Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation
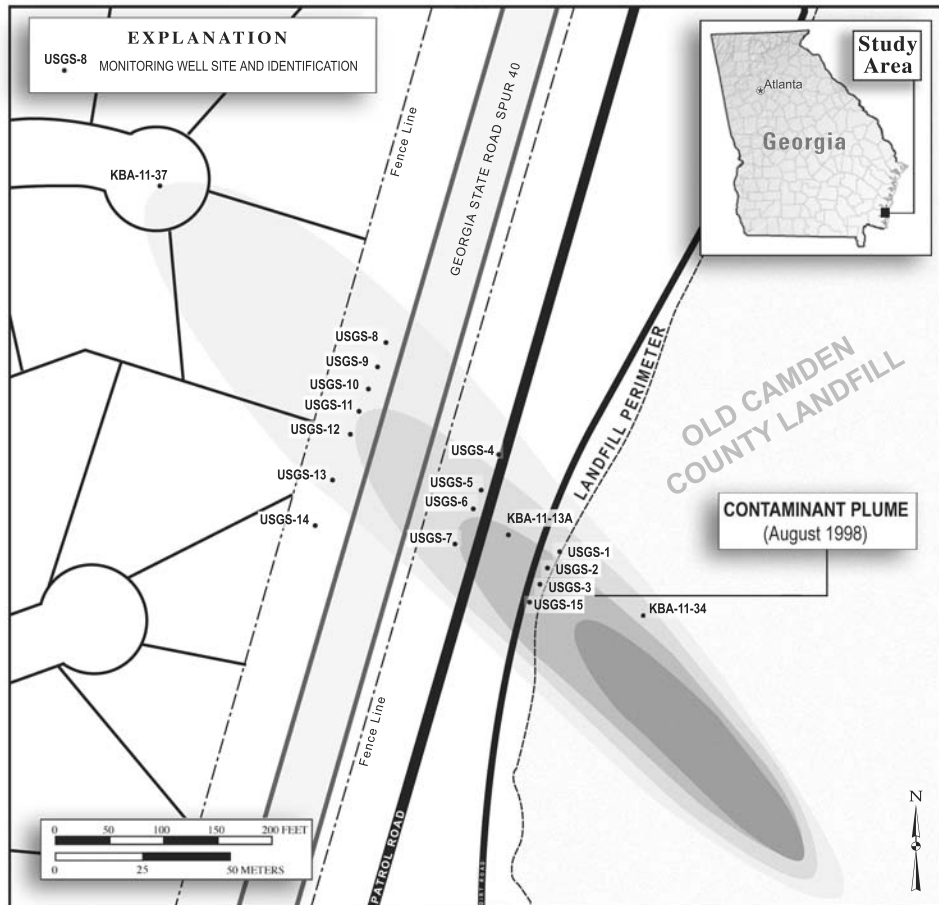
Water-Resources Investigations Report 03-4057

EXPLANATION

USGS-8   MONITORING WELL SITE AND IDENTIFICATION

Study Area

Atlanta

Georgia

KBA-11-37

Fence Line

GEORGIA STATE ROAD SPUR 40

LANDFILL PERIMETER

OLD CAMDEN COUNTY LANDFILL

USGS-8
USGS-9
USGS-10
USGS-11
USGS-12
USGS-13
USGS-14
USGS-4
USGS-5
USGS-6
USGS-7
KBA-11-13A
USGS-1
USGS-2
USGS-3
USGS-15
KBA-11-34

CONTAMINANT PLUME
(August 1998)

Fence Line

PATROL ROAD

0   50   100   150   200 FEET
0   25   50 METERS

N

Prepared in cooperation with the
**SOUTHERN DIVISION, NAVAL FACILITIES ENGINEERING COMMAND and the
NAVAL FACILITIES ENGINEERING SERVICE CENTER**

U.S. Department of the Interior
U.S. Geological Survey

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By Francis H. Chapelle, Mark A. Widdowson, J. Steven Brauner, Eduardo Mendez III, *and* Clifton C. Casey

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U.S. DEPARTMENT OF THE INTERIOR
GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY
Charles G. Groat, Director

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FIGURES

TABLE

CONVERSION FACTORS, TEMPERATURE, DATUMS, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
foot (ft)	0.3048	meter (m)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per year (ft/yr)	0.3048	meter per year (m/yr)
pounds (lbs)	0.4536	kilogram (kg)
gallon (gal)	3.785	liter (L)

Temperature in degrees Fahrenheit ($°F$) may be converted to degrees Celsius ($°C$) as follows:

$$°C = (°F - 32)/1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88); horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Abbreviations

<	less than
>	greater than
mg/L	milligram per liter
Mn/L	nanomoles per liter
µg/L	micrograms per liter

Acronyms

BTEX	benzene, toluene, ethylbenzene, and xylene
BTX	benzene, toluene, and xylene
DCE	dichloroethene
DO	dissolved oxygen
DOC	dissolved organic carbon
DOS	distance of stabilization
MCL	maximum concentration level
MNA	monitored natural attenuation
MTBE	methyl tertiary-butyl ether
NAC	natural attenuation capacity
NAPL	nonaqueous phase liquid
NAS	Natural Attenuation Software
PCE	perchloroethene
POC	particulate organic carbon
RCC	regulatory compliance concentration
TCE	trichloroethene
TEAP	terminal electron-accepting processes
TEX	toluene, ethylbenzene, and xylene
TOC	total organic carbon
TOR	time-of-remediation problem
TOS	time of stabilization
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride

Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation

By Francis H. Chapelle[1], Mark A. Widdowson[2], J. Steven Brauner[2], Eduardo Mendez III[2], *and* Clifton C. Casey[3]

ABSTRACT

Natural attenuation processes combine to disperse, immobilize, and biologically transform anthropogenic contaminants, such as petroleum hydrocarbons and chlorinated ethenes, in ground-water systems. The time required for these processes to lower contaminant concentrations to levels protective of human health and the environment, however, varies widely between different hydrologic systems, different chemical contaminants, and varying amounts of contaminants. This report outlines a method for estimating timeframes required for natural attenuation processes, such as dispersion, sorption, and biodegradation, to lower contaminant concentrations and mass to predetermined regulatory goals in ground-water systems.

The time-of-remediation (TOR) problem described in this report is formulated as three interactive components: (1) estimating the length of a contaminant plume once it has achieved a steady-state configuration from a source area of constant contaminant concentration, (2) estimating the time required for a plume to shrink to a smaller, regulatory-acceptable configuration when source-area contaminant concentrations are lowered by engineered methods, and (3) estimating the time needed for nonaqueous phase liquid (NAPL) contaminants to dissolve, disperse, and biodegrade below predetermined levels in contaminant source areas. This conceptualization was used to develop Natural Attenuation Software (NAS), an interactive computer program that estimates times of remediation associated with petroleum hydrocarbon and chlorinated ethene-contaminated aquifers. NAS was designed as a screening tool and requires the input of detailed site information about hydrogeology, redox conditions, and the distribution of contaminants. Because NAS is based on numerous simplifications of hydrologic, microbial, and geochemical processes, the program may introduce unacceptable errors for highly heterogeneous hydrologic systems. In such cases, application of the TOR framework outlined in this report may require more detailed, site-specific digital modeling. The NAS software may be downloaded from the Web site http://www.cee.vt.edu/NAS/.

Application of NAS illustrates several general characteristics shared by all TOR problems. First, the distance of stabilization of a contaminant plume is strongly dependent on the natural attenuation capacity of particular ground-water systems. The time that it takes a plume to reach a steady-state configuration, however, is independent of natural attenuation capacity. Rather, the time of stabilization is most strongly affected by the sorptive capacity of the aquifer, which is dependent on the organic matter content of the aquifer sediments, as well as the sorptive properties of individual contaminants. As a general rule, a high sorptive capacity retards a plume's growth or shrinkage, and increases the time of stabilization. Finally, the time of NAPL dissolution depends largely on NAPL mass, composition, geometry, and hydrologic factors, such as ground-water flow rates.

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An example TOR analysis for petroleum hydrocarbon NAPL was performed for the Laurel Bay site in South Carolina. About 500 to 1,000 pounds of gasoline leaked into the aquifer at this site in 1991, and the NAS simulations suggested that TOR would be on the order of 10 years for soluble and poorly sorbed compounds, such as benzene and methyl tertiary-butyl ether (MTBE). Conversely, TOR would be on the order of 40 years for less soluble, more strongly sorbed compounds, such as toluene, ethylbenzene, and xylenes (TEX). These TOR estimates are roughly consistent with contaminant concentrations observed over 10 years of monitoring at this site where benzene and MTBE concentrations were observed to decrease rapidly and are approaching regulatory maximum concentration limits, whereas toluene, ethylbenzene, and xylene concentrations decreased at a slower rate and have remained relatively high.

An example TOR analysis for chlorinated ethene NAPL was performed at the Kings Bay, Ga., site. NAPL removal action by in situ oxidation was performed here, and the NAS simulations indicated that TOR was highly dependent upon location within the plume (upgradient areas remediate faster than downgradient areas), and the organic carbon content (sorptive capacity) of the aquifer. In general, the NAS-estimated decreases in chlorinated ethene concentrations at different locations within the Kings Bay plume are roughly consistent with observed decreases over 3 years of monitoring. This comparison, however, also shows that observed patterns of contaminant concentration changes are much more complex than indicated by NAS. This, in turn, illustrates the general principle that hydrologic complexities of ground-water systems are not fully accounted for in simulation tools like NAS, and that TOR estimates made with such tools are inherently uncertain. Thus, although TOR estimates can be useful for evaluating different remediation strategies and goals for particular sites, these estimates should always be verified with site monitoring.

INTRODUCTION

Monitored natural attenuation (MNA) is the deliberate use of naturally occurring biodegradation, sorption, and dispersion processes to remediate contaminated ground-water systems. MNA is appropriate to use as a remedial strategy when "...it will meet site remediation objectives within a timeframe that is reasonable compared to that offered by other methods" (U.S. Environmental Protection Agency, 1999). Thus, estimating the amount of time required for natural attenuation processes to attain regulatory objectives is useful when evaluating MNA as a remedial technology. This report outlines a conceptual framework and a methodology for estimating the amount of time required for natural attenuation processes to lower contaminant levels to given regulatory goals.

In concept, estimating the length of time required for natural processes to remove a particular contaminant from a ground-water system is a simple mass-balance problem. If the initial mass of contaminant, M_o, (units of mass) present in a ground-water system is known, and if the rate that the contaminant is transformed or destroyed by natural attenuation processes, R_{NA}, (units of mass removed per unit time) is known, a mass-balance equation can be written:

$$[M_o - (R_{NA} \bullet t)] = M_{remaining},$$

where t is time and $M_{remaining}$ is the contaminant mass remaining at any time t. It follows that a TOR can be defined as the time required to lower contaminant mass below a given threshold ($M_{threshold}$):

$$[M_o - (R_{NA} \bullet t)] = M_{threshold},$$

$$\text{or}$$

$$t_{remediation} = [M_o - M_{threshold}]/R_{NA} = TOR, \qquad (1)$$

where the TOR is defined explicitly as given in equation 1, and refers to the length of time needed for a given mass of initial contaminant (M_o) to be lowered below a given regulatory threshold ($M_{threshold}$) by the rate of natural attenuation processes (R_{NA}) occurring in a ground-water system.

In addition to providing a working definition of TOR, equation 1 also indicates the kinds of information necessary to make remediation time estimates. This information includes an estimate of the mass of contaminant present, and an estimate of the rate of ongoing natural attenuation processes acting on the contaminant. The principal technical problem, therefore, is to obtain reliable estimates of these parameters. Clearly, the reliability of any remediation time estimates will be directly linked to the reliability of the parameter estimates. In addition, equation 1

shows that determining remediation times requires the definition of an acceptable contaminant mass threshold. This threshold must be predetermined to make remediation time estimates.

In practice, however, the problem is much more complex then indicated by equation 1. The rate of R_{NA}, particularly rates of biodegradation, may vary with time, so that the rate that contaminants are destroyed may not be constant ($R_{NA} \cdot t$) but rather a function of time

$$\left(\int_0^t R_{NA} dt \right).$$

Furthermore, many instances of ground-water contamination by petroleum hydrocarbons and chlorinated solvents can be traced to the release of NAPLs at or near land surface. These NAPLs typically seep downward through the unsaturated zone, reach the underlying saturated ground-water system, and dissolve to form contaminant plumes. Initially, contaminant plumes tend to grow and expand over time as NAPLs dissolve. At a certain point, however, rates of NAPL dissolution tend to come into equilibrium with the rate of contaminant removal by natural attenuation processes, and the plume comes into a quasi steady-state configuration. If the NAPL source continues to dissolve over time until it is exhausted, the contaminant plume will also shrink. Alternatively, some of the NAPL source might be removed by engineering methods (excavation, in situ oxidation, etc.), in which case the contaminant plume would tend to shrink faster than if the NAPL were left in place. Because of these complexities, equation 1 is useful primarily as a definition of "time of remediation" and is not suited to solve actual TOR problems.

To be practical, it is useful to divide the TOR problem into three distinct, but related, components (fig. 1). The first component is termed *distance of stabilization* (DOS), and involves estimating the maximum distance a contaminant plume can migrate from a source area of given contaminant concentration. If the maximum

distance that a plume migrates does not impact sensitive receptors so that no further remediation is deemed necessary, then the TOR is by default zero. Although cases of this kind may be the exception rather than the rule, it is important to be able to identify them when they do occur. In addition, DOS estimates can be useful in estimating contaminant concentrations in a source area that will preclude contaminant transport to nearby sensitive receptors. These estimates can be used to determine source-area remediation goals for engineered removal actions.

The second component is termed *time of stabilization* (TOS; fig. 1). This refers to the time it takes for a plume to shrink to a smaller configuration if a contaminant source is wholly or partially removed. In practice, this situation occurs when engineered methods are being considered to remediate contaminant source areas, and it is desirable to estimate the length of time it will take the contaminant plume to shrink to an acceptable configuration.

The third component is the *time of NAPL dissolution* (fig. 1). This refers to the time it will take for a NAPL body of given mass and composition to dissolve and disperse to the point where predetermined water-quality standards are met. This is usually the most important component associated with NAPL-contaminated ground-water systems.

In this report, each of these components are developed separately for practical and computational convenience. In practice, however, these issues are interrelated, and each is an important component of estimating times of remediation for contaminated sites.
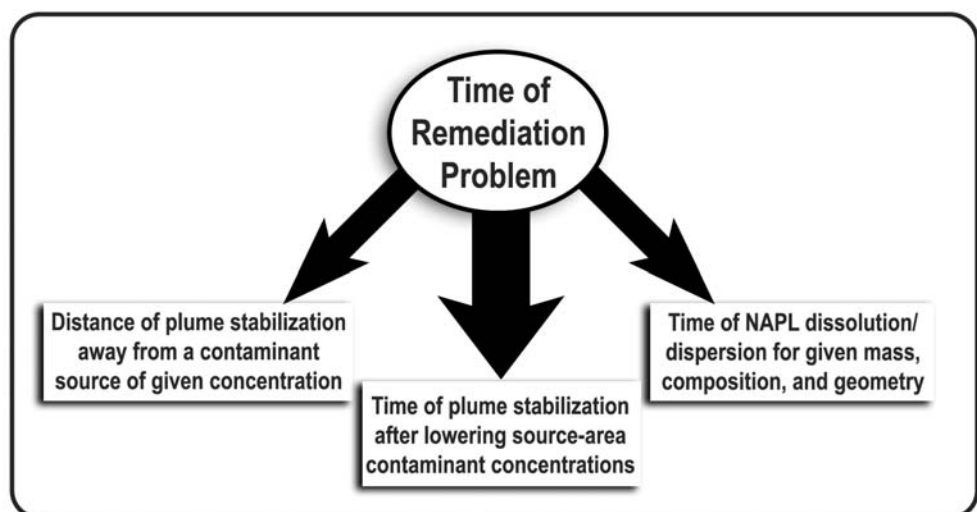

Figure 1. Conceptualization of the time of remediation problem.

Purpose and Scope

MNA is the careful use of naturally occurring contaminant-degrading and dispersing processes, in combination with environmental monitoring, to remediate contaminated ground-water systems (U.S. Environmental Protection Agency, 1997). All anthropogenic chemicals, including petroleum hydrocarbons, chlorinated solvents, metals, and radionuclides, are subject to natural attenuation processes. The effectiveness, however, of these processes and, thus, the time required for natural attenuation to remove environmental contamination, varies widely for different contaminants and for different ground-water systems (Rifai and others, 1995). This variability is not random and depends on the hydrologic, biologic, and geochemical attributes of particular ground-water systems. Because these attributes can be measured and interpreted in a logically consistent way, it is possible to estimate remediation times associated with natural attenuation processes. The purpose of this report is to describe a methodology for estimating TORs associated with MNA, and TORs associated with combining MNA with engineered contaminant-removal systems. The scope of this report includes MNA of petroleum hydrocarbons and chlorinated ethenes. The report begins with an in-depth description of the processes that contribute to natural attenuation, shows how these processes can be quantified into mass-balance equations, and uses these mass-balance equations to make TOR estimates.

NATURAL ATTENUATION OF PETROLEUM HYDROCARBONS

Biodegradation Processes

Biodegradation processes are an important component of the natural attenuation of petroleum hydrocarbons. These processes can transform toxic petroleum hydrocarbons, such as benzene, to environmentally innocuous compounds, such as carbon dioxide and water. Because (1) most petroleum products are a complex mixture of many hydrocarbons, and (2) different hydrocarbons are subject to widely varying biodegradation rates, however, these processes must be carefully assessed prior to applying MNA.

The effect of biodegradation processes on the mobility of petroleum hydrocarbons released to ground-water systems, and particularly the role of these processes in degrading and attenuating contamination, have not always been appreciated. As recently as 1981, papers using quantitative modeling techniques for evaluating hydrocarbon mobility did not consider the effects of microbial processes on hydrocarbon attenuation (Yazicigil and Sendlein, 1981).

By 1985, microbiologists had gathered clear evidence that biodegradation of petroleum hydrocarbons occurred in both aerobic and anaerobic aquifer systems. The most telling evidence that such processes were important, however, came from numerous field studies showing that petroleum hydrocarbons were selectively removed under a variety of conditions. One study in California (Hadley and Armstrong, 1991) surveyed 7,167 water-supply wells for evidence of chemical contamination. These researchers anticipated that petroleum hydrocarbon contamination, particularly benzene contamination, would be prevalent because gasoline spills had occurred from thousands of leaking underground tanks during the previous 50 years. To their surprise, however, very little evidence of benzene contamination of ground water was found. After reviewing the possible processes that could remove benzene from ground water, including sorption and evaporation, they concluded that biodegradation processes were the most likely reason for the puzzling "absence" of benzene.

The realization that microbial processes were important in the fate and transport of petroleum hydrocarbons in ground-water systems led to a number of investigations during the late 1980s. These studies form a basis for evaluating biodegradation as a natural attenuation process and as a possible strategy for remediating hydrocarbon contamination in ground-water systems.

Aerobic Oxidation

The ability of microorganisms to degrade petroleum hydrocarbons has been widely studied, and many of the biochemical pathways involved in degradation have been worked out in some detail. However, predicting how complex natural systems, particularly inaccessible ground-water systems, will react to hydrocarbon contamination is difficult. The shrinking of plumes containing benzene, toluene, ethylbenzene, and xylene (BTEX) in shallow ground-water systems had been widely reported during the

1980s, usually with little documented evidence. Barker and others (1987), however, reported the results of an experiment in which about 1,800 liters of ground water containing 2.4 mg/L benzene, 1.8 mg/L toluene, 1.1 mg/L each of *p*-xylene, *m*-xylene, and *o*-xylene, and 1,280 mg/L chloride were injected into a shallow aerobic aquifer. The chloride was added so that it would act as a conservative tracer. The resulting plume was then monitored by a dense network of multilevel piezometers. Samples from the monitoring wells were collected each day for 3 days after injection and usually each month thereafter.

By day 53, the combined effects of advection and dispersion had moved the chloride tracer plume from between 3 and 16 ft along the natural gradient prevailing in the aquifer, spreading to about three times its initial size as it moved. The benzene component of the plume reacted similarly to chloride in the first 53 days, spreading as it moved downgradient. The toluene component, however, was actually smaller at day 53 than at the beginning of the experiment. By day 108, the toluene component of the plume had virtually disappeared; furthermore, the benzene component of the plume had shrunk noticeably relative to the chloride tracer. By vertically integrating concentrations of benzene, toluene, and xylene (BTX) in the plume, the mass of each compound present as a function of time could be calculated. The mass of chloride, as expected, changed very little. The masses of each BTX compound, however, decreased rapidly. By 108 days, the mass of toluene and the BTEX isomers had decreased to nearly zero. Although benzene was more resistant to degradation than the other compounds, the mass of remaining benzene was virtually zero 400 days after injection.

This experiment differs from actual petroleum hydrocarbon spills in several ways. First, the large mass of aliphatic and alicyclic hydrocarbons present in all fuels were not included in the experiment. Thus, any effects of these compounds on BTX degradation were absent from the experiment. Because aliphatic compounds, however, are not soluble nor transported downgradient of petroleum spills in aqueous solution, this experiment accurately simulates conditions downgradient of petroleum spills. In part because of this lack of aliphatic hydrocarbons, aerobic conditions prevailed in the aquifer throughout the experiment. As aerobic bacteria may be more efficient hydrocarbon utilizers than anaerobic bacteria, this experiment probably records degradation rates as high as any that would be observed in ground-water systems.

The significance of the experiment reported by Barker and others (1987) is that it verified the numerous observations that BTX compounds were actively biodegraded in ground-water systems. Because of the aerobic conditions and the lack of an immiscible hydrocarbon phase capable of leaching BTX compounds over time, the time required for complete degradation in this experiment, however, was probably less than that required in most petroleum-product spills.

