods.

Key statistical tools for analyzing monitoring data trends that are not confirmed by a visual inspection of site data over time include the **Mann-Whitney** and the **Mann-Kendall** tests (Gilbert, 1987, Groundwater Services, 1999). These are statistical approaches for evaluating trends in a data set, such as concentration versus time data, at discreet locations.

The **Mann-Whitney U Test** (also called the Wilcoxon Rank-Sum Test, Gilbert, 1987) employs a **non-parametric** ranking procedure where a trend is reported from the overall ranking of different measurements, but not the magnitude of the measurements. It is currently being used by the State of New Jersey to determine plume stability (28 N.J.R. 1143). The test is performed for every contaminant at every monitoring well at a site where plume stability test is desired.

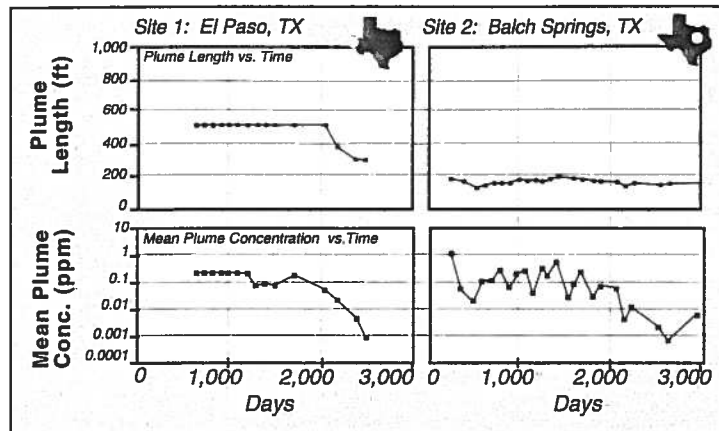


Figure 12.6 Example of Plume History Data for Two Petroleum Hydrocarbon Sites in Texas. Source: Newell and Connor, 1998 and Mace et al, 1997.

The Mann-Kendall Test is another non-parametric test (Gilbert, 1987) that can be used to define the trends in data using a ranking procedure. It requires four or more independent sampling events and compares each sampling event against every other sampling event. The worksheet on Figure 12.7 shows how to calculate the Mann-Kendall *S* statistic, where a positive *S* value indicates an increasing trend, and a negative *S* value indicates a declining trend. The *S* value and the total number of sampling events are used to determine whether a trend is probably present in the data.

The Mann-Kendall Test has been incorporated into an existing natural attenuation software package, the RNA Tool Kit, that uses an expanded implementation with three types of statistical information: the Mann-Kendall *S* statistic, a calculated confidence level, and the coefficient of variance for the sample data (Groundwater Services, 1999). Figure 12.8 shows a conceptual representation of the three types of information, where the *S* statistic shows the direction of the trend, the confidence factor shows how strong the trend is, and the coefficient of variation indicates how much scatter there is in the data. With this approach, sites can be classified as: expanding, probably expanding, stable, probably declining, declining, or not indicating a trend.

Example 12.1 PLUME HISTORY

A quarterly monitoring program shows the following benzene concentrations from a well at a site. Does the Mann-Kendall analysis *S* Statistic indicate the benzene concentration as Increasing, Decreasing, or as having No Trend?

MANN-KENDALL ANALYSIS OF PLUME:		MONITORING WELL NO: _____										CONTAMINANT: _____	
Concentration (mg/L)	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7	Event 8	Event 9	Event 10	Sum (# NO's) - (# YES's)		
Row 1: Event 1 > Event 2 ?													
Row 2: Event 2 > Event 3 ?													
Row 3: Event 3 > Event 4 ?													
Row 4: Event 4 > Event 5 ?													
Row 5: Event 5 > Event 6 ?													
Row 6: Event 6 > Event 7 ?													
Row 7: Event 7 > Event 8 ?													
Row 8: Event 8 > Event 9 ?													
Row 9: Event 9 > Event 10 ?													
Mann-Kendall Statistic (S) = TOTAL													

CHARACTERIZATION OF GROUNDWATER PLUME BASED ON DATA FROM THIS WELL

Use the Confidence Level Chart with the Mann-Kendall Statistic computed above (S) and the number of sampling events to estimate confidence level in the presence of a trend. $S < 0$ indicates a declining trend, while $S > 0$ indicates an increasing trend.

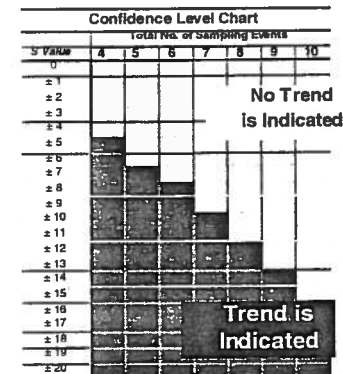


Figure 12.7 Worksheet for Mann-Kendall S-Statistic. Source: Groundwater Services, 1999.