Anaerobic Oxidation

One of the first consequences of petroleum hydrocarbon contamination of shallow ground-water systems is the establishment of anaerobic conditions near the plume. One well-documented example of this was a crude oil spill that occurred near Bemidji, Minn., in August 1979. Prior to the spill, the aquifer was aerobic (dissolved oxygen (DO) was about 10 mg/L) and did not contain substantial concentrations of methane. Soon after the spill, however, increased levels of microbial respiration created anaerobic conditions near the oil lens, and methane concentrations began to increase. This, in turn, provided an opportunity for studying the anaerobic degradation of petroleum hydrocarbons in an anaerobic ground-water system under field conditions (Baedecker and others, 1988; 1993). Concentrations of the BTEX compounds were observed to decrease substantially, as well as all alkylbenzene compounds. Because of the proximity to the oil lens, these concentration decreases could not be attributed to hydrodynamic processes and were interpreted as reflecting anaerobic microbial degradation (Cozzarelli and others, 1988).

Further evidence that microbial processes are involved with degradation is provided by the observed distribution of organic acids in the anaerobic plume. High concentrations of organic acids, particularly acetic acid, were observed near the oil lens. These acids have been shown to be intermediate products of anaerobic benzene and toluene degradation in laboratory experiments, and their presence is evidence that anaerobic microbial processes were actively degrading the hydrocarbons in this system. Downgradient of the oil lens, concentrations of the organic acids decreased as Fe(III) reduction replaced FHC methanogenesis as the principal anaerobic

metabolic process (Baedecker and others, 1988) and Fe(III) reduction (Lovley and others, 1989).

Biodegradation of Methyl Tertiary-Butyl Ether

MTBE was introduced in the 1970s as an octane replacement for tetraethyl lead, and is currently added to 30 percent of the gasoline consumed in the United States (Squillace and others, 1997). MTBE is a fuel oxygenate that lowers carbon monoxide emissions in accordance with the Clean Air Acts Amendment of 1990. MTBE is highly soluble in water, is readily transported in ground- and surface-water systems, has a low taste and odor threshold, and is tentatively classified by the U.S. Environmental Protection Agency (USEPA) as a possible human carcinogen. For these reasons, the potential contamination of drinking water supplies with MTBE has rapidly become a national concern. This concern has prompted the USEPA to establish a drinking water advisory of 20 to 40 µg/L for MTBE.

Leakage of MTBE-containing gasoline from underground storage tanks, and the migration of this gasoline to the water table can produce very high concentrations of MTBE in ground water. At a gasoline spill site in Beaufort, S.C., for example, contaminated ground water containing more than 10,000 µg/L dissolved MTBE was reported (Landmeyer and others, 1998). As this contaminated ground-water body passed through streambed sediments prior to discharging to a small stream, however, MTBE concentrations decreased dramatically due to microbial activity (Landmeyer and others, 2001). MTBE is commonly observed to biodegrade relatively slowly in ground-water systems, whereas biodegradation rates are much faster in surface-water sediments.

Sorption Processes

Sorption refers to the partitioning of a solute between the aqueous and solid phases present in aquifers. The solute may be adsorbed onto the surfaces of aquifer materials, or may be absorbed into the interior of the sorbent matrix. Thus, sorption can act either to remove solute from solution (adsorption), or to add solute to solution (desorption). These combined adsorption-desorption processes are called reversible sorption and can have important effects on the transport of solutes in ground-water systems. When a plume first develops from a new contaminant source, the sorptive capacity of the aquifer sediments is largely unfilled,

and as solutes migrate away from the source, they tend to adhere to aquifer sediments, gradually saturating the sorptive capacity of the aquifer material. This causes the transport of contaminants to be initially retarded relative to the velocity of ground water and, as time passes, the sorptive capacity of the sediments becomes saturated and the effects of retardation become less effective. The principal effect of sorption on the development of plumes is to retard the spread of contaminants, however, contaminant spread in not deterred. The steady-state configuration of plumes (that is, their extent when contaminant delivery from the source is balanced by the sum of the natural attenuation mechanisms) is independent of the sorption capacity of the aquifer. Low sorptive capacity aquifers, however, will reach the steady-state configuration sooner than high sorptive capacity aquifers.

Desorption, the processes by which solutes are released from contaminated aquifer sediments, is an important factor in any remediation effort. When aquifer sediments contain large amounts of contaminant mass in the adsorbed phase, they can continue to be sources of contaminants for long periods of time. This contributes to the contaminant "rebound" effect commonly observed in pump-and-treat remediation systems once the pumps are turned off, and can greatly increase the time needed to effect site cleanup. As a general rule, plumes develop rapidly in low-sorption capacity aquifers, and can be remediated rapidly as well. Conversely, in high-sorption capacity aquifers, plumes develop more slowly, and take longer to remediate. For these reasons, remediation strategies should include a quantitative evaluation of aquifer sorption capacity.

Advection and Dispersion

Advection refers to the migration of solutes resulting from the movement of the fluid phase in which the solutes are dissolved. In sandy aquifers with relatively high horizontal hydraulic conductivity (K >10 ft/d), advection is the dominant transport mechanism for relatively soluble contaminants such as chlorinated ethenes. If subsurface sediments were homogeneous, consideration of advective transport alone would account for much of the transport behavior of subsurface contaminants. However, the lithology and, thus, the hydraulic conductivity of ground-water systems, are highly heterogeneous. This heterogeneity causes variations in solute transport speed. If it were

possible to account for these variations, then advection could be used by itself to describe solute transport. Because these variations in advective transport are so complex, however, a meaningful account of them is not practical.

The traditional method for incorporating the unknowns associated with advective transport is by using what is termed hydrodynamic dispersion. Dispersion is a mechanical process that causes a solute to occupy a larger volume of porous media than would be expected by advection alone. In part, although dispersion accounts for the tendency of solutes to spread along concentration gradients, thus increasing the volume of the plume, dispersion is also a mathematical way of accounting for the uncertainty associated with hydraulic conductivity found in all ground-water systems. The most widely used form of the coefficient of hydrodynamic dispersion is:

$$D = D_o \tau + \alpha v, \qquad (2)$$

where D_o is the diffusion coefficient ($L^2 T^{-1}$) for the solute in question, τ is a dimensionless tortuosity factor, α is the dispersivity of the porous media (L), and v is pore-water velocity (LT^{-1}). Under conditions where ground-water flow is substantial, the first term of equation 2 (diffusion) is negligible compared to the second term, and it reduces to:

$$D = \alpha v. \qquad (3)$$

Thus, dispersion (advective "mixing") of a solute is proportional to the speed of ground-water flow (v) and the ability of the aquifer material to "mix" the water (α). In reality, dispersivity is a representation of uncertainty in the hydraulic conductivity of aquifers, and the uncertainty of ground-water velocity to transport solutes. Because this uncertainty increases exponentially with distance along a given flowpath, dispersivity also increases as the plume increases. This scale-dependent behavior is a characteristic feature of dispersivity (Gelhar and others, 1992).

Volatilization

When petroleum hydrocarbons are spilled onto soil, they tend to migrate downward under the pull of gravity until reaching the water table. Because gasoline and other fuels are lighter than water, they spread by forming a lens of free-phase hydrocarbon liquid floating on the water table. Above this lens, gases in the unsaturated zone tend to be at or near saturation with

the more volatile components that are present in the hydrocarbon. This is sometimes referred to as the zone where the air is at "residual saturation" with respect to the hydrocarbon. The diffusive transport of volatile hydrocarbons upward from the zone of residual saturation is one component of natural attenuation.

In addition to volatilization, the unsaturated zone is conducive to microbial growth. The volatile components of petroleum hydrocarbons, such as short-chained alkanes, cyclic alkanes, and aromatic components, are readily oxidized by many kinds of soil bacteria. The presence of air allows oxygen to diffuse into the system with the consequent potential for aerobic metabolism. Thus, in addition to volatilization losses, there are substantial losses of hydrocarbons due to biodegradation in the unsaturated zone.

NATURAL ATTENUATION OF CHLORINATED ETHENES

Biodegradation Processes

Biodegradation processes are an important component of the natural attenuation of chlorinated ethenes (Weidemeier and others, 1998), because biodegradation can transform chlorinated ethenes to environmentally innocuous compounds, such as carbon dioxide (CO_2), ethene, and chloride. Because some transformation products, such as vinyl chloride (VC), can increase the toxicity of chlorinated solvents, these processes must be carefully assessed in applications of MNA.

Chlorinated ethenes are subject to a variety of microbial degradation processes that include reductive dechlorination (Vogel and McCarty, 1985; Barrio-Lage and others, 1987, 1990; Bouwer, 1994; McCarty and Semprini, 1994; Vogel, 1994; Odum and others, 1995), aerobic oxidation (Hartmans and others, 1985; Davis and Carpenter, 1990; Phelps and others, 1991; Bradley and Chapelle, 1996, 1998a, 1998b; Bradley and others, 1998b), anaerobic oxidation (Bradley and Chapelle, 1996, 1998b; Bradley and others, 1998b), and aerobic cometabolism (Wilson and Wilson, 1985; Semprini and others, 1990, 1991; McCarty and Semprini, 1994; Semprini, 1995). Thus, assessing whether or not a particular degradation process is active in a hydrologic system is usually a complex task. Because the conditions under which these processes occur are known, identification of the presence or absence of

particular degradation processes at a given site is possible.

Reductive Dechlorination

Chloroethenes are relatively oxidized compounds, due to the presence of electronegative chlorine atoms, and can act as electron acceptors in microbial metabolism (Vogel and others, 1987). In the presence of a suitable electron donor and catalyst, hydrogen can replace a chlorine on a chlorinated ethene molecule. This microbially catalyzed process is called reductive dechlorination. A number of reports have described the accumulation of perchloroethene (PCE) and trichloroethene (TCE) transformation products in anaerobic ground-water systems and have attributed this phenomenon to microbial reductive dechlorination (Barrio-Lage and others, 1987, 1990; Bouwer, 1994; McCarty and Semprini 1994; Vogel 1994; Odum and others, 1995; Vogel and McCarty, 1985). The consensus today is that microbial reductive dechlorination is ubiquitous in anaerobic, chloroethene-contaminated aquifers, but the extent of dechlorination is highly variable from site to site (Bouwer, 1994; McCarty and Semprini, 1994; Vogel, 1994; Chapelle, 1996; Gossett and Zinder, 1996; McCarty, 1996).

The tendency of chlorinated ethenes to undergo reductive dechlorination decreases with decreasing number of chlorine substituents (Vogel and others, 1987; Bouwer, 1994; McCarty and Semprini, 1994; Vogel, 1994). PCE, with its four chlorine atoms, is a stronger oxidant than all of the naturally occurring electron-accepting species found in ground-water systems, with the notable exception of oxygen gas (O_2) (Vogel and others, 1987). Thus PCE readily undergoes reductive dechlorination to TCE except in aerobic aquifers. Reductive dechlorination of TCE to *cis*-dichloroethene (*cis*-DCE) occurs under Fe(III)-reducing conditions and in more strongly reducing environments. Reductive dechlorination of *cis*-DCE to yield VC apparently requires at least sulfate (SO_4)-reducing conditions (Vogel and others, 1987; Chapelle 1996), but proceeds more readily in methanogenic environments. VC, on the other hand, is the least oxidized of the chloroethenes. Consequently, reductive dechlorination of VC to the nonchlorinated product, ethene, is characteristically slow and significant only under highly reducing, methanogenic conditions (Vogel and McCarty, 1985; Barrio-Lage and others, 1987, 1990; Freedman and Gossett, 1989;

DiStefano and others, 1991; De Bruin and others, 1992; Bouwer, 1994; Ballapragada and others, 1995; Fennell and others, 1995; Maymo-Gatell and others, 1995; Odum and others, 1995; Wu and others, 1995). As a result of this decreasing reductive potential with decreasing number of chlorine substituents, reductive dechlorination of chloroethene contaminants is often incomplete in ground-water systems and frequently leads to the accumulation of *cis*-DCE and VC (Major and others, 1991; Kitanidis and others, 1993; McCarty and Reinhard, 1993; Haston and others, 1994; Weaver and others, 1995; Wilson and others, 1995).

The growing recognition that microbial reductive dechlorination is common in anaerobic aquifers, but rarely results in complete reduction to nonchlorinated products, undermined early efforts to exploit intrinsic microbial activity for remediation of chloroethene-contaminated ground water. Because VC is a USEPA priority pollutant, its observed production and accumulation in anaerobic aquifers represents a potential increase in risk to human health and the environment. Consequently, in situ production of VC by indigenous microorganisms increased regulatory concern over chloroethene contamination and prompted widespread application of physical remediation methods, such as pump-and-treat systems, in an effort to remediate contaminated ground water. Unfortunately, because ground-water systems are commonly hydrogeologically complex, pump-and-treat systems are generally slow and inefficient (Bouwer, 1994). The lack of an effective alternative, combined with subsequent advances in the understanding of microbial mechanisms for degrading chloroethenes, has led to a reexamination of bioremediation in chloroethene-contaminated aquifers in recent years.

An appreciation for the potential contribution of intrinsic microbial reductive dechlorination to chloroethene remediation in ground-water systems was delayed by the widely held perception that this process is accidental and of no benefit to the microorganisms carrying out the processes. Furthermore, because the molar concentration of chloroethenes in ground-water systems is generally low in all but the most contaminated source areas, it is generally thought that these compounds are not sufficiently concentrated to serve as primary substrates in microbial metabolism. In addition, the first pure cultures determined to be capable of reductive dechlorination were methanogens, which did not grow on chloroethenes and apparently

did not gain energy from the reaction. These organisms mediated slow and partial reductive dechlorination of PCE and TCE to yield DCE. Based on these observations, reductive dechlorination has commonly been viewed as an anaerobic cometabolism brought about by the accidental interaction of chloroethenes with enzymes and cofactors produced by the microorganisms for other metabolic purposes (McCarty and Semprini, 1994). This type of cometabolic dechlorinating process was considered ubiquitous in anaerobic systems but generally incapable of mediating complete reduction to nontoxic products like ethene.

This thinking began to change in 1993 when a number of investigations demonstrated that reductive dechlorination can be carried out by microorganisms that use chloroethene compounds as terminal electron acceptors for energy production. These microorganisms, collectively termed "halorespirers," are able to grow by using chloroethenes as sole terminal electron acceptors, and are capable of much higher rates of reductive dechlorination. Although halorespirers capable of reducing PCE or TCE to DCE are relatively common (Holliger and others, 1993; Krumholz and others, 1996; Sharma and McCarty, 1996; Maymo-Gatell and others, 1997), to date only one, Dehalococcus *ethenogenes*, has been shown to completely degrade PCE to ethene (Maymo-Gatell and others, 1997). If microorganisms, such as D. ethenogenes, are present in ground-water systems in substantial numbers, then complete reductive dechlorination to ethene may be a significant mechanism for chloroethene bioremediation in anaerobic aquifers.

At present, the general consensus is that, although complete microbial reductive dechlorination is possible in anaerobic aquifers, complete reductive dechlorination to ethene is rarely observed due to low electron donor availability, unfavorable reduction/oxidation (redox) conditions, or the potential absence of appropriate microorganisms. Thus, reductive dechlorination alone does not usually remediate chloroethene contamination in ground-water systems. In combination with aerobic and anaerobic mechanisms for microbial oxidation of DCE and VC, however, the process of reductive dechlorination can be an important component of the natural attenuation of chlorinated ethenes in ground-water systems.

Aerobic Oxidation

Although the tendency of chloroethenes to undergo reductive dechlorination decreases as the number of chlorine substituents decreases, the tendency to undergo oxidation increases with decreasing number of chlorine substituents (Vogel and others, 1987). As the least chlorinated of the chloroethenes, VC has the greatest tendency to undergo oxidation. Rapid microbial degradation of VC, including mineralization, has been observed in laboratory cultures and aquifer samples under aerobic conditions (Hartmans and others, 1985; Davis and Carpenter, 1990; Phelps and others, 1991; Bradley and Chapelle 1996, 1998a, 1998b; Bradley and others, 1998b). Moreover, under aerobic conditions, VC can be used as a sole carbon source for growth and metabolism (Hartmans and others, 1985; Hartmans and deBont, 1992). These observations indicate that, in addition to incidental oxidation via cometabolic mechanisms, VC can be utilized as a primary substrate for microbial oxidation under aerobic conditions.

The cometabolic oxidation of DCE under aerobic conditions has been demonstrated for a variety of cosubstrates including methane, phenol, toluene, and propane (McCarty and Semprini, 1994). In addition, several recent studies indicate that microbial oxidation of DCE to CO_2 can also occur aerobically in the absence of detectable cosubstrates (Bradley and Chapelle 1998b; Bradley and others, 1998b, 1998c). Mineralization of DCE without addition of a carbon cosubstrate has been documented in aquifer sediments (Bradley and Chapelle, 1998b; Bradley and others, 1998b, 1998c). DCE mineralization activity was observed in liquid cultures (106 final dilution) containing DCE as the sole carbon source and oxygen as the terminal electron acceptor (Bradley and Chapelle, 2000), which indicates that DCE can be a primary substrate without the need for a carbon co-substrate. Microbial growth with oxygen as an electron acceptor and DCE as sole carbon source has only recently been reported (J.M. Gossett, Cornell University, written commun., 2001).

Unfortunately, microbial oxidation of DCE and VC under aerobic conditions is of limited relevance in most ground-water systems. In the rare event that VC is directly released to aerobic aquifers [a possibility at PVC manufacturing sites, Hartmans (1995)], rapid aerobic mineralization of VC by aquifer microorganisms can be expected. For the overwhelming majority of sites, however, the presence

of DCE and VC in ground water is attributable to the existence of anaerobic conditions and the activity of reductive dechlorinating microorganisms. Addition of oxygen to ground water to stimulate aerobic contaminant biodegradation in an otherwise anaerobic aquifer system is expensive and in most cases impractical. Consequently, aerobic biodegradation of chloroethene contaminants in ground-water systems is probably limited to the edge of the contaminant plume where DO has not been depleted by microbial respiration (Bradley and others, 1998b). As discussed earlier, production and accumulation of VC requires the reducing conditions associated with SO_4-reduction and methanogenesis. Thus, because the co-occurrence of VC and aerobic conditions is rare in ground-water systems, aerobic oxidation of DCE and VC as primary substrates for microbial metabolism is not considered to be an important mechanism for chloroethene biodegradation. As was the case for cometabolic oxidation, it is worth noting that microbial oxidation of DCE and VC under aerobic conditions can be significant at the interface of ground-water and surface-water systems (Bradley and Chapelle 1998a, 1998b).

Anaerobic Oxidation

By 1995, efforts to utilize in situ bioremediation in chloroethene-contaminated aquifers had reached an impasse. Microbial reductive dechlorination of PCE and TCE was considered pervasive in anaerobic aquifers, but, in most systems, reductive dechlorination appeared to stop with DCE and VC. Likewise, the characteristic association of DCE and VC accumulation with anaerobic conditions disqualified aerobic microbial metabolism as a significant mechanism for bioremediation of these compounds under in situ conditions. Without a demonstrable mechanism for in situ biodegradation of chloroethenes to nontoxic products, state and Federal regulators were understandably reluctant to accept in situ biodegradation as a legitimate mechanism for remediation of chloroethenes in ground water.

The discovery in 1996 that microorganisms can oxidize VC to CO_2 under anaerobic conditions paved the way for regulatory acceptance of in situ bioremediation as a defensible mechanism for remediation of chloroethene-contaminated aquifers (Bradley and Chapelle 1996). Oxidation of VC can occur under anaerobic conditions if a sufficiently strong oxidant is available to drive microbial

degradation. Fe(III) oxides are strong oxidants that are ubiquitous in ground-water systems. In an experiment conducted with sediment from a Fe(III)-reducing aquifer, addition of Fe(III) to anaerobic microcosms resulted in VC mineralization rates comparable to those observed under aerobic conditions. Low but significant VC mineralization was also observed in anaerobic microcosms under ambient Fe(III) conditions. These results indicated that VC could be mineralized under anaerobic, Fe(III)-reducing conditions, and that the bioavailability of Fe(III) was an important factor affecting the rates of mineralization. More importantly, microbial oxidation of VC under Fe(III)-reducing conditions provided a potential anaerobic alternative to the slow and inefficient reductive dechlorination of VC to ethene.

For ground-water contaminants that serve as electron donors during biodegradation, such as petroleum hydrocarbons, the availability of competing terminal electron acceptors affects the efficiency of contaminant biodegradation (Borden, 1994, Chapelle and others, 1996a). Oxygen reduction is the most thermodynamically favored and, typically, the most efficient metabolic mechanism for biodegradation of reduced ground-water contaminants. Among the remaining terminal electron acceptors that are commonly observed in ground-water systems, the oxidation potential decreases in the order of $NO_3 > Fe(III) > SO_4 > CO_2$. Thus, in general, the potential for biodegradation of highly reduced ground-water contaminants is greatest under aerobic conditions and least under CO_2-reducing (methanogenic) conditions. Because DCE and VC are relatively reduced compounds, a similar pattern of decreasing oxidation potential under increasingly reducing conditions would be expected (Vogel and others, 1987).

The effect of redox conditions on DCE and VC oxidation was recently investigated in aquifer and bed-sediment microcosms (Bradley and Chapelle, 1998b). In that study, mineralization of DCE and VC to CO_2 decreased under increasingly reducing conditions, but significant mineralization was observed for both sediments under anaerobic conditions. VC mineralization decreased in the order of aerobic >Fe(III)-reducing >SO_4-reducing > methanogenic conditions. As one would expect given their difference in chlorine number, microbial oxidation of VC was greater than microbial oxidation of DCE for each electron-accepting condition. For both sediments,

microbial mineralization of DCE under aerobic conditions was at least twice that observed under anaerobic conditions. An interesting observation is that the rate and magnitude of DCE oxidation did not differ significantly among Fe(III)-reducing, SO_4-reducing, and methanogenic conditions. Based on this and other observations, it was concluded that microbial oxidation of DCE under these redox conditions involved an initial rate-limiting reduction to VC, which was subsequently oxidized to CO_2. This, in turn, suggested that direct oxidation of DCE requires a more powerful oxidant than Fe(III) oxides. A subsequent investigation demonstrated that aquifer microorganisms can anaerobically oxidize DCE to CO_2 under Mn(IV)-reducing conditions without an initial reduction to VC (Bradley and others, 1998c). Because Mn(IV) oxides are common in alluvial and glacial aquifer sediments, microbial oxidation of DCE may be significant in some anaerobic ground-water systems.

The ability of aquifer microorganisms to efficiently oxidize DCE and VC to nontoxic products under anaerobic conditions has important implications for the potential utilization of intrinsic biodegradation in ground-water systems. These results indicate that, in anaerobic aquifers, highly oxidized chlorinated chloroethenes, such as PCE and TCE, can be readily transformed to DCE and VC, which are susceptible to microbial oxidation under a number of anaerobic redox conditions. Thus, the combination of reductive dechlorination of PCE and TCE under anaerobic conditions, followed by anaerobic microbial oxidation of DCE and VC, provides a possible microbial pathway for complete degradation of chloroethene contaminants in ground-water systems.

Aerobic Cometabolism

Another potential process for microbial degradation of chloroethenes in ground-water systems is cometabolic oxidation. Wilson and Wilson (1985) reported that methanotrophic bacteria were capable of oxidizing TCE to CO_2 under aerobic conditions. Since then, a wide variety of aerobic microorganisms, which are able to oxidize TCE, DCE, and VC to CO_2 without accumulation of toxic intermediates, have been identified. These include methane, propane, ethene, aromatic compound, ammonium, isoprene, and VC oxidizers (see McCarty and Semprini, 1994). Cometabolic oxidation of chloroethenes does not supply energy for microbial growth or metabolism. Rather, for each of these processes, the responsible microorganisms contain nonspecific oxygenase that fortuitously oxidize chloroethenes to CO_2. Consequently, aerobic cometabolism of chloroethenes requires the presence of oxygen and a primary substrate to initiate the production of a suitable oxygenase.

Cometabolic oxidation is not considered to be a significant mechanism for intrinsic biodegradation of chloroethene contaminants in ground water. Cometabolic oxidation of chloroethenes by subsurface microorganisms has been successfully exploited for engineered remediation of chloroethene-contaminants in ground water (Semprini and others, 1990, 1991; McCarty and Semprini, 1994; Semprini, 1995). TCE contamination in aerobic aquifers can be biodegraded by methanotrophic microorganisms when methane is supplied to the subsurface in sufficient quantities to stimulate and support methanotrophic activity. Because methane and oxygen do not typically co-occur in ground-water systems, however, methanotrophic oxidation of chloroethenes is unlikely under nonengineered circumstances. A number of ex situ investigations have demonstrated that toluene oxidizers can cometabolize chloroethenes under aerobic conditions (Fan and Scow, 1993; Fuller and others, 1995; Hopkins and McCarty, 1995; Mars and others, 1996). Moreover, many ground-water contaminant plumes are the result of mixed waste releases and, as a consequence, contain chloroethenes and aromatic compounds like toluene. Unfortunately, contaminant plumes, which contain aromatic compounds in sufficient concentration to support cometabolic oxidation of chloroethenes, are characteristically anaerobic as a result of oxygen depletion by aerobic respiration. Consequently, significant cometabolic oxidation of chloroethenes in such systems would be, at most, a transient phenomenon. Because circumstances suitable for cometabolic oxidation of chloroethenes are rarely observed in ground-water systems, this process is generally not considered to be an important pathway for microbial degradation of chloroethene contaminants.

The interface between ground water and surface water is a nonengineered system in which cometabolic oxidation could potentially be a significant mechanism for biodegradation of chloroethene contaminants. Because ground-water contamination occurs most commonly in local flow systems (that is, flow systems hydrologically connected to land surface), plumes of contaminated ground water frequently discharge to nearby surface-water bodies. The streamed sediments

of these surface-water systems are commonly characterized by geochemical heterogeneity and remarkably active microbial communities. Because methanotrophic activity is commonplace in organic-rich, streambed sediments, discharge of chloroethene-contaminated ground water can reasonably be expected to support significant cometabolic oxidation of chloroethenes. In fact, complete oxidation of DCE and VC has been reported in streambed sediments characterized by mixed aerobic/methanogenic conditions (Bradley and Chapelle, 1997). These results suggest that cometabolic oxidation of chloroethene contaminants may be significant in stream and lakebed sediments.

Redox Conditions and the Biodegradation of Chlorinated Ethenes in Ground-Water Systems

Although microbial degradation processes of chlorinated ethenes are complex, they are predictable. Under some redox conditions, all chlorinated ethenes can serve as *electron acceptors* in microbial metabolism. In this case, microorganisms are respiring the chlorinated ethenes by transferring electrons to them. This process is also called reductive dechlorination. Under other redox conditions, microorganism can use lightly chlorinated ethenes, such as DCE and VC, as *electron donors*. In this case, microorganisms oxidize the chlorinated ethenes and use them as a source of energy in the form of electrons.
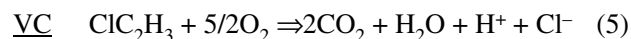
Under anoxic conditions, highly chlorinated ethenes, such as PCE and TCE, are subject to reductive dechlorination according to the sequence:

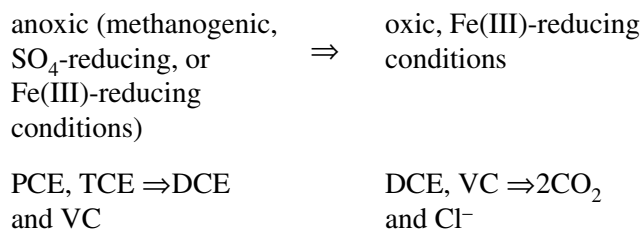PCE $\Rightarrow$ TCE+Cl $\Rightarrow$ DCE + 2Cl $\Rightarrow$ VC + 3Cl $\Rightarrow$ ethylene + 4Cl

The *efficiency* of dechlorination, however, differs for different redox conditions. Dechlorination of PCE and TCE to DCE occurs under mildly reducing conditions, such as nitrate (NO_3)- or Fe(III)-reduction, whereas the transformation of DCE to VC, or the transformation from VC to ethylene requires the more strongly reducing conditions of methanogenesis or SO_4 reduction (Vogel and others, 1987). Reductive dechlorination has been shown to be driven by molecular hydrogen (H_2) (DiStefano and others, 1991), and the efficiency of reductive dechlorination is directly related to the availability of H_2.

Concentrations of H_2 in ground-water systems are controlled by ambient microbial terminal electron-accepting processes (TEAPs). Under anaerobic conditions, H_2 is continuously produced by fermentative microorganisms metabolizing natural or anthropogenic organic matter. This H_2 is then utilized by respirative microorganisms that most commonly use Fe(III), SO_4, or CO_2 as terminal electron acceptors. Significantly, each of these TEAPs has a different affinity for H_2 uptake (Lovley and Goodwin, 1988). CO_2 reduction (methanogenesis) has the lowest H_2 affinity and steady-state H_2 concentrations in methanogenic aquifers are, therefore, relatively high (about 10 nM/L). SO_4 reduction has a slightly greater affinity for H_2 than methanogenesis and is characterized by slightly lower H_2 concentrations (1–4 nM/L). Fe(III) reduction (0.2–0.8 nM/L) and NO_3 reduction (<0.10 nM/L) have even greater affinities for H_2 and are characterized by progressively lower steady-state H_2 concentrations (fig. 2). Thus, the observation that reductive dechlorination is more efficient under methanogenic or SO_4-reducing conditions than under Fe(III)- or NO_3-reducing conditions reflects the greater availability of H_2 for reductive dechlorination, and not the activity of methanogenic or SO_4-reducing microorganisms (Smatlack and others, 1996).

The lightly chlorinated ethenes DCE and VC can be oxidized to CO_2 under oxic or Fe(III)-reducing conditions:

$\underline{DCE}$ $\quad Cl_2C_2H_2 + 2O_2 \Rightarrow 2CO_2 + 2H^+ + 2Cl^-$ $\quad$ (4)

$\underline{VC}$ $\quad ClC_2H_3 + 5/2O_2 \Rightarrow 2CO_2 + H_2O + H^+ + Cl^-$ $\quad$ (5)

Because DCE and VC are usually degradation products of reductive dechlorination, complete degradation of chlorinated ethenes is favored by sequential anoxic-oxic conditions. First, under reducing conditions, PCE and TCE is transformed to DCE and VC. Then, as ground water migrates to more oxic conditions, DCE and VC can be oxidized to CO_2:
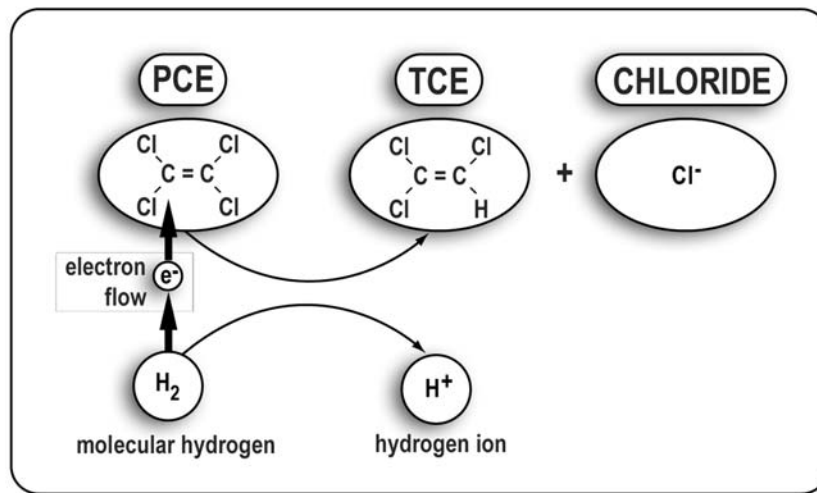
anoxic (methanogenic, SO_4-reducing, or Fe(III)-reducing conditions)	$\Rightarrow$	oxic, Fe(III)-reducing conditions
PCE, TCE $\Rightarrow$ DCE and VC		DCE, VC $\Rightarrow$ 2CO_2 and Cl^-

Figure 2. Schematic diagram showing how molecular hydrogen drives reductive dechlorination.

The efficiency with which chlorinated ethenes are completely degraded, therefore, is directly related to redox conditions present in an aquifer and to the succession of redox processes that chlorinated ethenes are exposed to along particular ground-water flowpaths. Thus, an important component to assessing the natural attenuation of chlorinated ethenes is to accurately delineate redox conditions in ground-water systems.

Delineating the Distribution of Redox Processes in Ground-Water Systems

The most common electron-accepting processes in ground-water systems are oxygen, NO_3, Fe(III), SO_4, and CO_2 reduction (methanogenesis) (fig. 3). Microorganisms that naturally inhabit ground-water systems couple the oxidation of an electron donor (usually organic carbon) with the reduction of electron acceptors. In doing so, microorganisms use the most energetically efficient electron acceptor available. The stoichiometry and Gibbs free energy (ΔG^o in units of kilocalorie/equivalent at pH 7.0, Stumm and Morgan, 1981, p. 453) of these processes can be represented by the generalized equations:
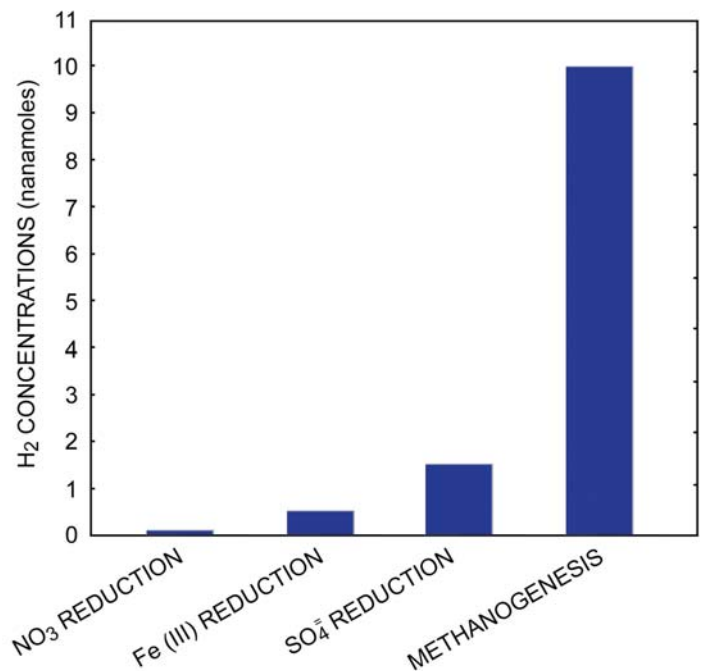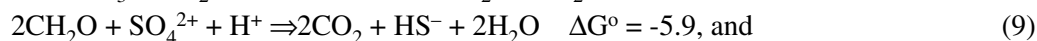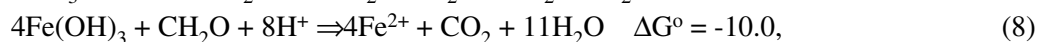
Figure 3. Characteristic H_2 concentrations associated with different terminal electron-accepting processes.

$$O_2 + CH_2O \Rightarrow CO_2 + H_2O, \quad \Delta G^o = \text{-29.0}, \tag{6}$$

$$4NO_3 + 4H^+ + 5CH_2O \Rightarrow 4NO_2 \Rightarrow 2N_2 + 5CO_2 + 7H_2O \quad \Delta G^o = \text{-19.6}, \tag{7}$$

$$4Fe(OH)_3 + CH_2O + 8H^+ \Rightarrow 4Fe^{2+} + CO_2 + 11H_2O \quad \Delta G^o = \text{-10.0}, \tag{8}$$

$$2CH_2O + SO_4^{2+} + H^+ \Rightarrow 2CO_2 + HS^- + 2H_2O \quad \Delta G^o = \text{-5.9, and} \tag{9}$$

$$2CH_2O \Rightarrow CH_4 + CO_2 \quad \Delta G^o = \text{-5.6.} \tag{10}$$

Because oxygen is the most efficient oxidant (that is, ΔG^o is the most negative), microorganisms will use oxygen preferentially to NO_3, Fe(III), SO_4, or CO_2. If oxygen is not available, however, microorganisms will preferentially use NO_3 over Fe(III), SO_4, or CO_2. If oxygen or NO_3 is not available, microorganisms will use Fe(III) over SO_4 or CO_2. Finally, if oxygen, NO_3, and Fe(III) are not available, microorganisms will use SO_4 preferentially to CO_2. Because CO_2 reducers are the least energetically favorable microorganisms, they can only become predominant in the absence of other more efficient electron acceptors. This observed behavior is commonly referred to as the ecological succession of terminal electron-accepting processes.

Because of ecological succession, microbial processes tend to segregate into distinct zones dominated by oxygen, NO_3, Fe(III), SO_4, and CO_2 reduction. Furthermore, given the different electron acceptors consumed (left side of eqs. 6–10) and final products produced (right side of eqs. 6–10), it is possible to logically deduce the zonation of microbial processes in ground-water systems.

If DO is present in ground water at concentrations greater than 0.5 mg/L, then oxygen reduction (eq. 6) will be the predominant microbial process. If DO concentrations are less than 0.5 mg/L, but NO_3 is present at concentrations greater than 1 mg/L, then NO_3 reduction (eq. 7) will be the predominant microbial process. Because nitrite (NO_2)

is an unstable intermediate product of NO_3 reduction (eq. 7), the presence of measurable NO_2 concentrations is indicative of NO_3 reduction. If ground water lacks DO, NO_3, or NO_2, but concentrations of Fe^{2+} are greater than 0.5 mg/L, then Fe(III) reduction (eq. 8) will be the predominant process. If ground water lacks Fe^{2+} but contains concentrations of SO_4 greater than 1 mg/L and hydrogen sulfide (H_2S) greater than 0.05 mg/L, then SO_4 reduction (eq. 9) will be the predominant process. Finally, if the water lacks DO, NO_3, Fe^{2+}, SO_4, and H_2S, but contains concentrations of methane greater than 0.2 mg/L, then methanogenesis (eq. 10) will be the predominant process. The logic of deducing predominant electron-accepting processes using observed changes of electron acceptor and final product concentrations in ground water is summarized in figure 4 (Chapelle and others, 1995).

In practice, this methodology commonly encounters uncertainties. Many products of microbial metabolism (such as Fe^{2+}, H_2S, and methane) can be transported by ground-water flow. In some cases where such transport is substantial, it is difficult to determine the exact redox zonation with this water-chemistry information. In these cases, direct measurement of dissolved H_2 can be used to identify ambient redox processes (fig. 4).

Based on this methodology, the following data are required to identify microbial redox processes in ground-water systems (table 1):

Table 1. Ground-water chemistry constituents used to identify microbial redox processes in ground-water systems, and common methods of analysis

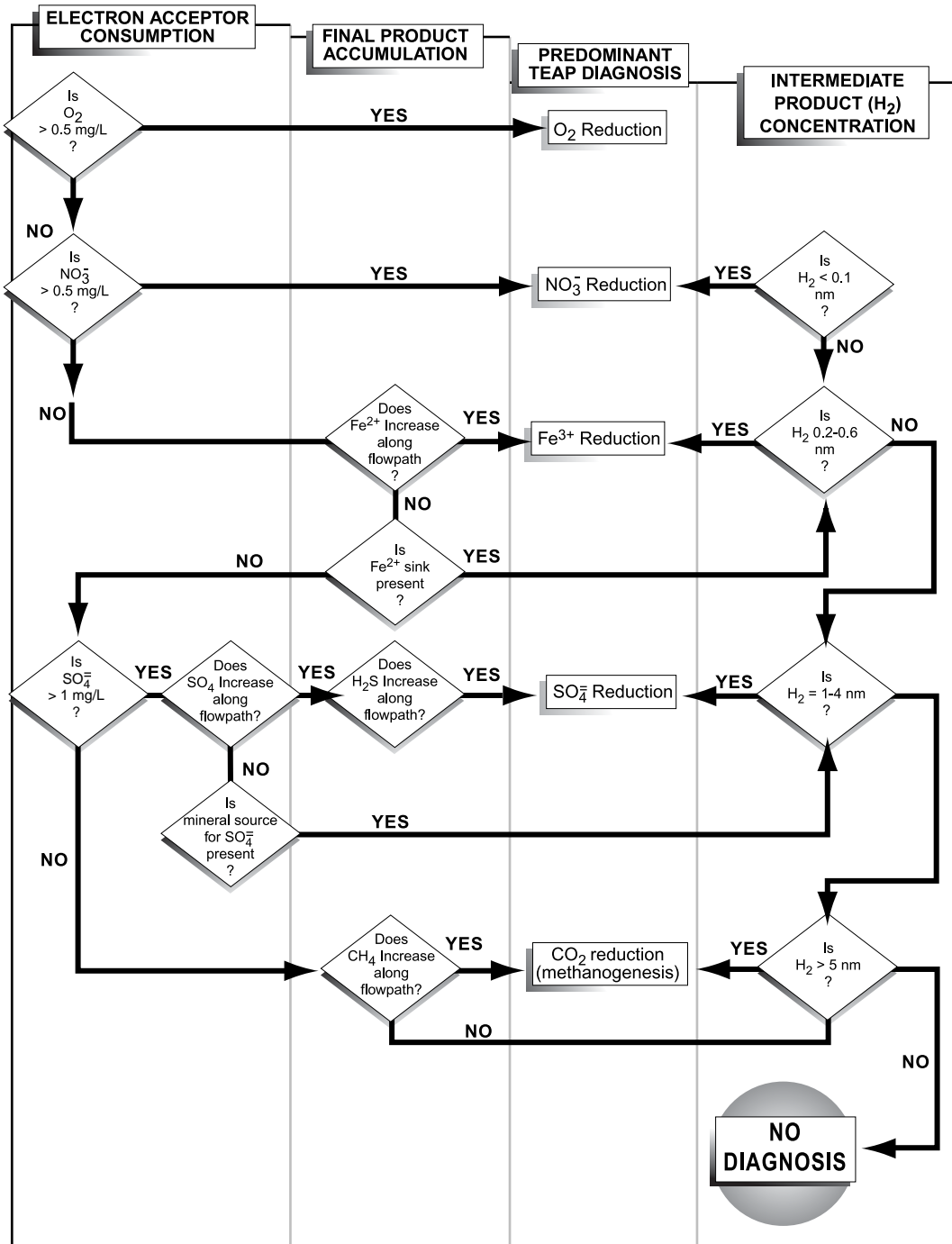| Analytical constituents	Method of analysis
Dissolved oxygen (DO)	Field kit
Nitrate (NO_3)	Ion chromatography
Nitrite (NO_2)	Ion chromatography
Dissolved ferrous iron (Fe^{2+})	Field kit
Sulfate (SO_4)	Ion chromatography
Hydrogen sulfide (H_2S)	Field kit
Dissolved methane (CH_4)	Gas chromatography
pH (units)	Meter
Dissolved hydrogen (H_2)	Gas chromatography

Figure 4. Flowchart for deducing terminal electron-accepting processes in ground-water systems.

Of these constituents, the most important—and commonly the most difficult measurement to make accurately—is DO. This is a skill-intensive constituent to measure in the field, and extreme care must be taken to avoid oxygenation of the water sample prior to analysis. DO meters are convenient, but do not reliably measure low (<0.5 mg/L) concentrations of oxygen. DO kits, on the other hand, can accurately distinguish between truly anoxic ground water and low concentrations of DO (Chemetrics, Inc., 1984). Concentrations of NO_3, NO_2, and SO_4 are most accurately measured in the laboratory using ion chromatography. H_2S and Fe^{2+} are most efficiently measured in the field with appropriate field kits (table 1). Samples for methane analysis can be collected in the field and analyzed in the laboratory. H_2 measurements are most reliable when made in the field (Chapelle and others, 1996b, 1997).

Organic Carbon Substrates that Support Reductive Biodegradation

Reductive dechlorination, the process in which chlorinated ethenes serve as electron acceptors in microbial metabolism, requires an organic carbon substrate (a source of electrons) to proceed. These organic carbon substrates initially are degraded by fermentative bacteria that produce molecular H_2 and other organic compounds. This H_2 then reacts directly with the chlorinated solvent, resulting in reductive dechlorination (fig. 2). Many different kinds of organic carbon, including petroleum hydrocarbons, naturally occurring particulate organic carbon (POC) in aquifer sediments, and natural dissolved organic carbon (DOC) in ground water can be fermented to H_2 to support reductive dechlorination. Organic carbon compounds differ substantially, however, in their ability to efficiently ferment and, therefore, the efficiency by which they can support reductive dechlorination. In particular, the ability to assess the efficiency by which natural DOC and POC are fermented is difficult. For these reasons, it is not currently technically feasible to quantitatively measure the mass of fermentable total organic carbon (TOC) available in ground-water systems.