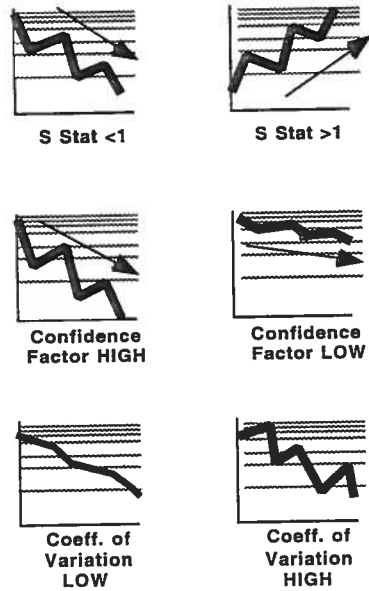


Figure 12.8 Conceptual Model for use of Mann-Kendall Test in Plume Stability Analysis. Source: Groundwater Services, 1999.

Date Sampled	Benzene Concentration (mg/L)
11/1/93	3.18
2/1/94	3.455
5/1/94	3.022
8/1/94	4.876
11/1/94	1.635
2/1/95	2.561
6/1/95	2.329
8/1/95	0.95

Solution. As shown in Figure 12.9, the Mann-Kendall worksheet indicates that the benzene in this well exhibits a DECLINING trend. To provide a more detailed interpretation of the results, the confidence factor and coefficient of variation can also be analyzed.

MANN-KENDALL ANALYSIS OF PLUME:		MONITORING WELL NO: _____										CONTAMINANT: _____	
Concentration (mg/L)	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7	Event 8	Event 9	Event 10	Sum (# NO's) - (# YES's)		
3.18	3.455	3.022	4.876	1.635	2.561	2.329	0.95						
Row 1: Event 1 > Event 2 ?	NO	YES	NO	YES	YES	YES	YES				2-5 = -3		
Row 2: Event 2 > Event 3 ?		YES	NO	YES	YES	YES	YES				1-5 = -4		
Row 3: Event 3 > Event 4 ?			NO	YES	YES	YES	YES				1-4 = -3		
Row 4: Event 4 > Event 5 ?				YES	YES	YES	YES				0-4 = -4		
Row 5: Event 5 > Event 6 ?					NO	NO	YES				2-1 = +1		
Row 6: Event 6 > Event 7 ?						YES	YES				0-2 = -2		
Row 7: Event 7 > Event 8 ?							YES				0-1 = -1		
Row 8: Event 8 > Event 9 ?													
Row 9: Event 9 > Event 10 ?													
Mann-Kendall Statistic (S) = TOTAL											-16		

CHARACTERIZATION OF GROUNDWATER PLUME BASED ON DATA FROM THIS WELL

Use the Confidence Level Chart with the Mann-Kendall Statistic computed above (S) and the number of sampling events to estimate confidence level in the presence of a trend. S<0 indicates a declining trend, while S>0 indicates an increasing trend.

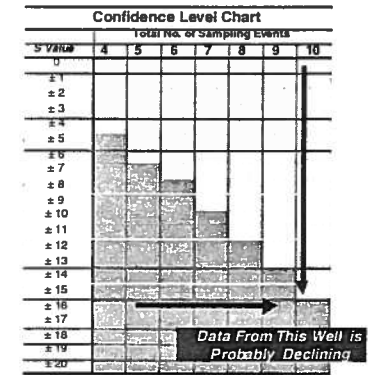


Figure 12.9 Example of Mann-Kendall S-Statistic Calculation. S Statistic is -16, indicating that a declining trend is probably present.

TABLE 12.5 Geochemical and Rate Indicators of Natural Attenuation

SCOPE and DATA REQUIREMENTS: In the absence of an adequate historical database, secondary evidence of plume attenuation may be established based on geochemical indicators measurements or calculation of a site-specific first-order decay rate. Requires plume delineation and geochemical analyses.

• Geochemical Indicators of Bioremediation	Quantify on-going natural attenuation processes based on comparison of electron acceptor and metabolic by-product concentrations between upgradient wells and plume wells. Also use indicators such as dissolved hydrogen to determine if microbial environment (e.g., aerobic, nitrate reducing, iron reducing, sulfate reducing vs. methanogenic conditions).
• Site-Specific First-Order Decay Rate from Centerline Concentration vs. Distance Plots	Derive site-specific biological natural attenuation rates for organic constituents dissolved in groundwater using centerline concentration data vs. distance. The result is a lumped decay rate, where all attenuation processes (sorption, dispersion, and biodegradation) are lumped together. Note that this decay rate is not equivalent to a biodegradation rate used in solute transport models or rates derived from concentration vs. time plots.