Although the ability to quantify the available mass of fermentable organic carbon available to support reductive dechlorination is difficult, the geochemical conditions resulting from organic carbon metabolism in an aquifer is relatively easy to assess. For these reasons, it is more appropriate for assessments of natural attenuation to focus on ambient geochemical conditions than on measuring available organic carbon.

Daughter Products Indicating Biodegradation

Concentrations of chlorinated ethenes and their degradation products give a direct indication of the presence or absence of microbial degradation (both reductive and oxidative) processes. In many cases, the production of *cis*-1,2-DCE, VC, and chloride ions along aquifer flowpaths is direct evidence of reductive dechlorination intrinsic bioremediation. VC and some DCE isomers could be primary contaminants in some ground-water systems. VC, however, is not normally present as a primary contaminant in solvent spills associated with military activities, because VC was not used as a solvent. Thus, the presence of VC in ground water associated with a chlorinated ethene spill is strong evidence of reductive dechlorination. Also, *cis*-1,2-DCE (rather than *trans*-1,2-DCE) is usually produced from the reductive dechlorination of TCE. As a rule of thumb, if *cis*-1,2-DCE comprises more than 80 percent of the total DCE, then the DCE is likely of biogenic origin (Wiedemeier and others, 1998). Thus, VC and *cis*-1,2-DCE can be indicators of microbial reductive dechlorination.

Sorption Processes

Sorption refers to the distribution of a solute between the aqueous phase and the solid phase. The solute may be adsorbed onto the surfaces of the solid matrix, or may be absorbed into the interior of the sorbent matrix. Sorption can, therefore, act either to remove solute from solution (adsorption) or to add solute to solution (desorption). These combined adsorption-desorption processes are called *reversible sorption* and can have important effects on the transport of solutes in ground-water systems (Schwarzenbach and Westall, 1981).

When a plume first develops from a newly in-placed contaminant source, the sorptive capacity of the aquifer sediments is largely unfilled; but as solutes migrate away from the source, they tend to adhere to

aquifer sediments and gradually fill the sorptive capacity of the aquifer material. This causes the transport of contaminants to be initially retarded relative to the velocity of ground water. As time passes, however, the sorptive capacity of the sediments is filled, and the effects of retardation become increasingly less evident. The principal effect of sorption on the development of plumes is to delay, or retard, the spread of contaminants; but, contaminant spread is not deterred. The steady-state configuration of plumes (that is, their extent when contaminant delivery from the source is balanced by the sum of the natural attenuation mechanisms) is independent of aquifer sorption. Low sorptive capacity aquifers, however, will reach the steady-state configuration sooner than high sorptive capacity aquifers.

Desorption, the processes by which solutes are released from contaminated aquifer sediments, is an important factor in any remediation effort. When aquifer sediments contain large amounts of contaminant mass in the adsorbed phase, they can continue to be sources of contaminants for long periods of time. This contributes to the contaminant "rebound" effect commonly observed in pump-and-treat remediation systems once the pumps are turned off, and can greatly increase the time needed to effect site cleanup. As a general rule, plumes develop rapidly in low-sorption capacity aquifers and can be remediated rapidly as well. Conversely, in high-sorption capacity aquifers, plumes develop more slowly and take longer to remediate. For these reasons, remediation strategies should include a quantitative evaluation of aquifer sorption capacity.

Measuring Biodegradation Rates

One approach to measuring biodegradation rates is to collect aquifer material, construct either static or flow-through microcosms in the laboratory, and measure the decrease in concentrations of particular compounds, or the production of $^{14}CO_2$ from radiolabeled compounds (Chapelle and others, 1996a). These methods are advantageous in that they can be applied to a wide range of hydrologic systems, because results can be obtained in timeframes of weeks or months, and because abiotic controls can be used to separate biotic from abiotic effects. The laboratory

approach, however, introduces uncertainties due to sediment disturbance and the difficulty of reproducing in situ conditions.

Another approach to measuring biodegradation rates is to track the loss of contaminants along ground-water flowpaths. This approach also is subject to various uncertainties, particularly in separating the effects of microbial processes from abiotic processes, such as hydrodynamic dispersion, advection, and sorption. Uncertainty is associated with estimating contaminant mass from a limited number of data points in a heterogeneous medium.

Microbial utilization of substrates (contaminants) conforms to enzyme saturation (Monod) kinetics according to the Michaelis-Menton equation:

$$V = [v_{max}/K_s + S] (SB), \qquad (11)$$

where V is the rate of substrate uptake (moles per time), v_{max} is the maximum rate of substrate uptake (moles of substrate per time per gram of cells), K_s is the substrate concentration at which $v = \frac{1}{2} v_{max}$ (moles of substrate per liter), S is substrate concentration (moles per liter), and B is the amount of cells (grams). At low substrate concentrations where $S \sim K$ (that is, substrate uptake is not limited by enzyme availability), and when the microbial population is neither increasing or decreasing with time, the Michaelis-Menton equation is approximated by first-order kinetics:

$$V \sim kS, \qquad (12)$$

where k is a rate constant (units of 1/time). In many substrate-limited ground-water systems, first-order kinetics are an adequate approximation of contaminant degradation, and this approach has been widely used to simulate solute transport of organic contaminants. This simplification, however, is not recognized as an appropriate approach for sites with (1) high contaminant concentrations (>1 mg/L; Bekins and others, 1998) where the availability of degradation enzymes is substantially less than the availability of the contaminant; (2) contaminant concentrations that are toxic to microorganisms; (3) more than one substrate that limits microbial degradation rates; and/or (4) increasing or decreasing microbial populations.

One method for estimating biodegradation rates from field data is based on a dispersion model approach (Buscheck and Alcantar, 1995; Chapelle and others,

1996a). This method was originally developed for dissolved BTEX compounds, but can be applied to dissolved chlorinated solvents as well.

The dispersion-model approach assumes that the plume is at steady-state conditions, (that is, the plume is not expanding or contracting with time), and that the equation

$$C(x) = C_o \exp - \left[\frac{-v + \sqrt{v^2 + 4Dk}}{2D} \right] x \qquad (13)$$

describes the exponential decrease in solute concentrations away from a constant source (Chapelle and others, 1996a). The decrease is proportional to ground-water velocity (<), the coefficient of hydrodynamic dispersion (D), and the biodegradation rate constant (k). This solution does not take into account transverse dispersion. The seepage velocity of ground water can be estimated by applying a modification of Darcy's equation, and the coefficient of hydrodynamic dispersion can be estimated from the scale of the plume. Given these estimates, k can be estimated by curve-fitting solutions of equation 13 to field data.

For chlorinated ethenes, this procedure is complicated because TCE, DCE, and VC are produced as daughter products from PCE as well as being degraded. TCE, DCE, and VC concentration changes along a flowpath segment reflect the difference between production and degradation. Thus, for TCE, *cis*-1,2-DCE, and VC, this procedure yields apparent degradation rate constants that underestimate actual degradation rate constants. In addition to underestimating degradation rate constants for daughter products, this method introduces several other sources of uncertainty, including those related to (1) source concentrations, (2) ground-water flow rates, (3) adequate sampling within the plume, and (4) deviations from steady-state conditions within the plume. Although these sources of uncertainty can be reduced by extensive data collection and the use of more sophisticated models, they cannot be entirely eliminated. Because of these uncertainties, it is clear that degradation rate constants obtained with these methods should be regarded as rough estimates.

Sources of Uncertainty in Biodegradation Rate Estimates

Estimating biodegradation rate constants using field data is subject to numerous sources of uncertainty that need to be explicitly considered in any application. These uncertainties include (1) variation of ground-water flow rates, (2) uncertainty in adequately sampling contaminant concentrations within the plume, and (3) deviations from steady-state conditions within the plume. Variation of ground-water flow rates in time and space due to heterogeneity of hydraulic conductivity and hydraulic gradient changes due to recharge events occurs in all shallow aquifers. This is an important source of uncertainty in estimating biodegradation rate constants because an n-fold error in ground-water flow velocity (v) results in an n-fold error in calculated biodegradation rate constant (k) (eq. 13). If variations in ground-water flow with time are large, then the steady-state assumption inherent in equation 13 is not appropriate, and time-dependent solutions of equation 1 must be used (Rifai and others, 1995). Furthermore, if transverse dispersion is substantial in a system, then a two- or three-dimensional treatment of the problem is more appropriate (Weaver and others, 1996). Adequate sampling of contaminant concentrations in a plume can also be a substantial source of uncertainty in evaluating the behavior of chlorinated ethene concentrations (Cherry, 1996). Contaminant concentrations are observed to vary substantially between the "core" and "fringes" of plumes. These variations can substantially affect biodegradation rate estimates.

These procedures clearly show that there are numerous sources of uncertainty inherent in quantifying biodegradation rate constants using field data. Furthermore, many of these uncertainties are difficult or impossible to quantify. Although uncertainties can be reduced by extensive data collection, they cannot be eliminated entirely regardless of the effort expended. For these reasons, biodegradation rate constants and estimates of natural attenuation capacity obtained using these methods should be regarded as estimates.

TIME OF REMEDIATION ASSOCIATED WITH NATURAL ATTENUATION

Summing the Processes that Contribute to Natural Attenuation

In this report, the TOR ($t_{remediation}$) is defined in equation 1 as

$$t_{remediation} \geq [M_o - M_{threshold}]/R_{NA},$$

where M_o is the initial mass of contaminant present in the system, $M_{threshold}$ is the threshold for remaining contaminant mass, which is the remediation goal, and R_{NA} is the rate that natural attenuation removes contaminants from the system. Many factors affect R_{NA} in ground-water systems, including hydrodynamic dispersion, advection, sorption, and biodegradation. These processes can be summed mathematically to give overall concentration changes of a contaminant C with time ($\partial C/\partial t$). Thus, $\partial C/\partial t$ is equal to the sum of hydrodynamic dispersion

$$D\frac{\partial^2 C}{\partial x^2},$$

advection $\quad -v\frac{\partial C}{\partial x}$,

sorption, $\quad -\frac{\rho_b b K_d}{n}\frac{\partial C}{\partial t}$,

and biodegradation $-R^{bio}$, as well as accounting for sources of contaminants leaching from NAPLs, such as petroleum hydrocarbons or chlorinated solvents $+ R^{NAPL}$. When these source and sink terms for a contaminant C are summed, they give a mass-balance equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho_b K_d}{n}\frac{\partial C}{\partial t} - R^{bio} + R^{NAPL}, \quad (14)$$

where

C = aqueous concentration of contaminant (ML^3),

t = time (T),

x = distance (L),

D = coefficient of hydrodynamic dispersion (L^2T^{-1}),

v = average linear pore velocity of ground water (LT^{-1}),

ρ_b = bulk density of the porous medium (dimensionless),

K_d = an equilibrium sorption coefficient (dimensionless),

n = porosity (dimensionless),

R^{bio} = removal of contaminant due to biodegradation, and

R^{NAPL} = addition of contaminant dissolving from NAPL,

which describe the transport of a contaminant. Equation 14 has been widely used to assess natural attenuation processes (Newell and others, 1996), and is useful for (1) assessing the natural capacity of an aquifer system to attenuate contaminants, (2) estimating the distance a contaminant plume will migrate from a source, (3) estimating the time a contaminant plume will take to develop from a source or the time it will take for a contaminant plume to collapse once a source is removed, and (4) estimating the time it will take for a NAPL source to dissolve and dissipate. Each of these applications have specific uses and will be discussed in detail.

Natural Attenuation Capacity

The concept of "assimilative capacity" is well known in soil science (Charbeneau and Daniel, 1993, p. 15.1) and surface-water hydrology (Chapra, 1996, p. 11) and refers to the capacity of a system to absorb and/or transform pollutants to innocuous byproducts. By analogy, a "natural attenuation capacity" can be defined for ground-water systems as being the ability to lower contaminant concentrations along aquifer flowpaths.

In surface-water systems, assimilative capacity depends upon hydrologic (streamflow, mixing, and hydrodynamic dispersion) and biological (biological oxygen demand) factors, and is assessed using analytical or digital water-quality models. Similarly, the natural attenuation capacity of ground-water systems depends upon hydrologic (dispersion and advection) and biological (biodegradation rates) factors that can also be assessed using quantitative models. As discussed previously, the sum of dispersive, advective, sorptive, and biodegradative processes acting on a solute in a one-dimensional flow system is given by equation 14.

Appropriate procedures for solving equation 14 depend on the ground-water system in question and the specific problems being addressed. When a contaminant plume has reached approximate steady-state conditions (that is, the plume is not expanding or

contracting with time and MC/Mt=0), the sorption term becomes small relative to the other three terms, and the solute-transport equation simplifies to the ordinary differential equation:

$$D\frac{d^2C}{dx^2} - v\frac{dC}{dx} - kC = 0 \qquad (15)$$

For boundary conditions of C = C$_0$ at x = 0, and C = 0 as x $\rightarrow \infty$, equation 15 has the particular solution:

$$C(x) = C_o\exp-\left[\frac{-v + \sqrt{v^2 + 4Dk}}{2D}\right]x \qquad (16)$$

Equation (16) indicates that the steady-state solute concentration decrease away from a constant source is dependent on hydrodynamic dispersion (D), the biodegradation rate constant (k), and ground-water pore velocity (<). With this usage, a positive value of k indicates contaminant loss. The slope of the steady-state solute concentration profile along a flowpath is proportional to the value of:

$$-\left[\frac{-v + \sqrt{v^2 + 4Dk}}{2D}\right] \qquad (17)$$

The term *natural attenuation capacity* (abbreviated NAC), as used in this report, refers to the quantity given in equation 17, which has units of inverse length (L^{-1}). Conceptually, it may be thought of as the contaminant-lowering capacity of an aquifer per unit length (feet or meters) of flowpath.

The concept of natural attenuation capacity as defined in equation 17 is useful because it illustrates those characteristics of a hydrologic system that affect the efficiency of natural attenuation. For example, if the biodegradation rate constant is small (~0.001 d^{-1}) relative to the ground-water velocity (about 1 ft/d) and aquifer dispersivity (10 ft), the NAC of the system also will be small (0.009902 ft^{-1}). Because of this small NAC, contaminants will be transported relatively long distances downgradient of a source area (fig. 5). Conversely, if the biodegradation rate constant is high (0.01 d^{-1}) relative to ground-water velocity (0.2 ft/d) and aquifer

dispersivity (1 ft), the NAC will be proportionally higher (0.0477 ft^{-1}) and the transport of contaminants will be restricted closer to the source area (fig. 5). More quantitatively, NAC can also be useful in providing estimates of the distance of plume stabilization, given different contaminant concentrations at the source area. This, in turn, can provide estimates as to what contaminant concentration at the source area is required to meet a regulatory goal at a given distance downgradient.

Distance of Stabilization

The distance that contaminants are transported in a ground-water system depends on the NAC and the contaminant concentrations at the source area. This distance, termed the distance of stabilization (DOS), can be estimated by solving equation 16 for distance (x), yielding

$$(ln\ C_o/C)/NAC = x, \qquad (18)$$

where NAC is given by equation 17. Thus, given a target concentration C, an initial source-area concentration C$_o$, and the NAC of an aquifer, the distance it will take for the aquifer to lower contaminant concentrations to the target C [usually maximum concentration levels (MCLs), which are established by regulatory agencies (U.S. Environmental Protection Agency, 1991)] can be calculated directly from equation 18.
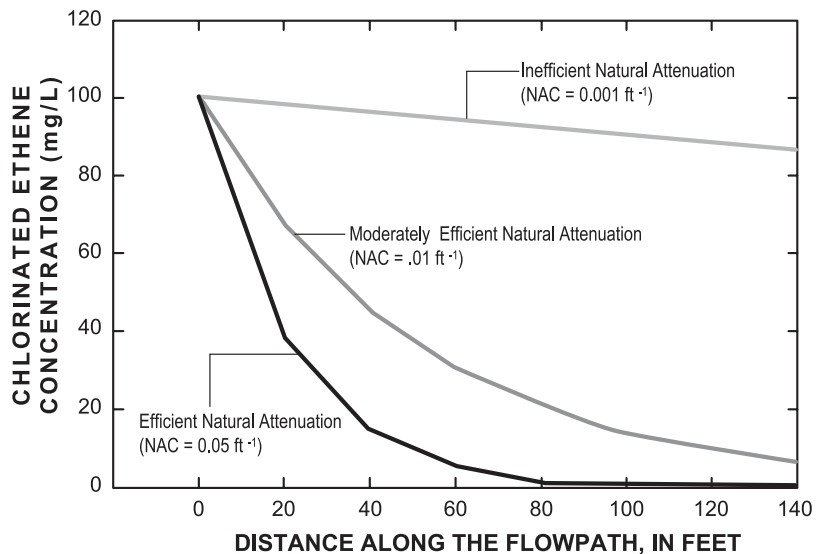

Figure 5. Effects of natural attenuation capacity on contaminant concentration declines along ground-water flowpaths.

This reasoning identifies two ways in which the NAC of a ground-water system can be used to achieve site remediation. The first depends on whether the NAC is sufficient to achieve plume containment without additional remediation procedures. In this case, monitored natural attenuation may be an acceptable stand-alone remedial strategy. In many other cases, however, the NAC may not be sufficient as a stand-alone remediation strategy. In those cases, engineering methods (for example, excavation, in situ chemical oxidation, and in situ bioremediation) need to be used to lower source-area concentrations to levels where the NAC present in the aquifer can lower contaminant concentrations to MCLs at a given point of compliance. This methodology is consistent with recent USEPA guidance, which has stressed that natural attenuation is usually appropriate when used in conjunction with engineered reduction of contaminant sources:

> "In the majority of cases where monitored natural attenuation is proposed as a remedy, its use may be appropriate as one component of the total remedy, that is, either in conjunction with active remediation or as a follow-up measure" (U.S. Environmental Protection Agency, 1999, p. 1).

The manner in which natural attenuation and active remediation measures (such as source removal, pump-and-treat, chemical oxidation, or enhanced bioremediation) are combined depends in part on the distance to stabilization given by equation 18.

Time of Stabilization

Distance of stabilization calculations are useful for estimating the maximum extent of a contaminant plume, and estimating maximum allowable source-area concentrations. These steady-state solutions, however, do not provide any indication of how long it takes for the plumes to reach steady state. The time of stabilization (TOS) is often an important regulatory consideration. This problem can be addressed using time-dependent solutions of equation 14. Analytical solutions to equation 14 have been found for a several sets of initial and boundary conditions. For the case of a semi-infinite aquifer with a constant source, a time-dependent solution for equation 14 is given by Domenico (1987). This solution makes it possible to evaluate some of the factors affecting TOS.

First, it may seem intuitively obvious that the higher the NAC, the faster a plume would come to stabilization. Application of the analytical solution for a hypothetical chlorinated ethene case (fig. 6A), however, shows that this is not the case. In fact, this plot shows that as NAC increases, TOS remains constant. Thus, although NAC greatly affects the *distance* that a plume will migrate, it does not affect the *time* it will take the plume to stabilize. Secondly, it seems intuitively reasonable that the closer the target contaminant concentration C is to the initial contaminant concentration C_o, the shorter the TOS. Again, however, application of the analytical solution shows that this is not the case. Figure 6B shows that the predicted TOS does not vary with different ratios of C/C_o, which reflects the exponential nature of the biodegradation kinetics used to simulate plume stabilization.

Sorption processes, however, do have an important effect on the time to stabilization. Figure 6C shows a plot of TOS and percent organic matter in the aquifer (the greater the percentage of organic matter, the higher the sorption coefficient). As the organic matter content of the aquifer increases and, thus, the sorptive capacity of the aquifer increases, the predicted time to stabilization increases dramatically. This is a general result. The sorptive capacity does not affect the *distance* of stabilization, but it has a large effect on the *time* of stabilization. Time to stabilization is also affected by contaminant type. Figure 6D indicates a plot of TOS and organic matter content for MTBE, benzene, and TCE. The results indicate that the stabilization time of MTBE, the least strongly adsorbed compound, is the least affected by organic carbon content. Stabilization times of TCE and benzene, on the other hand, are progressively more affected by aquifer organic carbon content. Based on these results, TOS seems to be most affected by aquifer organic content (sorptive capacity) and by contaminant type (which also affects sorptive capacity). Some qualitative judgments about times of remediation are possible just by considering the observable properties of the aquifer and contaminants in question.