12.4.2 Geochemical Indicators and Rates

Geochemical Indicators. Geochemical indicators and rates provide supplement information that natural attenuation processes are active at the site (see Table 12.5). There are three general types of geochemical indicators:

1. Consumption of electron acceptors used for direct oxidative reactions. The apparent loss of dissolved oxygen, nitrate, and sulfate in the plume area is typically used as a geochemical indicator of direct oxidation of petroleum hydrocarbons, but does not relate to the direct loss of chlorinated solvents (see Tables 12.6 and 12.7).
2. Production of metabolic by-products. At petroleum hydrocarbon sites, ferrous iron and methane are typically used as indicators of anaerobic biodegradation of dissolved petroleum hydrocarbon contaminants. At chlorinated solvent sites, the presence of daughter products is evaluated. For example, key chlorinated solvent daughter products for chlorinated ethenes are *cis*-DCE (*cis*-DCE is a strong indicator of biodegradation of TCE, while *trans*-DCE typi-

cally originates from released source materials); vinyl chloride (the daughter product of DCE biodegradation under anaerobic biodegradation), and ethene (the daughter product of vinyl chloride biodegradation). (For a more detailed discussion of daughter products, see Chapter 7 or Wiedemeier et al., 1999).

3. Presence of appropriate redox/microbial environments. At some chlorinated solvent sites, dissolved hydrogen is measured to indicate whether the site is under nitrate reducing, iron reducing, sulfate reducing, or methanogenic conditions. Biodegradation of chlorinated solvents via reductive dechlorination (the most important dechlorination reaction for many chlorinated solvents) is favored in sulfate reducing and methanogenic environments (Wiedemeier et al., 1999).

TABLE 12.6 Geochemical Indicators at Petroleum Hydrocarbon (Fuel) Sites With Naturally Occurring Biodegradation

GEOCHEMICAL INDICATOR	GEOCHEMICAL INDICATOR CONCENTRATION	
	Inside of Plume	Outside of Plume
Dissolved Oxygen	Low	Higher
Nitrate	Low	Higher
Manganese	Higher	Low
Ferrous Iron (dissolved)	Higher	Low/ND
Sulfate	Low	Higher
Methane	Higher	Low/ND

ND: Non-detect

Note that different geochemical indicators are used at petroleum hydrocarbon rather than chlorinated solvent sites. For petroleum hydrocarbon plumes, the dissolved contaminants (primarily BTEX compounds) serve as electron donors and dissolved oxygen, nitrate, solid ferric iron, sulfate, and carbon dioxide serve as electron acceptors (see Table 12.6). The disappearance of the electron acceptors in the plume indicates active biodegradation processes that are consuming the dissolved petroleum hydrocarbons. Because ferric iron is a solid phase, and because carbon dioxide has numerous other sources and sinks, the presence of their metabolic by-products (ferrous iron and methane, respectively) are used to indicate that these reactions are ongoing (Wiedemeier et al., 1999). Newell et al. (1996) shows a statistical evaluation of geochemical indicators for 28 air force petroleum hydrocarbon sites.

TABLE 12.7 Geochemical Indicators at Sites with Chlorinated Solvents That Undergo Naturally Occurring Biodegradation via Reductive Dechlorination (e.g., PCE, TCE, TCA, Carbon Tetrachloride)

GEOCHEMICAL INDICATOR	GEOCHEMICAL INDICATOR CONCENTRATION	
	Inside of Plume	Outside of Plume
Dissolved Oxygen	Low	Higher
Nitrate	Low	Higher
Manganese	Higher	Low
Ferrous Iron (dissolved)	Higher	Low/ND
Sulfate	Low	Higher
Methane	Higher	Low/ND
Daughter Products	Present	ND
Dissolved Hydrogen	Higher	Low/ND

ND: Non-detect

For chlorinated solvent plumes, the dissolved contaminants (e.g., PCE, TCE, DCE, TCA, DCA, etc.) serve as electron acceptors and dissolved hydrogen (produced from fermentation of other organics) is used as the electron donor (Wiedemeier et al., 1999). This type of reaction occurs only under deeply anaerobic conditions, and therefore the redox state of the aquifer is an important indicator for determining the likelihood of biodegradation. The redox state can be determined using field measurements by evaluating the presence of inorganic species (e.g., presence of oxygen indicates the site is not anaerobic), by evaluating the presence of organic by-products (i.e., methane), or by evaluating the presence of dissolved hydrogen concentrations. Table 12.7 shows the types of geochemical indicators at sites where biodegradation of chlorinated solvents is indicated.

Rate Calculations. In some natural attenuation protocols, rate calculations are used as evidence to demonstrate that natural attenuation processes are active. There are different kinds of rates, and application of rate calculations should be performed carefully to ensure proper interpretation (Rifai and Newell, 1998).

One of the most common type of rate calculations uses centerline plume concentrations that are plotted on semi-log paper against distance from the source (ASTM, 1998a; Rifai and Newell, 1998). A bulk attenuation rate (referred to as " k ") is then calculated using the slope and ground water seepage velocity (see Figure 12.10). The resulting rate value, if positive, indicates that concentrations are declining between the source and the edge of plume due to the combined effects of dispersion, biodegradation, and other natural attenuation pro-

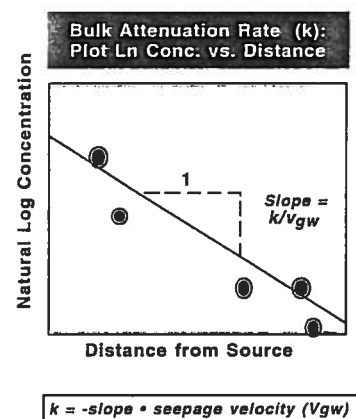


Figure 12.10 Calculation Approach for Site-Specific Lumped Attenuation Rates.

cesses acting on dissolved contaminants that have left the source zone. Note that this calculation is appropriate only when the plume is known to be stable or shrinking, and that the process of calculating a rate provides a value that typically is not used for any further calculations or compared to anything. In effect, the rate calculation just indicates that concentrations are declining.

A second type of rate calculation is the plotting of concentrations at a particular well against time. This rate (referred to as " k_t " for k of source) primarily reflects how the source loading has changed over time. For stable plumes, k_t will be zero. For shrinking plumes, the k_t term will indicate how quickly the loading rate from the source (primarily from dissolution from nonaqueous phase hydrocarbons at most sites) is declining over time. Note that this type of rate is very different from the bulk attenuation rate described above. The k_t term can be used in other calculations, such as to estimate what concentrations will be in the future by extrapolating past concentration vs. time trends.

A third type of rate calculation uses a computer model or a specialized calculation to remove the effects of sorption and dispersion, and to determine the biodegradation rate λ . The λ rate reflects the rate of biodegradation of the contaminant and nothing else. As with the bulk attenuation rate, this calculation is appropriate only when the plume is known to be stable or shrinking. It has been the author's experience that for many fuel release sites with BTEX plumes, biodegradation is the primary attenuation process and therefore λ will be close to the bulk attenuation rate k .

The biodegradation rate λ can be calculated using different calculation approaches based on tracers or analytical models (Wiedemeier et al., 1999). An automated **attenuation rate**

model, FATE V, is also available to calculate λ from site specific contaminant and hydrogeologic data (Nevin et al., 1997).

Example 12.2 GEOCHEMICAL INDICATORS

A fuel hydrocarbon site exhibits the following pattern of geochemical indicators: Dissolved oxygen is depleted in the plume area (2.5 mg/L outside plume, 0.7 mg/L inside plume). Sulfate is depleted in the plume area (120 mg/L outside plume, 10 mg/L inside plume). Nitrate concentrations are low (< 1 mg/L) outside and inside the plume area. Methane and ferrous iron exhibit high concentrations in the source area of the plume (4.2 mg/L and 16 mg/L, respectively), but have no detectable concentrations outside the plume. What do the geochemical indicators indicate?

Solution. These geochemical indicators show that vigorous aerobic and anaerobic biodegradation of petroleum hydrocarbons is ongoing at this site.

Example 12.3 GEOCHEMICAL INDICATORS

A chlorinated solvent site with PCE exhibits the following pattern of geochemical indicators: Dissolved oxygen is slightly depressed in the plume area (2.5 mg/L outside the plume vs. 2.0 mg/L inside plume). Nitrate and sulfate concentrations are unchanged inside versus outside the plume. No methane or dissolved hydrogen or daughter products were observed. What do the geochemical indicators indicate?

Solution. These geochemical indicators show that the site is aerobic, and it is unlikely that PCE will biodegrade.

Example 12.4 BULK ATTENUATION RATE CALCULATION

A site has BTEX concentration versus distance data for four wells located 160 ft apart. What is the bulk attenuation rate (i.e., the rate that reflects the combined effect of dispersion, sorption, and biodegradation)? The site has a ground water seepage velocity of 58 ft/yr.