Time of Nonaqueous Phase Liquid Dissolution

The preceding analyses of aquifer properties that affect DOS and TOS are based on analytical solutions of equation 14 for generalized conditions that treat contaminants as a point source of constant concentration. In reality, aquifers are most commonly
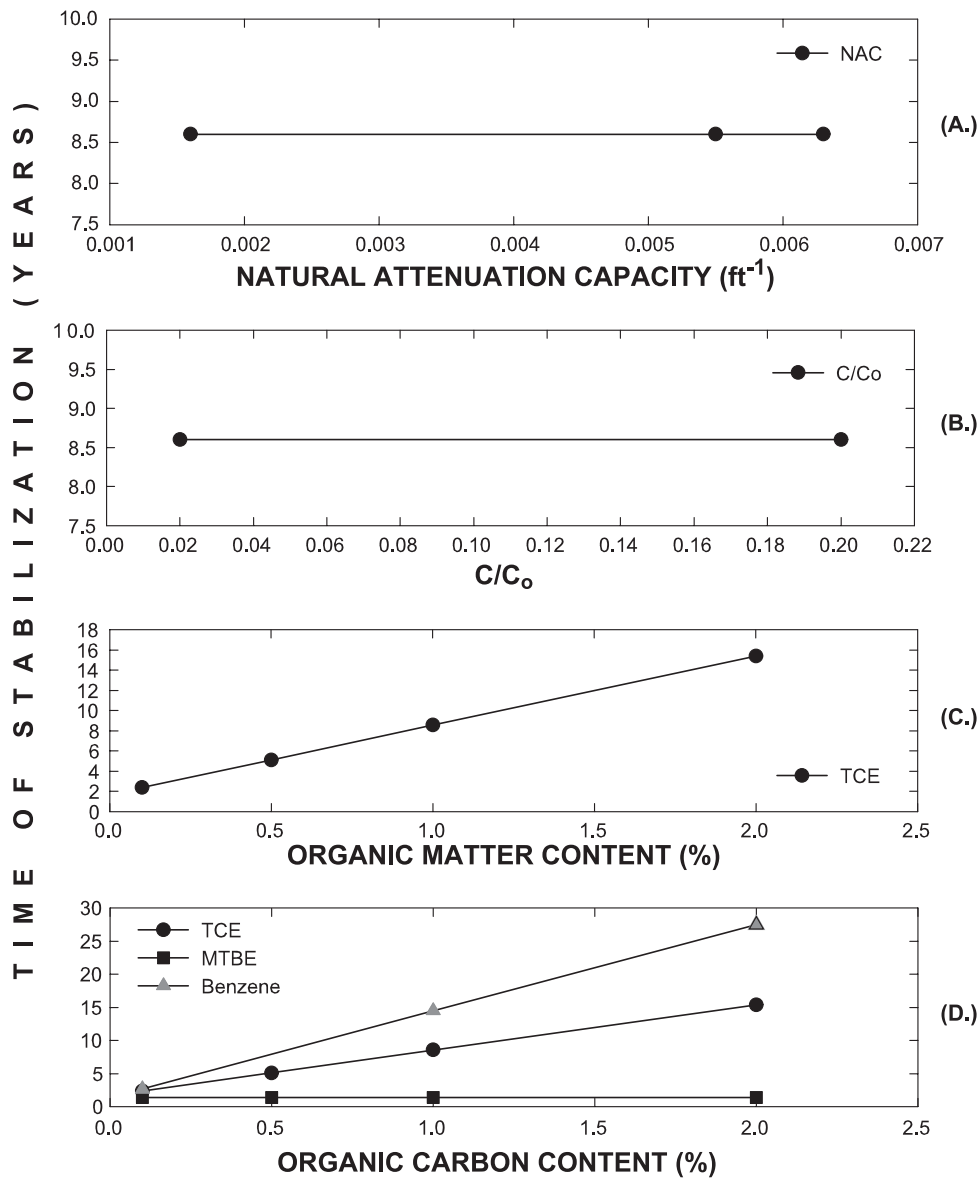
Figure 6. Effects of (A) natural attenuation capacity, (B) initial contaminant concentration, (C) organic matter content of aquifer material, and (D) contaminant composition on times of stabilization.

contaminated by petroleum hydrocarbons and/or chlorinated ethenes that seep into the aquifer as NAPLs. When a large amount of NAPL is present, the behavior of contaminant plumes that develop can be approximated by the constant source assumption. In reality, however, the ultimate TOR depends on how rapidly NAPL dissolved and how rapidly the dissolved constituents are attenuated. Thus, realistic estimates of TOR require a quantitative treatment of NAPL behavior.

The dissolution and biodegradation of NAPL cannot be treated realistically by simple analytical

solutions to equation 14. Rather, the more flexible boundary and initial conditions made possible by numerical solutions are required. In this report, the numerical model SEAM 3D (Waddill and Widdowson, 1997) is used to estimate NAPL dissolution rates. The treatment of NAPL in SEAM 3D follows that of Imhoff and others (1993), and is based on the concept that the driving force for NAPL dissolution is the difference between the actual aqueous concentration of a solute (S_{ls}) and the aqueous concentration of a solute in equilibrium with a given NAPL (S_{ls}^{eq}). The NAPL source term in equation 14 is given by:

$$R_{Source,ls}^{NAPL} = max[0, k^{NAPL}(S_{ls}^{eq} - S_{ls})], \qquad (19)$$

where $R_{Source,ls}^{NAPL}$ is the solute concentration at the source used in equation 14, k^{NAPL} is the dissolution rate of the NAPL, and $(S_{ls}^{eq} - S_{ls})$ is the difference between the equilibrium concentration of a solute in equilibrium with NAPL and the actual concentration at any given time. The equilibrium concentration of solute (S_{ls}^{eq}) can be calculated from Raoult's law as:

$$(S_{ls}^{eq}) = f_{ls}(S_{ls}^{sol}),$$

where f_{ls} = mole fraction of the solute, and S_{ls}^{sol} = solubility of the solute. With each timestep of the model, S_{ls}^{NAPL} is updated as

$$\frac{dS_{ls}^{NAPL}}{dt} = \frac{n}{\rho_b}R_{source, ls}^{NAPL}. \qquad (20)$$

This treatment allows simulation of a given mass of NAPL in an aquifer, contained within a specified volume of aquifer, that is acted on by given hydrologic conditions. Furthermore, this treatment allows the calculation of contaminant concentration due to NAPL dissolution at any point in the model domain. For the purposes of this report, the term "time of NAPL dissolution" refers specifically to the time required to lower *aqueous* phase contaminants associated with a NAPL source below a given threshold directly downgradient of the NAPL. This definition is adopted because the ability to directly measure NAPL mass is technically difficult and subject to numerous uncertainties. On the other hand, measuring aqueous concentrations of contaminants directly downgradient of a NAPL source area is much easier to accomplish.

By using the mathematical treatment described above, some factors that affect the time of NAPL dissolution can be illustrated. Clearly the most important factor is the mass of NAPL present in the aquifer. For a given NAC (0.0093 ft^{-1}), the TOR calculated with SEAM 3D varies almost linearly with respect to mass of contaminant (fig. 7A). This behavior reflects the progressive dissolution of NAPL (eq. 20), because dissolution occurs at the surface of the NAPL body. Also, the rate of NAPL dissolution varies in

proportion to rates of ground-water flow. For example, for a NAPL mass of 200 lbs and a rate of ground-water flow of 100 ft/yr, time of NAPL dissolution is about 33 years (fig. 7A). If the rate of ground-water flow is decreased by a factor of 2 to 50 ft/yr, then the time of NAPL dissolution increases by a factor of 2 to 62 years (fig. 7A).

Time of NAPL dissolution is also affected by the dimensions of the NAPL body. For example, if a NAPL body 20 ft long and 10 ft wide has a thickness of 10 ft, a NAPL mass of 10 lbs would have a time of dissolution of about 37 years. Assuming, however, the thickness is decreased to 1 ft, the time of dissolution increases to 76 years (fig. 7B). Note also that as the NAPL thickness decreases, the more curvilinear the relation between NAPL mass and the time of dissolution becomes (fig. 7B). This reflects the surface area of NAPL subjected to dissolution (fig. 7B). This kind of analysis also indicates that time of dissolution is relatively unaffected by NAC, the organic matter content of the aquifer, and the kind and amount of electron acceptors available. These factors greatly affect the length of plume stabilization and the time of plume stabilization (fig. 6), but not the time of NAPL dissolution. This happens because natural attenuation mechanisms (principally biodegradation) operate more effectively on dissolved constituents than on NAPL. Thus, whereas the size of the plume emanating from a NAPL source, and the time to stabilization of that plume is highly dependent on NAC and aquifer organic matter content, respectively, the time of NAPL dissolution is more dependent on NAPL mass, NAPL geometry, and ground-water flow rates (fig. 7).

TIME OF REMEDIATION SOFTWARE

The TOR problem, as developed in preceding sections, can be logically divided into (1) distance of plume stabilization, (2) time of plume stabilization, and (3) time of NAPL dissolution problems (fig. 1). Each of these issues can be addressed using particular solutions of the TOR equation (eq. 14), which can be developed according to specific needs. In this report, software was developed based on useful (but limited) solutions to equation 14 to address these three classes of TOR
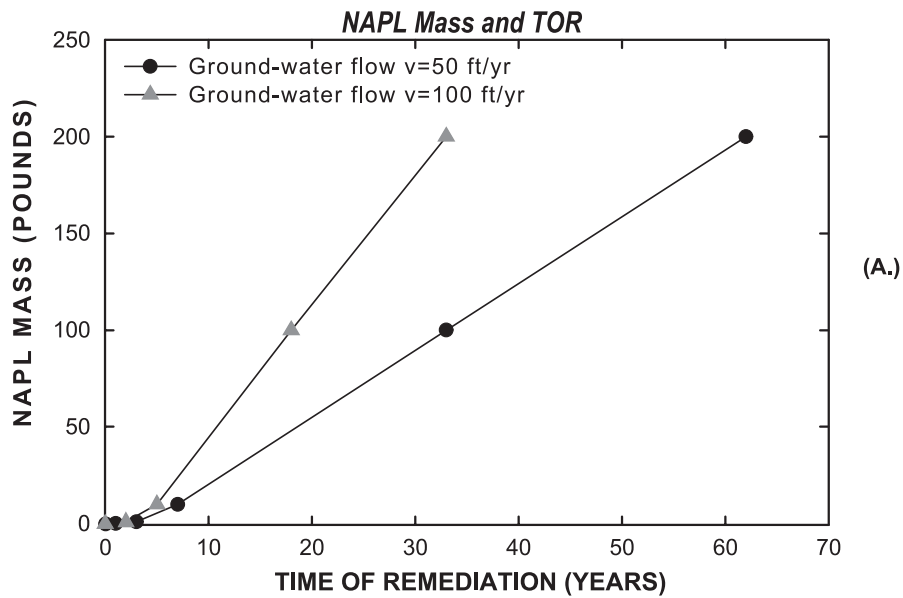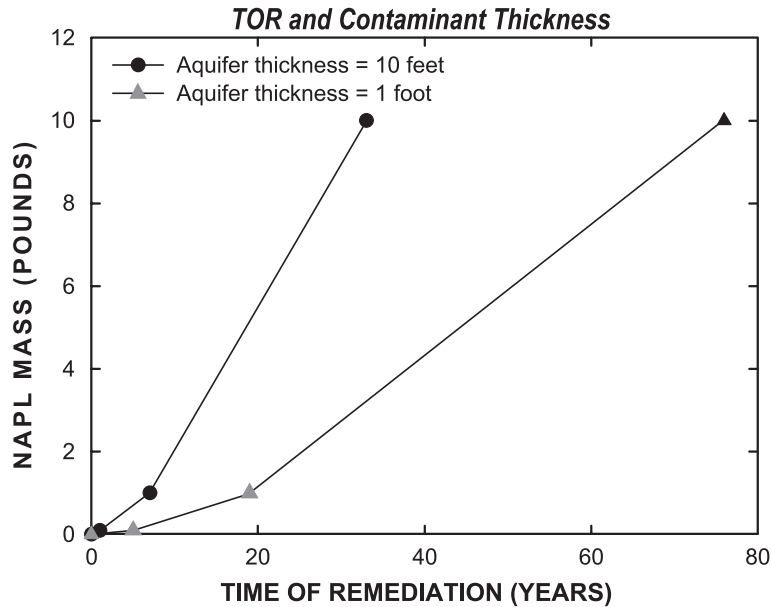
Figure 7. Time of nonaqueous phase liquid (NAPL) dissolution versus (A) NAPL mass, and (B) NAPL mass in differing aquifer thickness.

problems. The software was designed to aid the user in assembling and organizing the data needed to make TOR estimates, to obtain appropriate and useful solutions of the TOR equation, and to illustrate the various uncertainties inherent in TOR estimates. The software, termed Natural Attenuation Software (NAS), is meant to be used as a tool to assist hydrologists in making TOR estimates. No attempt has been made to make NAS applicable to all, or even most, TOR problems. Rather, NAS is designed around numerous simplifications of hydrologic, microbial, and geochemical processes that, although convenient, will introduce unacceptable error to some problems. The NAS software can be downloaded from the Web site http://www.cee.vt.edu/NAS/ (accessed February 29, 2003).

Overview of Natural Attenuation Software

The NAS tool is designed for application to ground-water systems consisting of porous, relatively homogeneous, saturated media, such as sands and gravels, and is designed specifically for petroleum hydrocarbon and chlorinated ethene contaminants. First, detailed site information about hydrogeology, redox conditions, and contaminant concentrations must be entered. NAS cannot be applied without extensive site characterization, and the software is intentionally designed to require these data before the analysis can proceed. If the data that NAS requires are not available, then TOR estimates cannot and should not be made.

A flowchart describing how the NAS software can be used to address TOR questions is shown in figure 8. After data entry, NAS estimates site-specific ground-water flow rates, biodegradation rates, and sorption properties. Based on these estimates, NAS then produces either analytical or numerical solutions of the TOR equation. The analytical solutions are specific to plume concentration questions, such as what is the DOS for given source-area contaminant concentrations, and what is the TOS if source-area concentrations are changed. For the DOS question, NAS calculates what the maximum source-area
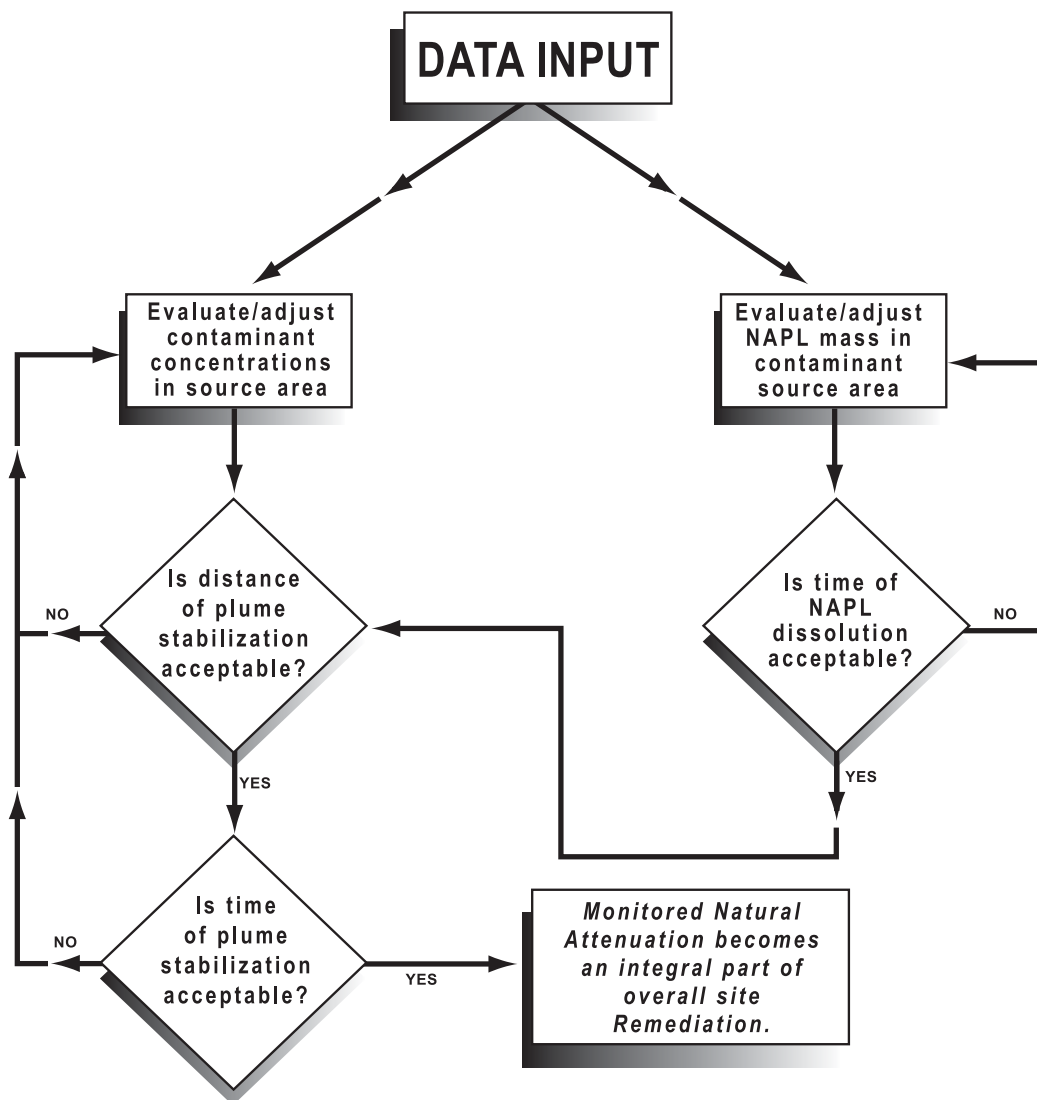
Figure 8.   Flowchart showing how NAS can be applied to time of remediation problems.

concentration that can be allowed, based on a regulatory maximum concentration level at a given point downgradient of the source. Then, NAS estimates how long it will take for the plume to reach the lower steady-state configuration once source-area concentrations have been lowered by engineering methods. When the DOS and the TOS are acceptable, based on site-specific regulatory criteria, MNA can become an integral component of site remediation (fig. 8).

In the case of NAPL contaminants, either chlorinated solvents or petroleum hydrocarbons, NAS uses the SEAM 3D code (Waddill and Widdowson, 1997) to solve equation 14. The solution provided by NAS is tailored to estimate the length of time required by a given NAPL mass to dissolve and lower contaminant concentrations at the source area below a given user-supplied threshold. In principle, the numerical solution could then be used to estimate the distance of stabilization for the remaining residual concentration. Because this would substantially lengthen the amount of time required to make a simulation, however, this is not presently practical for distance and TOS problems. Rather, once the NAPL time to remediation calculation is completed, aqueous contaminant concentrations derived from the time of NAPL dissolution analysis can be used to make DOS and TOS estimates using the analytical solution (fig. 8).

Data Requirements and Input Using Natural Attenuation Software

When the NAS package is opened, the user can begin by clicking the button "Start a Project" (fig. 9A). This opens a dialog box in which the user can provide the facility and site names, and other appropriate information. The first task is to select the units to be used. Once the units are entered, a "next" button pops up that allows the user to move ahead. Throughout the program, the user is not allowed to move to the next step until the required information is entered. The next dialogue box queries the user as to the nature of the contaminants (petroleum hydrocarbons or chlorinated ethenes). If petroleum hydrocarbons are selected, the user has the option of considering MTBE and naphthalene in addition to BTEX compounds. If chlorinated ethenes are selected, the user must specify whether PCE or TCE is the source compound. NAS can be applied to mixes of petroleum hydrocarbons and chlorinated ethenes, but only by considering these classes of compounds in separate simulations.

After the contaminants have been properly identified, NAS returns to the main menu, illuminates the "Enter Site Data" button, which the user can click to open a dialogue box to enter site data. Hydraulic conductivity is entered as a range of values for maximum, average, and minimum (fig. 9B); the range of values at each site can be determined by hydraulic testing in the field (Bouwer, 1989). Similarly, values of hydraulic gradient are input as a range of values to accommodate variability of hydraulic gradient at a site and is a major source of uncertainty in estimating remediation times. Hydrogeologic data entry is completed by entering values for site porosity, aquifer thickness, and percent organic matter (fig. 9B). The percent organic matter (loss on ignition) is needed to estimate the sorptive capacity of aquifer material.

The next site data required by NAS is contaminant-concentration data from along the axis of the plume. First, NAS queries the user about the sampling date and the number of wells available along the centerline of the plume. The user then creates a data table for each well, and inputs the well identifiers, the distance along the flowpath for each well, and contaminant concentrations. After these data are entered, NAS queries the user for redox chemistry data about the site. These data can be added for the same wells used for contaminant concentrations, or other wells can be used. The user then is queried about what redox measurements are available, and creates a table for data entry. NAS follows a flowchart similar to figure 4 to identify predominant redox processes. If the data indicate an ambiguous redox diagnosis (as commonly happens), then NAS will query the user to make the determination directly. A redox diagnosis must be made for NAS to continue. Because biodegradation rates are redox-dependent, NAS includes the capability for determining different biodegradation rates for different redox zones and is capable of considering up to four different redox zones that contain four different rates of biodegradation. NAS requires contaminant data from at least three wells in a given redox zone to assign zone-specific biodegradation rates.