Solution. Plotting the *natural logarithm* of the concentration versus distance yields the plot below, with a best-fit line having a slope of -0.05 (unitless) (see Figure 12.11). The seepage velocity is 58 ft/yr, or 0.16 ft/day. When multiplied together, this yields a bulk attenuation rate k of:

$$k = -\text{slope} \cdot \text{seepage velocity}$$

$$k = -(-0.05) \cdot (0.16 \text{ ft/day})$$

$$k = 0.008 \text{ day}^{-1}$$

$$\text{bulk attenuation half-life} = \ln(2)/k \text{ (see Chapter 7)}$$

$$\text{bulk attenuation half-life} = 0.693/0.008/\text{day}$$

$$\text{bulk attenuation half-life} = 87 \text{ days}$$

The effects of sorption, dispersion, and biodegradation combine to reduce dissolved BTEX concentrations by half every 87 days once the BTEX leaves the source (and assuming the BTEX is no longer flowing through any other source zones).

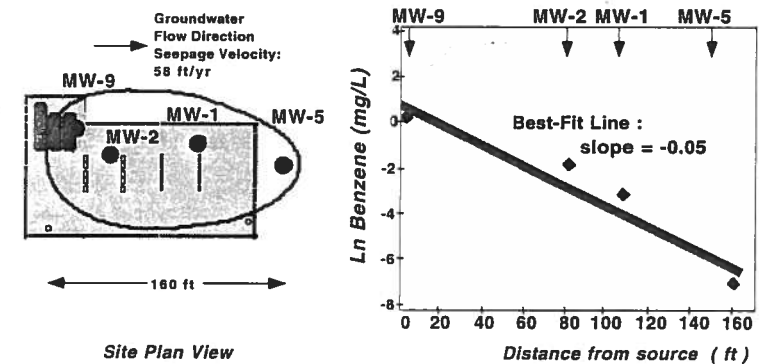


Figure 12.11 Site Plan View with Data Used for Rate Calculation.

12.4.3 Modeling Studies

Solute transport models are often used as a line of evidence for natural attenuation studies to support claims that the plume is stable and that geochemical indicators show ongoing biodegradation (see Table 12.8). Perhaps the most important task for a modeling study is to determine whether natural attenuation processes are sufficient to prevent further migration of the plume. The modeling approach is to build a transient (time dependent) model with a best-guess time for the source release. After calibrating the model to the observed plume, the simulation time is increased. If the plume does not expand in the model, then modeling supports the contention that natural attenuation processes are controlling the plume. If the model indicates that the plume has the potential to expand, then this line of evidence is not supportive that the plume is controlled.

In general, plume history data provides more reliable indication of plume stability than models if the plume history is long relative to the time required for the contaminants to

Table 12.8 Use of Models to Demonstrate Lines of Evidence

SCOPE and DATA REQUIREMENTS: When applicable, support primary and secondary evidence using modeling studies.	
<ul style="list-style-type: none"> Use of Natural Attenuation Models 	<p>Compile data regarding source size and strength, time since release, advection, dispersion, adsorption, and biodegradation processes occurring at the site and enter into model. Increase simulation period in model to determine if plume has potential to expand based on best understanding of site attenuation processes. Representative models for fuel sites: BIOSCREEN, BIOPLUME III. Representative models for chlorinated solvent sites: BIOCHLOR, MODFLOW/RT3D.</p>

travel between key monitoring wells near the edge of the plume. Modeling plays a more important role in sites where natural attenuation processes are more complex or where there is limited or no historical data.

Commonly used natural attenuation models include BIOSCREEN and BIOPLUME II or III for fuel sites, and BIOCHLOR and MODFLOW/RT3D for chlorinated solvent sites (see Chapters 8 and 10).

12.4.4 Case Study

Key results from a natural attenuation study performed at Keesler AFB site in Biloxi, Mississippi by Newell et al. (1995) are shown below. Additional case studies of natural attenuation studies at both fuel and chlorinated sites are presented by Wiedemeier et al. (1999).

At Keesler AFB, a gasoline service tank at the base released gasoline into Coastal Deposit sands, an unconfined water bearing unit. One tank was removed in 1987 and then three more tanks were removed in 1996. Although no free product was observed in the monitoring wells, residual NAPL was detected in two soil samples using short-wave ultraviolet light and Sudan IV hydrophobic dye. A ground water monitoring system installed in 1995 was used to delineate a BTEX plume that was determined to be approximately 41,000 sq ft in area (about 320 ft in length by 140 ft in width). The highest concentration of benzene observed at the site in 1995 was 3.55 mg/L.

Plume History. Plume history data were available for only one location. Total BTEX concentrations in this area were 1.5 mg/L in 1991 and 1.2 mg/L in 1995, which indicate a stable or slowly shrinking plume.

Geochemical Indicators. Geochemical data indicated that both aerobic and anaerobic biodegradation are occurring at the site. Dissolved oxygen concentrations fell from background levels of over 2.0 mg/L outside the plume area to approximately 0.4 mg/L inside the plume, indicating anaerobic conditions in the core of the BTEX plume (see Figure 12.12).