Following redox data entry, NAS produces a summary of the data for the user to view. In addition, NAS uses the data to estimate biodegradation rates (based on contaminant concentration changes along the flowpath), redox zonation (based on redox chemistry
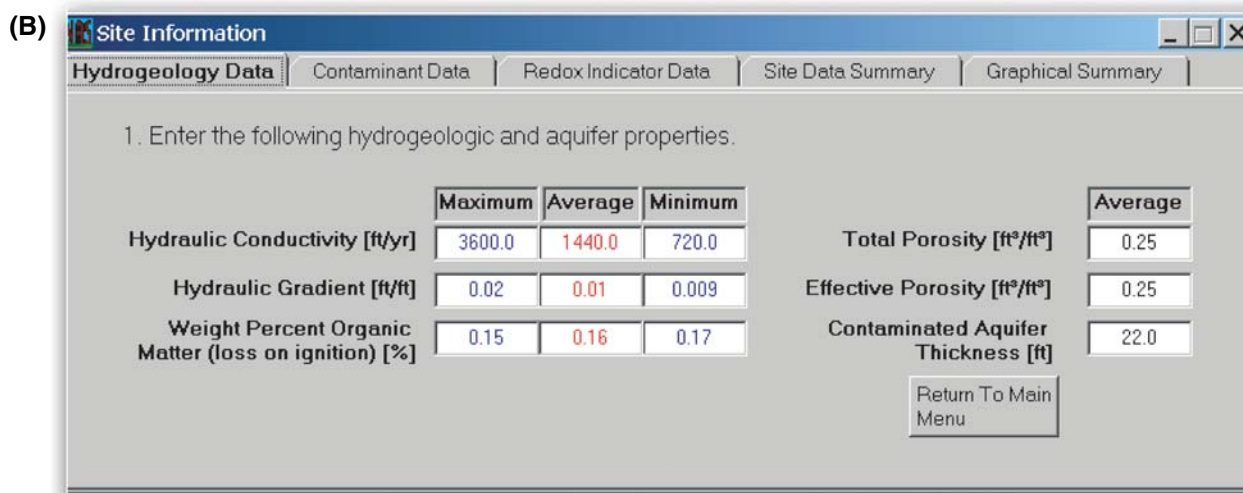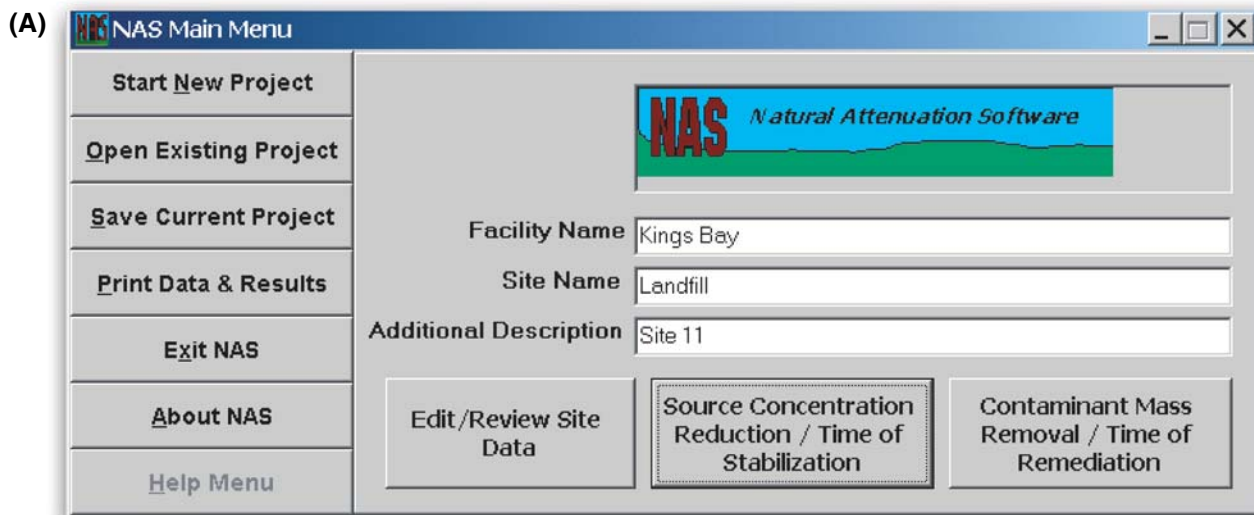
Figure 9. Initial computer screens of (A) NAS and (B) the hydrogeology data entry of NAS.

data), and sorption parameters (based on contaminant type and organic matter content). When the user returns to the main menu, the buttons for "Source Concentration Reduction/Time of Stabilization" and "Contaminant Mass Removal/Time of Remediation" are illuminated. The "Time of Stabilization" button activates the analytical solutions. NAS then asks the user to input the distance between the contaminant source and the relevant point of contact (POC) at the site. When the POC is provided, NAS queries the user to input the width of the contaminant source. When the source width is provided, NAS queries the user to input the regulatory compliance concentration (RCC) at the POC. This is usually the MCL for contaminant of concern. When the user clicks the "calculate" button, NAS displays the maximum, best-estimate, and

minimum TOS (fig. 10A). In addition, NAS displays the target source-area concentration (the maximum concentration allowable at the source for natural attenuation to lower contaminants below the RCC at the POC). By clicking the "graphical view" button, the solutions can be displayed visually (fig. 10B).

By returning to the main menu, the user can proceed to time of NAPL-based time of NAPL dissolution calculations. This part of NAS uses a numerical solution (SEAM 3D) of the TOR equation to make these estimates. When the "Contaminant Mass Removal/Time of Remediation" button is clicked, the user is queried about the length (length is perpendicular to the direction of flow) and width (width is parallel to the direction of flow) of the NAPL body. When these dimensions are entered, the user is then queried about
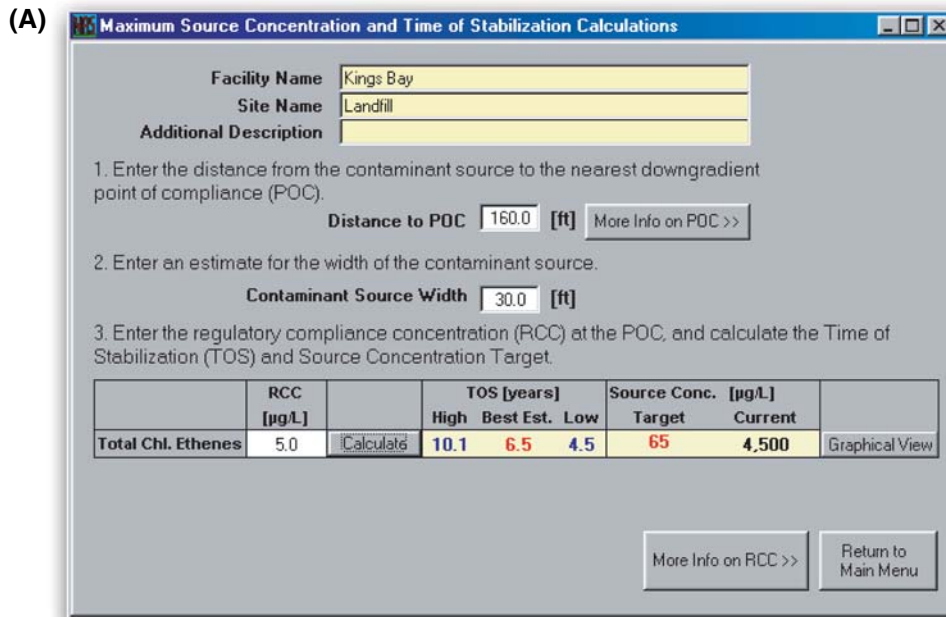
(A)

(B)
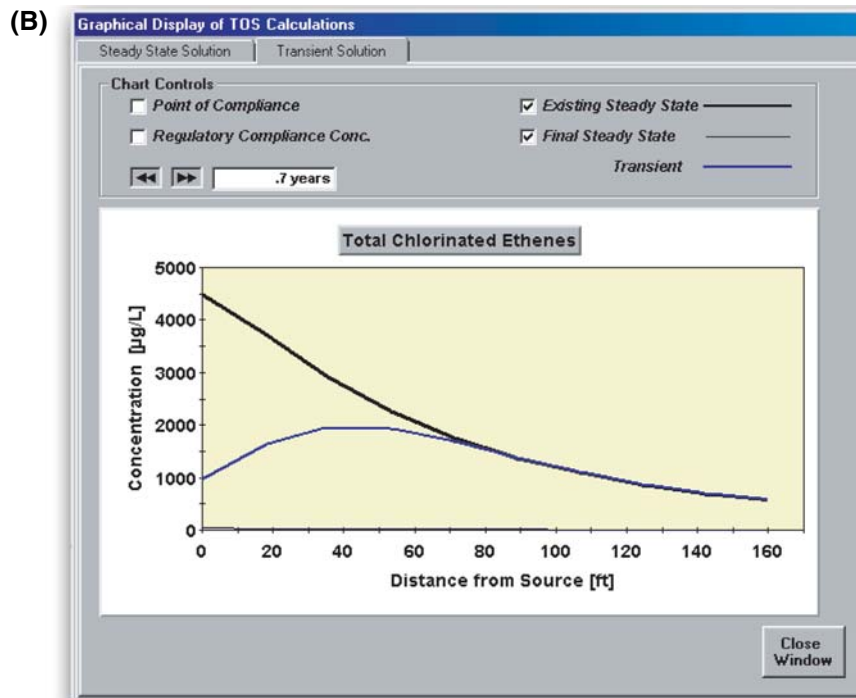
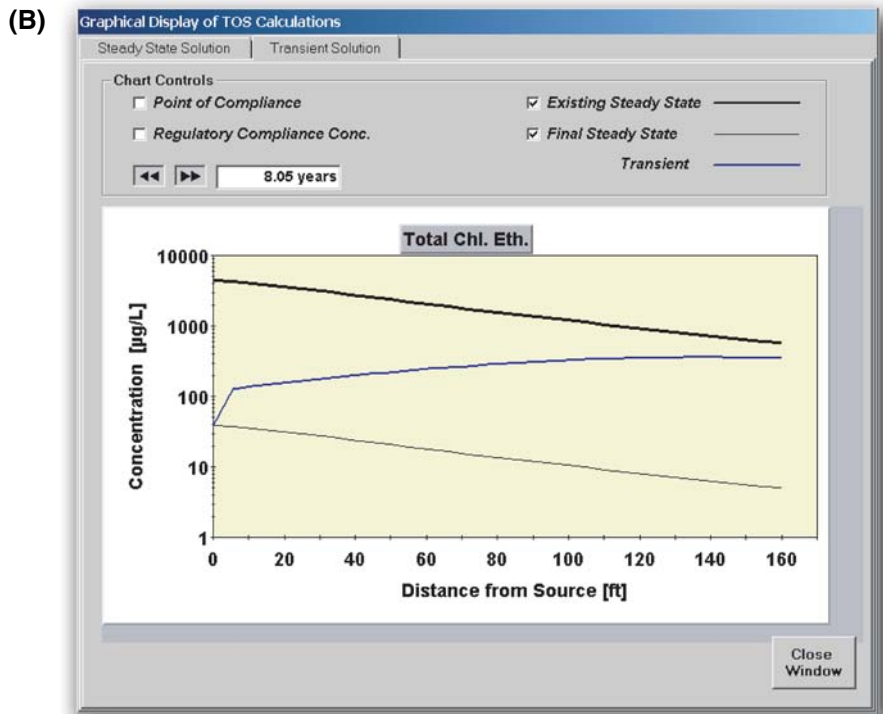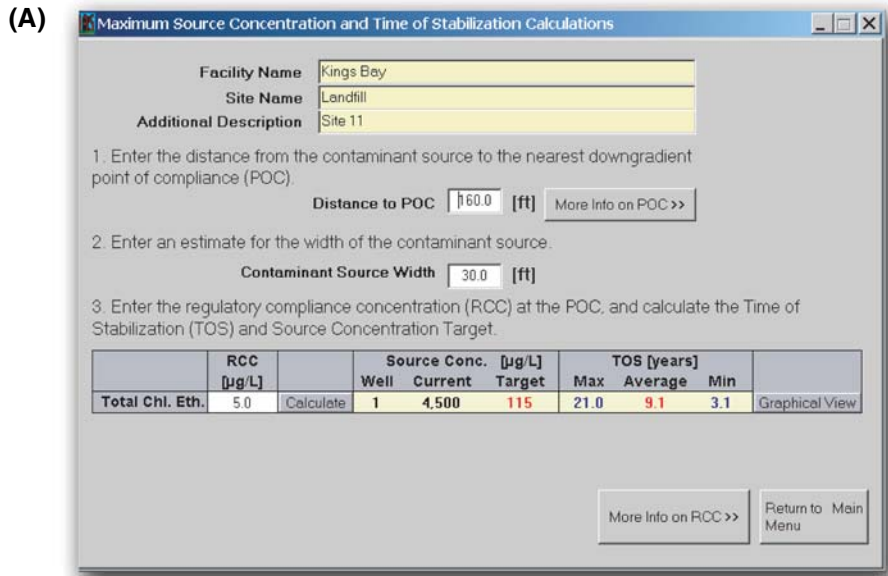**Figure 10.** NAS computer screens of (A) distance and time of stabilization, and (B) graphical representation of time-of-stabilization calculations.

the thickness of the NAPL body and the percentage of contaminants present in the NAPL. When this information is provided, NAS queries the user to enter the electron acceptors present at the site, including oxygen, NO_3, bioavailable Mn (if data are available), bioavailable Fe(III) (if data are available), and SO_4. Once the electron acceptor data are provided, the user may move to the next screen, which asks for the

amount of NAPL present in the source area. The user can specify a single mass or a range of mass estimates. NAS then asks for the mass removal options being considered, which range from no removal to complete removal (although complete removal obviates any additional TOR calculation). The user can specify a simulation time of up to 100 years (any simulation time longer than 100 years is considered to have too many

(A)

(B)

Figure 10. (Continued) NAS computer screens of (A) distance and time of stabilization, and (B) graphical representation of time-of-stabilization calculations.

potential sources of error to be meaningful in the context of the NAS tool), and run the simulation by clicking the "Execute TOR Calculation" button, which runs the SEAM 3D model with the NAPL package; the simulation can take several minutes. After the solution(s) have been calculated, the user is asked to specify an aqueous contaminant concentration level that represents site remediation. NAS then returns the length of time needed to reach that remedial goal (fig. 11).
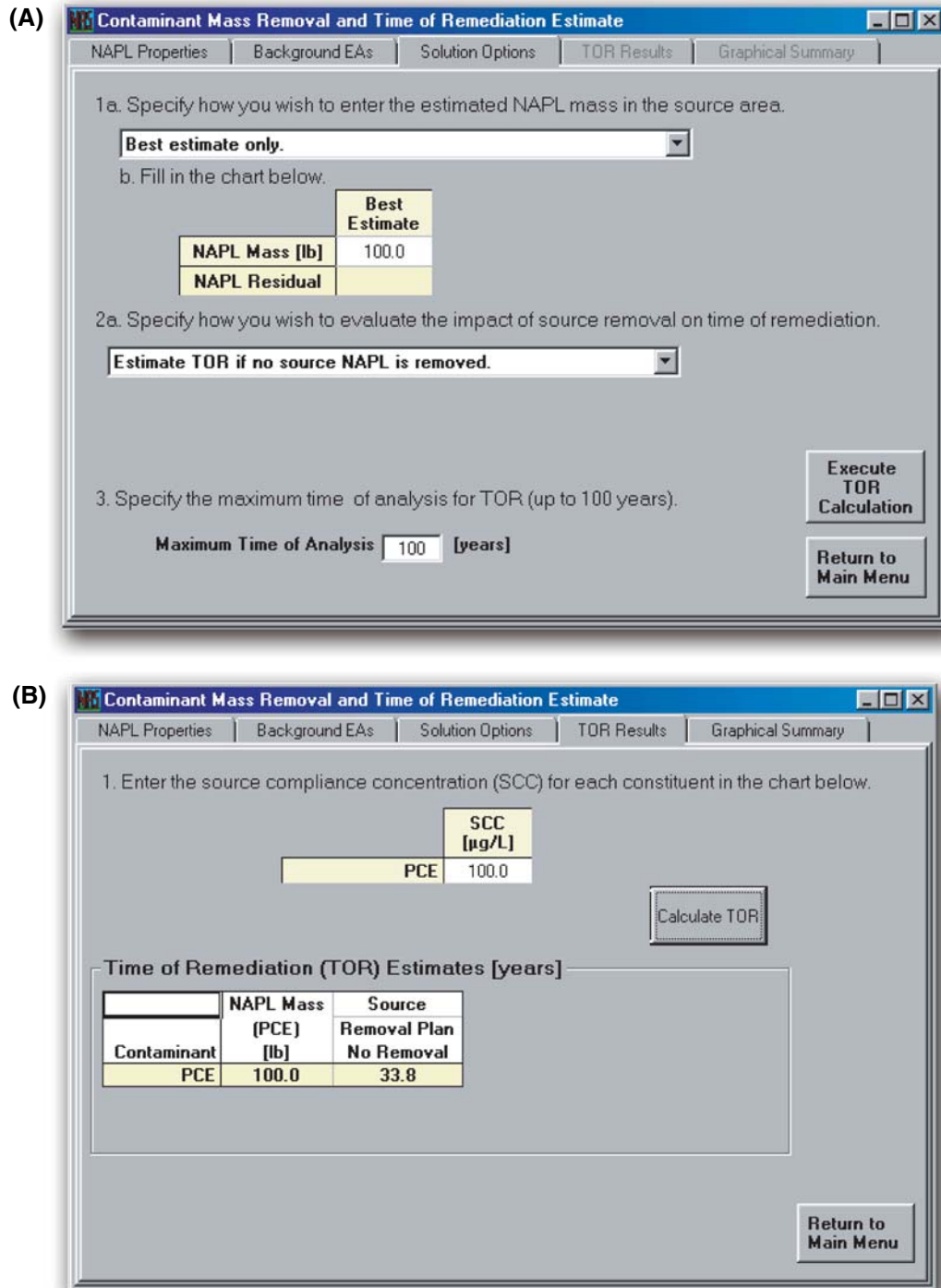
Figure 11. NAS computer screens of (A) data input for nonaqueous phase liquid time-of-dissolution calculations, and (B) example of time-of-dissolution results.

TIME OF REMEDIATION EXAMPLES

The TOR methodology was applied to two sites at Naval Facilities because of the substantial regulatory interest in evaluating times of plume stabilization/NAPL remediation at each site. Furthermore, the U.S. Geological Survey conducted data-collection activities at each of these sites. TOR assessments were performed for petroleum hydrocarbon releases at the Laurel Bay site, Marine Corps Air Station, Beaufort, S.C., and chlorinated ethene releases at Naval Submarine Base, Kings Bay, Ga.

Gasoline Nonaqueous Phase Liquid Example: Laurel Bay, South Carolina

The Laurel Bay site in Beaufort, S.C., is a U.S. Geological Survey Toxic Substances Hydrology Program research site (Landmeyer and others, 1998) located in the lower Coastal Plain physiographic province, which is underlain by fine-grained, well-sorted sands of aeolian origin. The site is an active gasoline station at the Marine Corps Exchange. In 1991, a leak was discovered in one of the underground gasoline storage tanks. The leaking tanks were removed along with substantial quantities of contaminated aquifer sediments in accordance with State guidelines (South Carolina Department of Health and Environmental Control, 1995). In 1993, the U.S. Geological Survey began to assess the migration of contaminants in the ground-water system. By 1996, a well-developed plume of BTEX- and MTBE-contaminated ground water had developed at the site.

The physical layout of the site, ground-water levels, and the locations of monitoring wells are shown in fig. 12. As is commonly the case at such sites, most of the monitoring wells were placed at locations that helped delineate the size and shape of the plume. As such, only a few wells are actually located in the centerline of the plume and, therefore, useful for estimating biodegradation rates. Contaminant-concentration data from wells outside the plume centerline can be a major source of error when estimating biodegradation rates, and such data should be avoided. As of 1996, five wells (1, RW, MSL-1, 8, 19, and 21) were located in the central part of the plume oriented along the direction of ground-water flow (fig. 12). Of these five wells, two (1 and RW) are located in the NAPL source area. The potentiometric map shows a major discontinuity in ground-water

levels near the downgradient ditch that is the discharge area for the local flow system. The rapid change of water elevation near the ditch causes the flow to accelerate as it approaches the ditch. As such, flow velocities in the upgradient part of the system are lower than in or near the ditch. As a result, and because NAS assumes a constant velocity, only wells upgradient of the potentiometric discontinuity were used to estimate biodegradation rates in NAS.

Contaminant and redox data collected at the Laurel Bay site were used as input into NAS and are summarized in figure 13. Also shown in figure 13 are the estimated biodegradation rates for benzene, toluene, ethylbenzene, xylene, MTBE and total BTEX, as well as the natural attenuation capacity of the aquifer for these compounds, as calculated by NAS. The calculated biodegradation rates, although similar to rates observed at other gasoline spill sites (Weidemeier and others, 1996), are relatively low. The estimated biodegradation rate for MTBE in particular is very low at the Laurel Bay site, and is consistent with laboratory studies of MTBE biodegradation in sediments conducted at this site (Landmeyer and others, 1998). Largely because of these low biodegradation rates, the natural attenuation capacity of the aquifer is similarly low—only 0.0061 ft^{-1} for total BTEX (fig. 13B).

Maximum source-area concentration and TOS estimates given by NAS are shown in figure 14. Given the low NAC of the system, NAS estimated that the target source-area concentrations required to biodegrade contaminants below regulatory thresholds prior to discharge at the downgradient drainage ditch are fairly low; concentrations are 758 µg/L for total BTEX, 168 µg/L for benzene, and 2,362 µg/L for MTBE. NAS also estimated that it would take between 4.1 and 6.2 years for the plume to stabilize to these lower source-area concentrations if a removal action were undertaken.