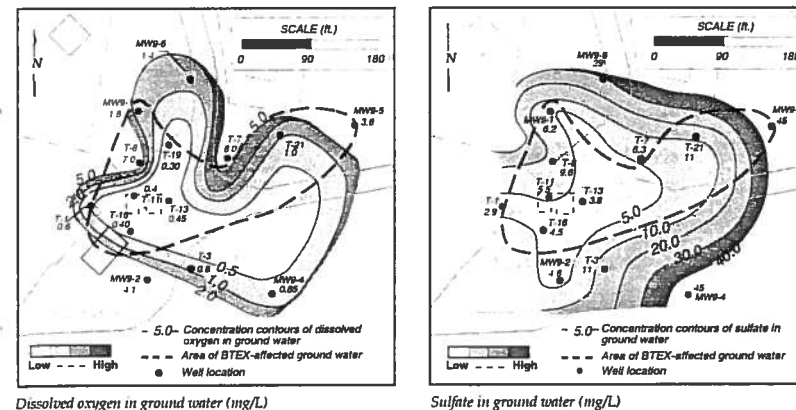


Figure 12.12 Distribution of electron acceptors in ground water, April 1995, Keesler AFB, Mississippi. Source: Wiedemeier et al., 1999.

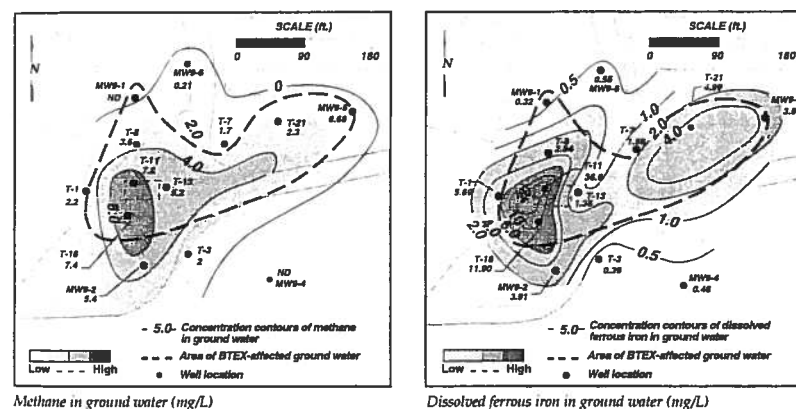


Figure 12.13 Metabolic by-products in ground water, April 1995, Keesler AFB, Mississippi. Source: Wiedemeier et al., 1999.

Sulfate data showed considerable depletion of this electron acceptor in the center of the plume, with background levels of 26.2 mg/L falling to 3.8 mg/L inside the plume (see Figure 12.12).

Metabolic by-product data also showed extensive anaerobic biodegradation processes. Both ferrous iron and methane showed strong correlation with the dissolved plume (see Figure 12.13). Maximum concentrations of ferrous iron and methane at the site were 36.6 mg/L and 7.4 mg/L, respectively, compared to non-detect or near non-detect concentrations in clean background wells for both compounds. No rate calculations were performed for the natural attenuation demonstration at this site.

Based on the geochemical indicators, the ground water contains significant biodegradation capacity (also called expressed assimilative capacity, defined as the mass of contaminant that can be removed by one liter of ground water moving from a clean background zone through the plume area. The calculated biodegradation capacity at the site was 16.7 mg/L, with most of this capacity coming from sulfate reduction and methanogenesis.

Ground Water Modeling. The BIOSCREEN Natural Attenuation Model (Newell et al., 1996) (see Chapter 8) was used as an additional line of evidence at the site (Newell et al., 1996; Wiedemeier et al., 1999). The model was calibrated to match the observed data using two different biodegradation models (both the first order decay and instantaneous reaction model). The model was then used to indicate that the plume was "no longer growing in size," and that the source mass was slowly being degraded by natural attenuation processes.

12.4.5 Key Natural Attenuation Issues

Implementation of natural attenuation often brings up three important issues regarding the need for source remediation, the natural and duration of long-term monitoring, and the appropriateness of natural attenuation for expanding plumes. The discussion below summarizes some of the key arguments relevant to each question.

Source Remediation. From a regulatory perspective, source removal is often still prescribed as a requirement before natural attenuation is implemented. For example, the EPA MNA directive (EPA, 1997) states that source control is a "fundamental component of any monitored natural attenuation remedy," and it is expected that source control "will be evaluated for all contaminated sites and that source control measures will be taken at most sites."

From a technical and risk perspective, however, the applicability of source control is more difficult to determine. At most sites that have organic contaminants, much of the source is actually in the form of residual nonaqueous phase liquids (NAPLs) that are very difficult to remove with current technologies. In practical terms, removal of these sources would entail relatively large expensive excavation projects to ensure that the source has been removed. Removal of mobile NAPL or areas of contaminated vadose zone soils is possible, but at many sites these sources do not increase the risk associated with the site. For example, Freeze and McWhorter (1997) concluded that at sites with DNAPL in low permeability units, "very high mass removal efficiencies are required to achieve significant long-term risk reduction with technology applications of finite duration. Further, it is unlikely that current technologies can achieve such efficiencies in heterogeneous low-permeability soils that ex-

hibit dual porosity properties and preferential pathways." At these types of sites, source removal would be very difficult and not provide any reduction in risk at the site.

Performance Monitoring. At many sites, the questions are of how long monitoring should continue and in what form is asked. The EPA's MNA directive (EPA, 1997) states that "Performance monitoring is required as long as contamination levels remain above required cleanup levels on any portion of the site. Typically, monitoring is continued for a specified period (e.g., one to three years) after cleanup levels have been achieved to ensure that concentration levels are stable and remain below target levels."

At many sites, however, site managers make the case that once a plume has been shown to be shrinking, and if the concentrations are all below risk-based levels, and if no off-property issues or discharge issues are present, then long-term monitoring need not extend for years and years. The rationale is that strong scientific evidence and extended empirical data demonstrate that the plume will behave predictably, and that additional data collection does not increase the reliability of the remedy or provide any other beneficial effect. In summary, there are a wide variety of views on how much long-term monitoring is enough. This question typically is resolved on a site-by-site basis.

Expanding Plumes. The focus of this chapter has been on using plume stability to indicate that natural attenuation is a viable remediation alternative. In theory, natural attenuation can be used for expanding plumes, and some states such as Texas are exploring the use of natural attenuation for expanding plumes as long as the plumes do not expand too much (i.e., less than a couple of hundred feet). The 1997 EPA directive states that "monitored natural attenuation would more likely be appropriate if the plume is not expanding..."

In practice, the use of natural attenuation for rapidly expanding plumes is more difficult to apply, as it is difficult to predict how long the plume will extend before stabilizing. The best applications of natural attenuation to expanding plumes are for cases where the plume, if expanding, is expanding slowly (such as for a chemical with a very high retardation factor or one undergoing biodegradation).

12.5 RISK-BASED CORRECTIVE ACTION (RBCA)

The Risk-Based Corrective Action (RBCA) process was developed by an ASTM Committee (ASTM, 1995, 1998b) to establish a comprehensive process for management of both human health and ecological risks associated with chemical releases to soil or ground water. The RBCA program was originally devised for petroleum release sites (ASTM, 1995), and was extended for chemical release sites (non-petroleum sites) in 1998. This section reviews the key concepts behind RBCA and its application to ground water problems.

Natural attenuation and RBCA are similar in two ways: (1) They are both relatively new methods for managing contaminants in the environment; and (2) They both account for the ability of nature to attenuate contaminants as they move through the environment.

Effective risk management via RBCA at chemical release sites entails (1) identification of applicable risk factors on a site-specific basis and (2) development and implementation of

appropriate protective measures in the timeframe necessary to prevent unsafe conditions. Key elements of the risk-based site evaluation process include:

- **Exposure Pathway Screening:** Identify potential mechanisms for exposure of human or ecological receptors on a site-specific basis. For many contaminated sites, the ground water pathway with ingestion of ground water will be important. Other pathways that are typically reviewed include inhalation of vapor and particulates, dermal contact with soil, ingestion of soil and dust leaching from soils to ground water, and discharge to surface water.
- **Risk-Based Cleanup Objectives:** For each complete exposure pathway, evaluate potential for exposure in excess of safe limits based on tiered evaluation of soil and ground water cleanup limits. For example, a common risk level for carcinogenic chemicals is 1 excess cancer death per 100,000 or 1,000,000 exposed persons.
- **Remedy Selection:** Develop risk-based exposure control strategy based on the nature and timing of the potential impact. The remedy might be active remediation or natural attenuation to reduce concentrations, containment to interrupt exposure pathways, or institutional controls to remove potential receptors.

12.5.1 RBCA Tools

Modeling tools can prove helpful at various points of the RBCA site evaluation process, including exposure pathway screening, tiered evaluation of clean-up standards, remedy selection, and design of the compliance monitoring program. Software tools combine fate and transport models (which help quantify the effects of natural attenuation between source and receptor), exposure factors (which indicate how much chemical gets ingested by potential receptors, chemical and toxicological properties (which determine how mobile and how toxic a contaminant is) and risk levels (which are typically determined by regulatory agencies). Figure 12.14 shows how site information, exposure data, toxicity factors, and risk levels perform RBCA calculations in one commonly used software package (Connor et al., 1998; Connor and Bowers, 1998).