These estimates cannot be directly verified at the Laurel Bay site because, although some sediment excavation occurred during tank removal, the excavation did not remove all of the gasoline-contaminated sediments. Predicted benzene concentrations based on time-of-stabilization estimates were compared to measured concentration declines of benzene in the plume. Figure 15 shows predicted concentration declines in well MW-8, assuming a complete source-removal action in 1994 compared to measured concentrations of benzene taken between 1994 and 2000. Interestingly, measured concentration
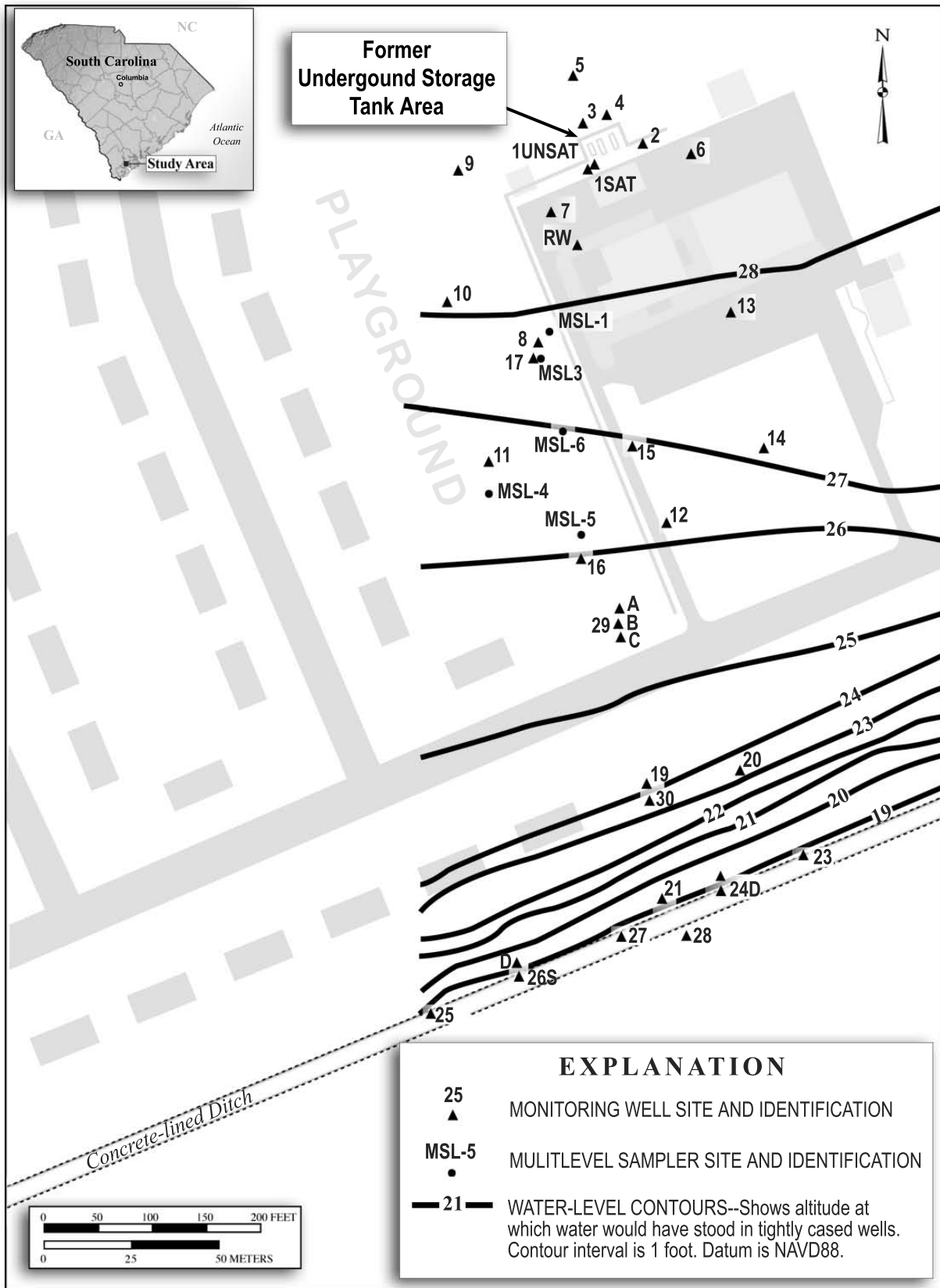
Figure 12. Site map, locations of observation wells, and potentiometric surface of the Laurel Bay site, South Carolina.
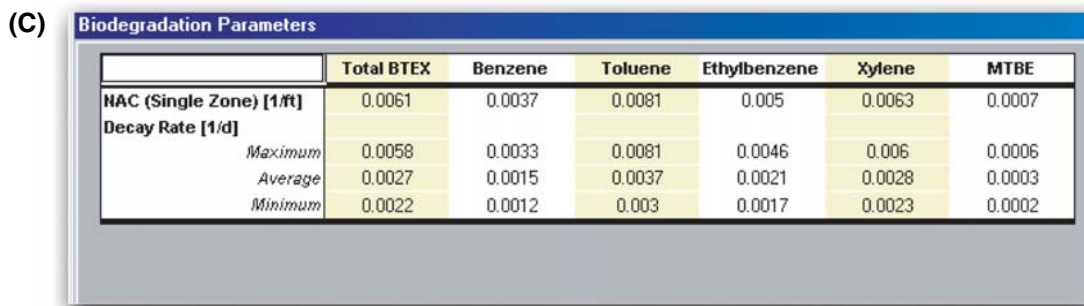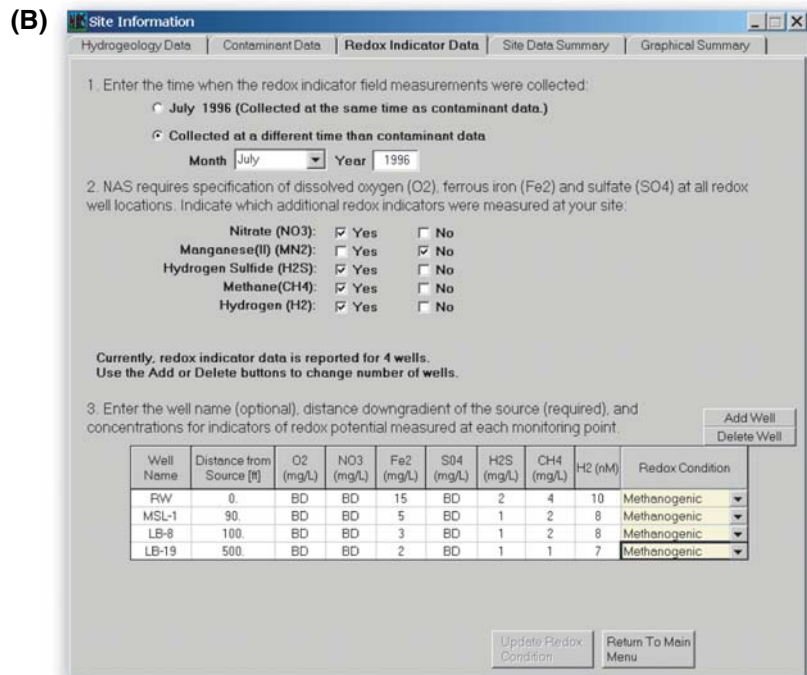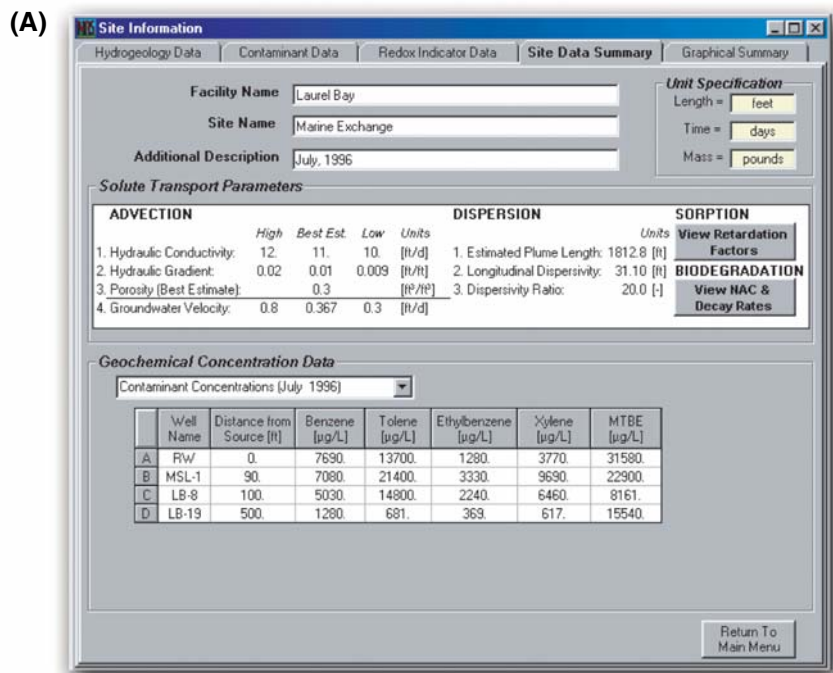
(A)

(B)

(C)

Figure 13. NAS computer screens of (A) summary of contaminant data, (B) redox data, and (C) summary of biodegradation rate and natural attenuation capacity estimates made from these data for the Laurel Bay site.
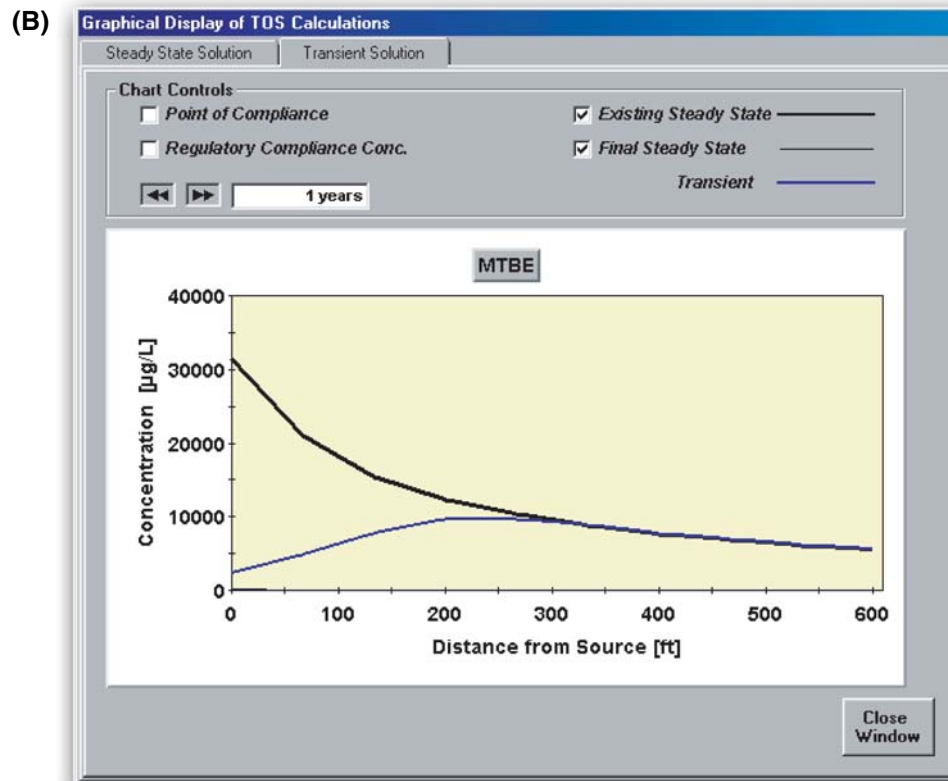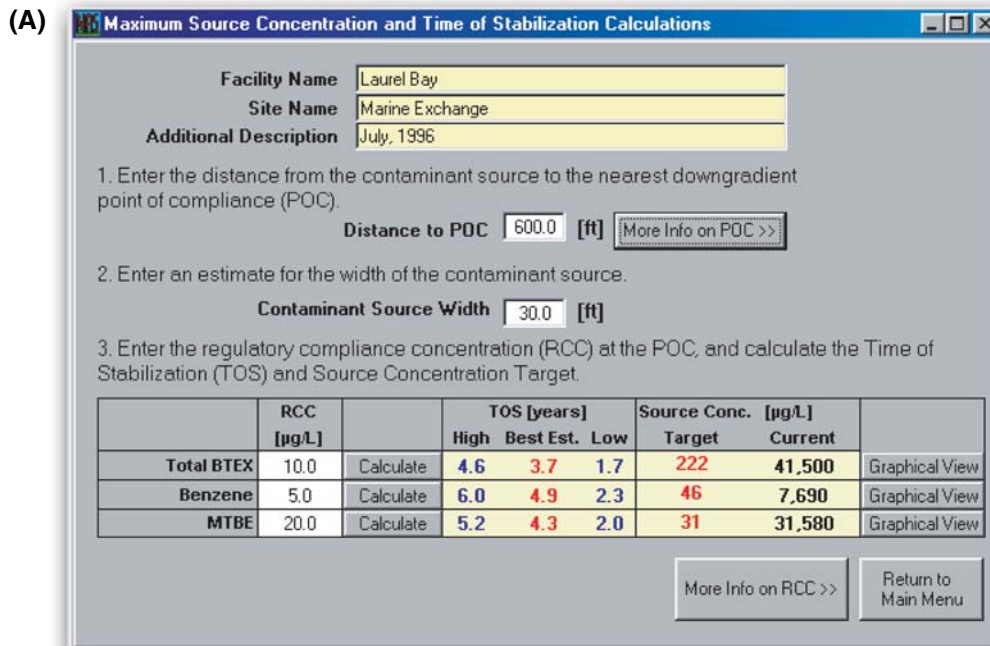
(A)

(B)

Figure 14. NAS computer screens of (A) summary of time-of-stabilization and distance of stabilization estimates, and (B) graphical view of time-of-stabilization estimates for the Laurel Bay site.
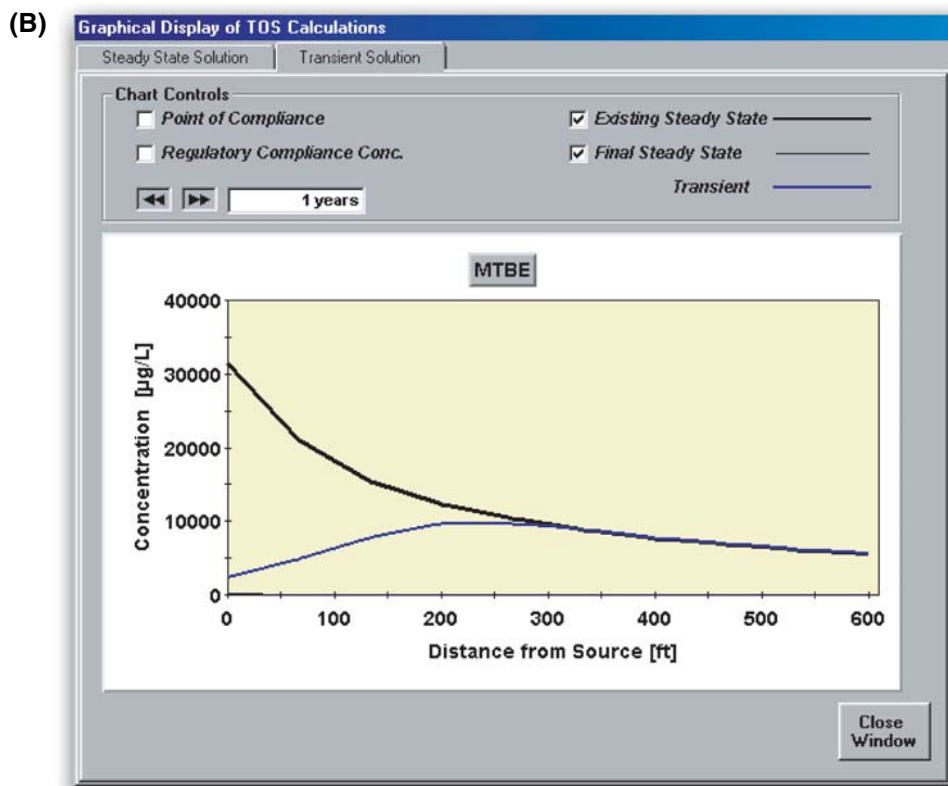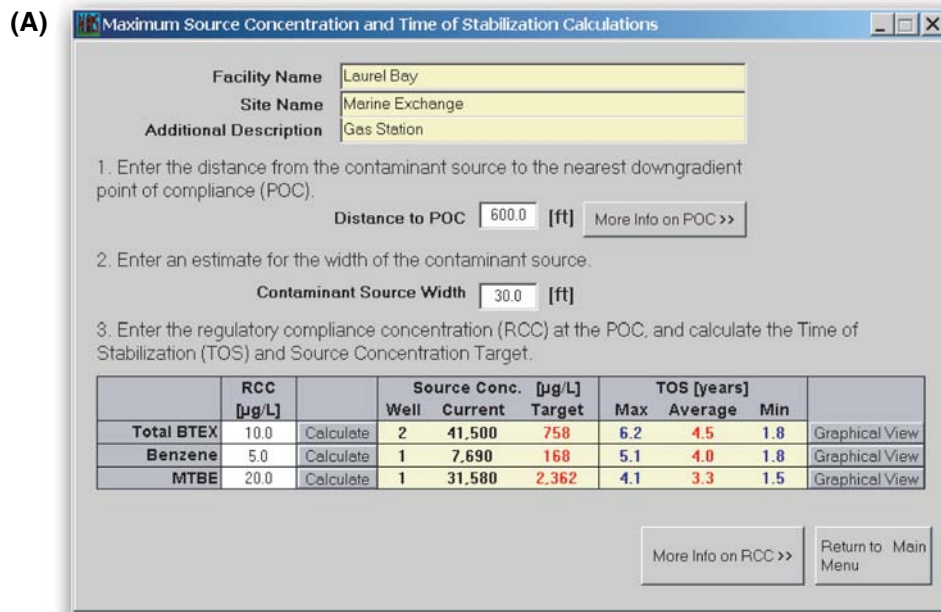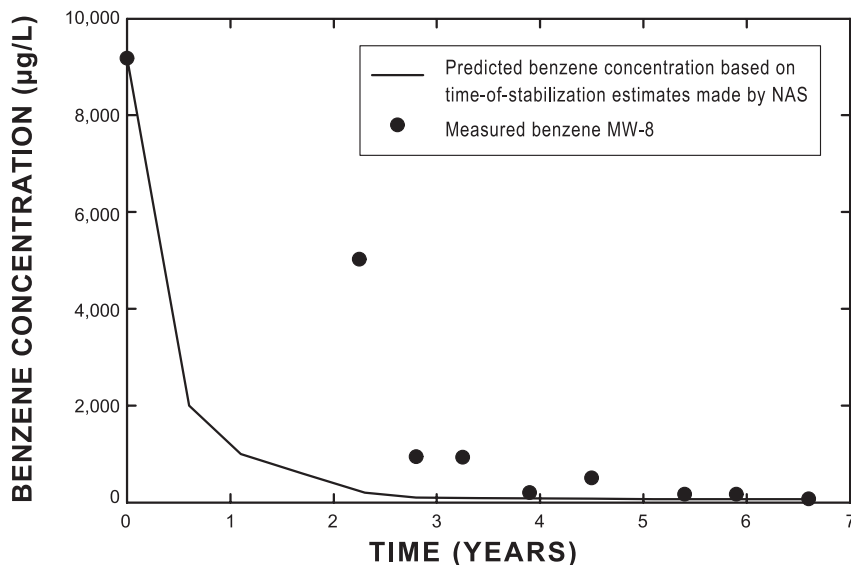
Figure 14. (Continued) NAS computer screens of (A) summary of time-of-stabilization and distance of stabilization estimates, and (B) graphical view of time-of-stabilization estimates for the Laurel Bay site.

Figure 15. Predicted benzene concentrations using time of stabilization estimates at well MW-8 plotted versus measured benzene concentrations over time at the Laurel Bay site.

declines of benzene follow a pattern consistent with a complete source-removal action, which seems counterintuitive; however, the observed NAPL dissolution behavior at this site suggests a possible explanation.

The amount of NAPL that was released at Laurel Bay is not known precisely, but fuel inventory records suggest that between 100 and 500 gal of gasoline leaked into the aquifer. Given the density of gasoline (about 7 lbs/gal), it is estimated that between 500 and 1,000 lbs of gasoline NAPL was delivered to the ground-water system. Gasoline NAPL, on average, contains 2 percent benzene, 10 percent toluene, 1 percent ethylbenzene, 4 percent BTEX, and (in this case) 10 percent MTBE. Using these percentages for the NAPL at Laurel Bay, NAS can be used to estimate times of remediation for different masses of NAPL.

Estimated times of NAPL dissolution and concentration decreases to the levels indicated by the distance-to-stabilization estimates (fig. 14) for total BTEX, benzene, and MTBE, and assuming that NAPL masses ranging from 10 to 1,000 lbs, are shown in figure 16A. The analysis suggests that for the highly volatile compounds, benzene and MTBE, the TOR is fairly brief and is about 10 years for NAPL masses ranging between 100 and 1,000 lbs. Because ground-

water chemistry data are available from the source area for the 10 years following the spill (well 1SAT), the predictions made by NAS can be tested. Figure 16B shows MTBE, benzene, and total BTEX concentrations in the source area (well 1SAT) as a function of time beginning in 1993. These data show that benzene and MTBE concentrations were initially high, but have decreased over time. In contrast, total BTEX concentrations have decreased, but not as rapidly as benzene and MTBE. By 2001 (about 10 years after the spill), measured concentrations of both MTBE and benzene reached the remediation level as suggested by the NAPL dissolution estimates, whereas less soluble toluene, ethylbenzene, and xylene (TEX) compounds did not. This analysis indicates that the NAPL dissolution rates estimated by NAS are consistent with measured values.

The observed rapid NAPL dissolution at the Laurel Bay site (fig. 16B) provides a possible explanation for the observation that concentration declines in the plume mimic those that would be expected if a source-removal action had been undertaken. For a number of hydrologic reasons, but most obviously because ground-water flow rates at this site are relatively high (about 1 ft/d), NAPL dissolution of the most soluble components of gasoline (benzene and MTBE) is relatively efficient (fig. 16B). This efficient dissolution results in the MTBE and benzene plume acting almost like a source-removal action. The more insoluble TEX components, however, more closely resemble the long-term source area that exists at this site. These data show that the TOR for benzene and MTBE is shorter (about 10 years) than the TOR for total BTEX (about 40 years). The behavior observed at the Laurel Bay site is expected to be similar to the behavior observed at other gasoline spills throughout the United States. This reflects the lower solubility of the TEX compounds relative to benzene and MTBE, suggesting that in the absence of source-area removal, the overall remediation time will be longer for TEX compounds than for benzene and MTBE.
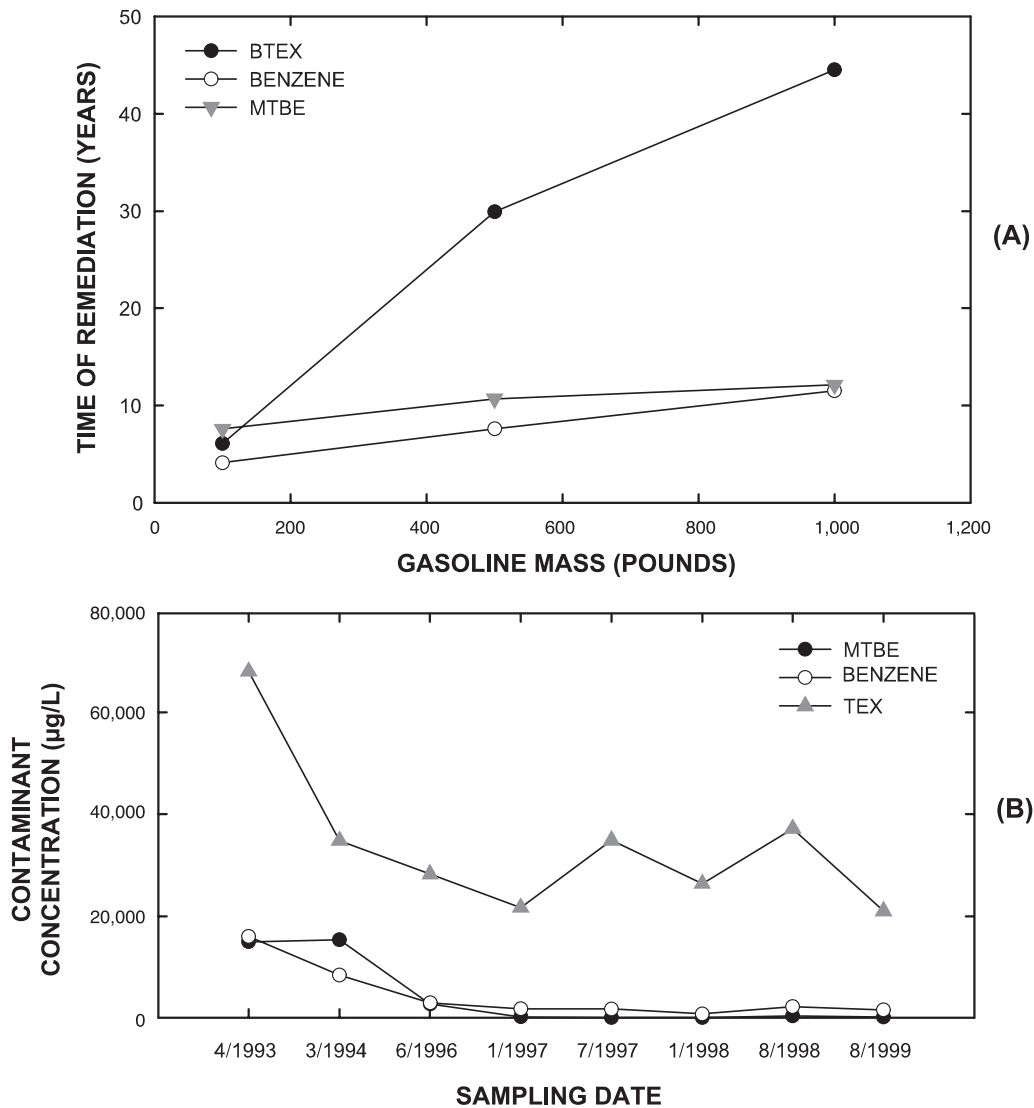
Figure 16. (A) Estimated time of nonaqueous phase liquid dissolution for MTBE, benzene, and total BTEX using NAS, and (B) observed source-area contaminant concentration decreases in source-area well EX-1 at the Laurel Bay site.