12.5.2 Key Concept: Natural Attenuation Factor (NAF)

For a given exposure pathway, the clean up standard (referred to in RBCA studies as a Site-Specific Target Level or SSTL) represents a in source zone soils or ground water that is protective of a human or ecological receptor located some distance away at the **point of exposure (POE)**. For example, for the ground water exposure pathway, the SSTL is the contaminant concentration in ground water at the source zone that will prevent unsafe exposure to a receptor located at the POE (e.g., a person who uses a drinking water well located some distance downgradient).

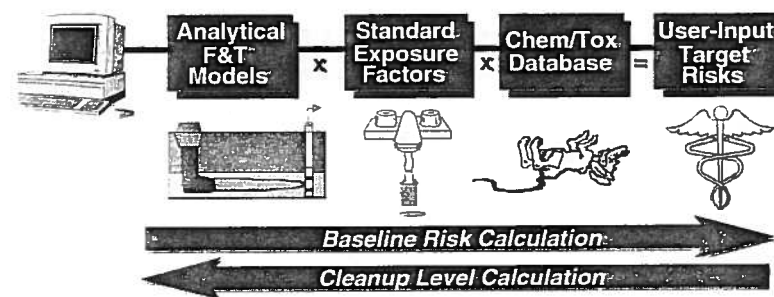


Figure 12.14 Calculation Scheme for RBCA Software Calculation. Forward Calculation Involves Entering Site Concentrations To Determine Risk at Site. Backward Calculation Involves Entering Safe Risk Levels To Determine Safe Concentration Levels at Site. Source: Connor et al., 1998.

For each complete exposure pathway, SSTL values for the source medium can be back-calculated from safe exposure levels at the POE using the following general expression: $SSTL = RBEL \times NAF$

Where

RBEL = Risk-based exposure limit at POE
 NAF = Natural attenuation factor defining natural reduction in contaminant concentrations during transport from source to POE.

In the case of the ground water pathway, the NAF can be calculated by simply comparing the source concentration and concentration at the POE if the data are available and if the plume is no longer expanding. If these conditions are not met, then natural attenuation models are used to estimate the NAF. Most RBCA software packages (e.g., Connor et al., 1998) use analytical solute transport for most RBCA calculations.

Example 12.5 RBCA Calculation.

A site containing benzene and toluene in ground water has a domestic ground water well located 1000 ft downgradient from the source zone. If this well is the closest ground water Point of Exposure (POE) for this site, what are the SSTLs (site specific target level) for benzene and toluene that will protect the people using the downgradient well? Assume that the BIOSCREEN model predicts that both benzene and toluene concentrations are reduced by a factor of 100 times by advection, dispersion, sorption,

and biodegradation processes between the source and the POE. Note that the drinking water standard (the RBEL in this case) for benzene is 0.005 mg/L and that of toluene is 1 mg/L (in other words benzene is much more hazardous to human health when ingested than toluene is).

ANSWER:

$$\text{SSTL} = \text{RBEL} \times \text{NAF}$$

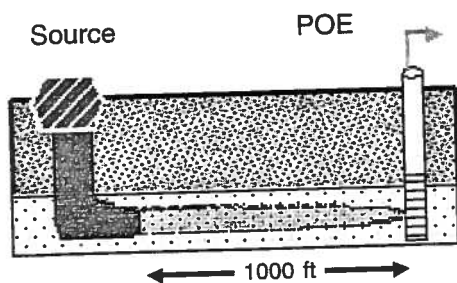
$$\text{NAF} = 100 \text{ from BIOSCREEN}$$

$$\text{RBEL} = 0.005 \text{ mg/L for benzene}$$

$$\text{RBEL} = 1 \text{ mg/L for toluene}$$

$$\text{SSTL for benzene} = 0.050 \text{ mg/L}$$

$$\text{SSTL for toluene} = 10 \text{ mg/L}$$



If the ground water at the source has concentrations less than these SSTLs, then no further action is required, and natural attenuation can be used to manage the plume. If source ground water concentrations are greater than one or both SSTLs, then either (1) the source needs to be remediated to reduce concentrations, (2) the plume needs to be cut off using pumping or some other containment approach, or (3) an institutional remedy needs to be implemented where the receptors need to be moved off well water and future ground water use is prohibited. The RBCA process does have limitations; for example, ecological risk is not explicitly calculated in many RBCA studies and off-site property damages issues complicate the implementation of RBCA. However, RBCA is becoming an accepted approach for managing contaminants in ground water at many sites.

SUMMARY

Natural attenuation and risk-based corrective action (RBCA) have emerged as accepted methods for managing contaminated ground water at many sites. Both approaches account for naturally occurring processes that reduce the concentration of contaminants in the subsurface. Natural attenuation is demonstrated by evaluating plume history, geochemical indicators, and model predictions. A RBCA evaluation calculates the risk associated with a site and using models, exposure data, and toxicity data, yields a safe clean-up standard at the source zone.

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