The Laurel Bay example points out the following important aspects of making TOR estimates for gasoline NAPLs:

1. Even when substantial numbers of observation wells are available at a site, the number of wells that intersect the central part of the plume and, therefore, are useful for documenting biodegradation rates, are commonly limited. This limited data places considerable uncertainty on the derived biodegradation rates.

2. When the site exhibits relatively low natural attenuation capacity, the target concentrations in the source area will be relatively low as well.

3. When the sediment lacks organic matter, the TOS is relatively rapid.

4. For relatively soluble components of NAPL, such as benzene and MTBE, the TOR can be fairly brief (in this case, on the order of 10 years). For less soluble TEX components, the TOR can be much longer (in this case, as much as 50 years).

Chlorinated Ethene Example: Kings Bay, Georgia

The site used for this example is an abandoned landfill known as the Old Camden Road landfill located at the Naval Submarine Base, Kings Bay, Ga. A dense

network of monitoring wells was used to delineate the contaminant plume, as it existed in 1998 (fig. 17), and to follow contaminant concentration changes over time. The site is underlain by sediments of back-barrier and barrier-island origin. The most permeable sands (hydraulic conductivity about 8.2 to 5.5 ft/d) underlying the site are present at depths between 30 and 35 ft, and were deposited by a prograding barrier island (Leeth, 1999). This permeable zone is underlain and overlain by finer-grained sediment, which are characterized by low hydraulic conductivity. The hydraulic gradient ranges between 0.004 and 0.006 ft/ft, resulting in an average ground-water flow velocity of about 50 ft/yr. The hydrologic, geochemical, and contaminant data for this site are summarized in figure 18.

The redox data at this site indicate SO_4-reducing conditions in and near the source area grading to Fe(III)-reducing conditions downgradient (fig. 18). In addition, the contaminant-concentration data indicate a distinct change in biodegradation rates for total chlorinated ethenes that coincide with the change in redox conditions. This discontinuity between redox-dependent biodegradation rates can be simulated by means of the multizone model capability of NAS. Biodegradation rates for individual chlorinated ethenes and total chlorinated ethenes are summarized in figure 19. In general, these biodegradation rates are consistent with rates observed at other anoxic, chlorinated ethene-contaminated sites (Wiedemeier and others, 1999), and with rates estimated previously at this site (Chapelle and Bradley, 1998).

The maximum source concentration and time-of-stabilization calculations performed by NAS are summarized in figure 20. This analysis suggests a maximum source-area concentration for total chlorinated ethenes of 130 µg/L, given a point of
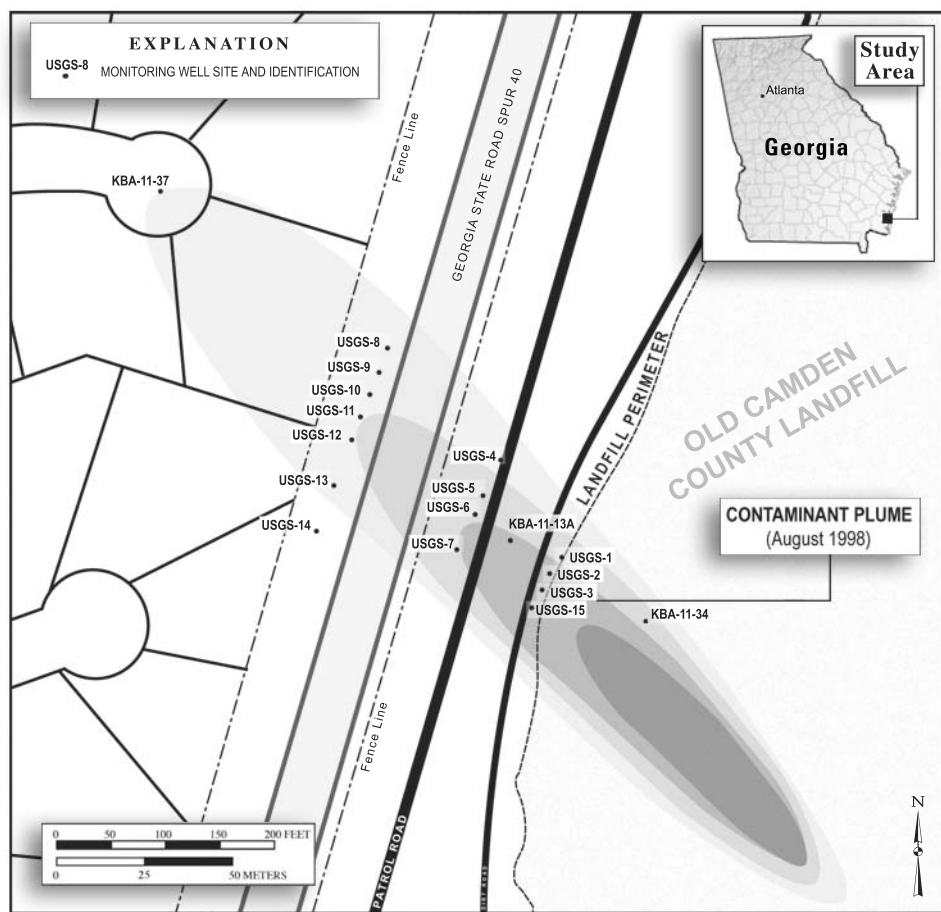

Figure 17. Location of total chlorinated ethene plume prior to in situ oxidation and locations of monitoring wells.

Site Information

Hydrogeology Data | Contaminant Data | Redox Indicator Data | **Site Data Summary** | Graphical Summary

Facility Name: Kings Bay
Site Name: Landfill
Additional Description: Site 11

Unit Specification
Length = feet
Time = days
Mass = pounds

Solute Transport Parameters

ADVECTION

	Maximum	Average	Minimum	Units
1. Hydraulic Conductivity:	8.2	6.8	5.5	[ft/d]
2. Hydraulic Gradient:	0.006	0.005	0.004	[ft/ft]
3. Porosity (Average):		0.25		[ft³/ft³]
4. Groundwater Velocity:	0.197	0.136	0.088	[ft/d]

DISPERSION

	Units
1. Estimated Plume Length:	846.2 [ft]
2. Longitudinal Dispersivity:	22.80 [ft]
3. Dispersivity Ratio:	20.0 [-]

SORPTION
View Retardation Factors

BIODEGRADATION
View NAC & Decay Rates

Concentration Data

Contaminant Concentrations (November 1998)

Well Name	Distance from Source [ft]	PCE [µg/L]	TCE [µg/L]	cis-DCE [µg/L]	Vinyl Chl. [µg/L]	Total Chl. Eth. [µg/L]
KBA-34	0.	3500.	1000.	BD	BD	4500.
USGS-3	110.	2.	511.	1270.	112.	1895.
13A	160.	0.5	32.5	158.	76.	267.
USGS-5	220.	BD	BD	54.	166.	220.
USGS-10	380.	BD	BD	24.	31.	55.
KBA-37	630.	BD	BD	10.	2.	12.

Return To Main Menu

Site Information

Hydrogeology Data | Contaminant Data | **Redox Indicator Data** | Site Data Summary | Graphical Summary

1. Enter the time when the redox indicator field measurements were collected:
   ○ November 1998 (Collected at the same time as contaminant data.)
   ◉ Collected at a different time than contaminant data
   Month: November Year: 1998

2. NAS requires specification of dissolved oxygen (O2), ferrous iron (Fe2) and sulfate (SO4) at all redox well locations. Indicate which additional redox indicators were measured at your site:

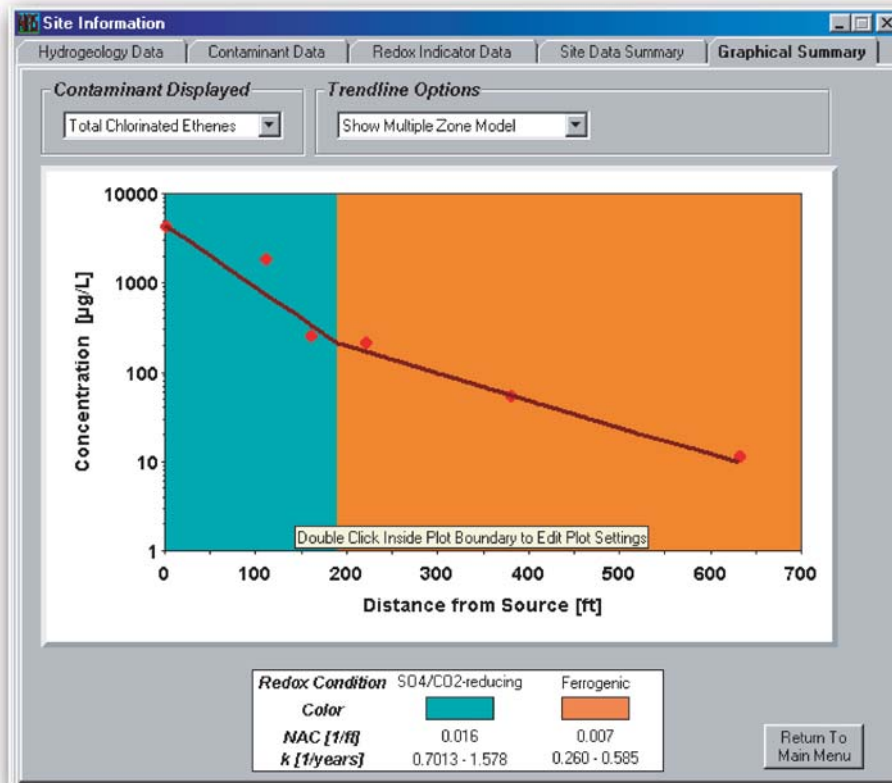|		
Nitrate (NO3):	☑ Yes	☐ No
Manganese(II) (MN2):	☐ Yes	☑ No
Hydrogen Sulfide (H2S):	☑ Yes	☐ No
Methane(CH4):	☑ Yes	☐ No
Hydrogen (H2):	☑ Yes	☐ No

3. Number of redox indicators along the centerline of the plume.

   Currently, redox indicator concentration data is reported for 6 wells. Add/Delete Wells

4. Enter the well name (optional), distance downgradient of the source (required), and concentrations for indicators of redox potential measured at each monitoring point.

	Well Name	Distance from Source [ft]	O2 (mg/L)	NO3 (mg/L)	Fe2 (mg/L)	SO4 (mg/L)	H2S (mg/L)	CH4 (mg/L)	H2 (nM)	Redox Condition
A	KBA-34	0.	0	0	1	10	0	5	2	SO4/CO2-reducing
B	usgs-3	110.	0	0	0.39	6.48	0	3.8	1.66	SO4/CO2-reducing
C	KBA-13A	160.	0	0	0.24	3.27	0.577	5.1	1.55	SO4/CO2-reducing
D	usgs-5	220.	0	0	0.26	0	0.385	5.6	0.5	Ferrogenic
E	usgs-10	380.	0	0	0.41	10	1.5	6	0.81	Ferrogenic
F	KBA-37	600.	0	0	0.3	10.2	0.1	0.3	0.3	Ferrogenic

Update Redox Condition   Return To Main Menu

Figure 18. Summary of hydrologic, contaminant, and redox characteristics of the Kings Bay site.

Figure 19. Discontinuity in biodegradation rates between redox zones, and summary table of estimated biodegradation rates at the Kings Bay site.
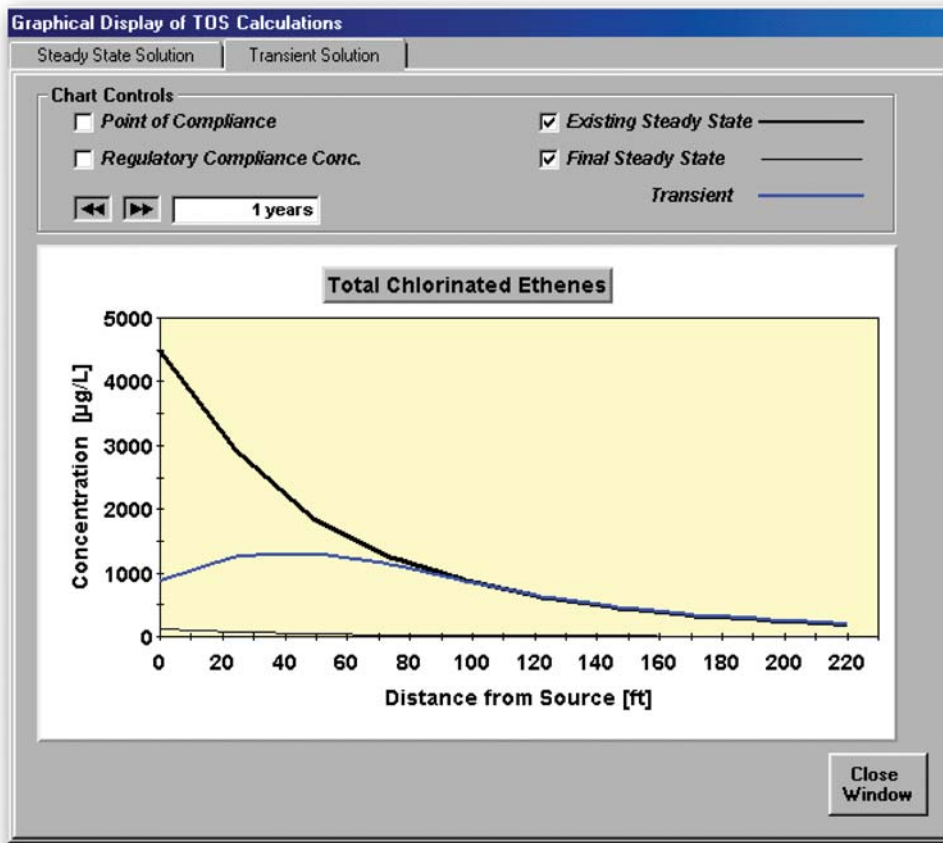
Figure 20. Summary of time and distance of stabilization estimates for the Kings Bay site.

contact 220 ft downgradient (roughly corresponding to the Navy property line) and an MCL at the property line of 5 µg/L. This is much lower than the source area concentration as of 1998 (about 4,500 µg/L), suggesting that a reduction in source-area concentrations was needed at this site. A previous source-area concentration analysis (Chapelle and Bradley, 1998) produced similar results, and based on this analysis, a source-area remediation was undertaken at this site with a source-area target concentration of 100 µg/L. A series of in situ oxidation source-removal actions was initiated in late 1998, which resulted in source-area PCE concentrations being lowered to <100 µg/L from the 4,000 to 5,000 µg/L range.

This source-removal action raises the question of how long it will take the plume to shrink to equilibrium with the lower concentration source area. The TOS calculations performed by NAS are plotted with sediment organic matter concentration and shown on fig. 21A. Because the organic matter composition of these sediments ranges from 0.1 to 0.5 percent, the analysis suggests that the TOS for this system will range from about 7 to 15 years, with a best estimate of 11 years. These estimates suggest that even though much of the contaminant mass was removed by in situ oxidation in 1999, the contaminant plume will persist for the foreseeable future.

Also of interest at Kings Bay are TOR estimates for residual NAPL present in the landfill. Excavations
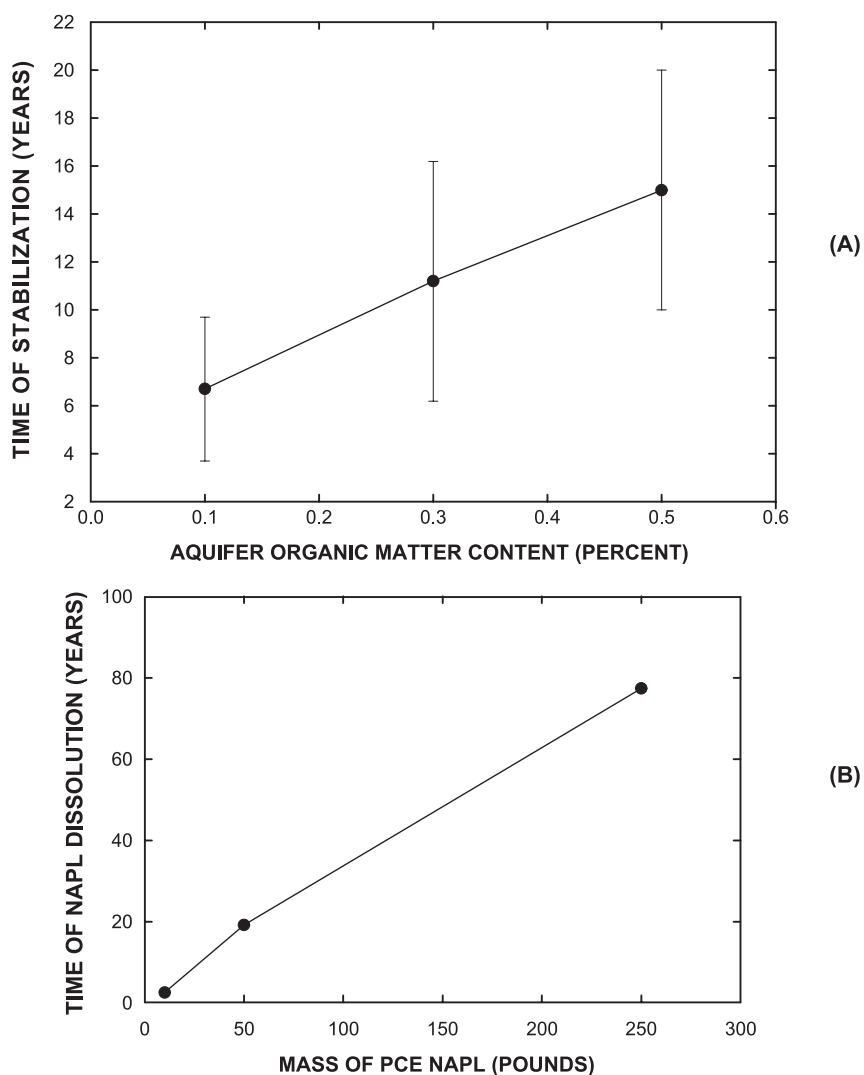

Figure 21. Estimated (A) time of stabilization for plume following nonaqueous phase liquid (NAPL) removal and (B) time of NAPL dissolution versus NAPL mass at the Kings Bay site.

at the landfill have revealed the presence of plastic 5-gal buckets partially filled with NAPL PCE. Thus, undiscovered sources of NAPL are probably present at this site. Because containers ranging from about 1 to 25 gal were disposed of at this site, NAPL masses at particular points in the landfill could likely vary from about a pound (a few ounces of PCE) to as much as 250 lbs (19 gal of PCE).

Figure 21B shows a TOR analysis at this site for NAPL masses ranging from 10 to 250 lbs. The results suggest that low masses of NAPL (about 10 lbs) will disperse fairly quickly (about 3 years), whereas larger masses (250 lbs) would require as much as 77 years. This is roughly consistent with the observed behavior of PCE at this site where a contaminant plume, emanating from a high-concentration source area associated with the disposal of a PCE mass (about 200 lbs), has been observed to persist for at least 30 years (fig. 17).

This time-of-NAPL dissolution analysis illustrates the utility of source-area removal technologies to lower the TOR associated with natural attenuation processes. For masses of PCE exceeding 50 lbs (about 6 gal), times of remediation without source removal would likely exceed 20 years (fig. 21B). On the other hand, if 90 percent of the NAPL mass is removed via in situ oxidation by Fenton's reagent, the TOR could be lowered to less than 5 years (fig. 21B). Thus, combining engineered NAPL removal with natural attenuation of an existing plume can be a useful remedial strategy.

The TOS estimates made with NAS can be compared to monitoring data

at the Kings Bay site. Monitoring data from 1998 to present (2001) for four wells located at different distances along the flowpath are shown in figures 22 and 23. At the most upgradient well (USGS-3), located in the zone injected with Fenton's reagent, concentrations of chlorinated ethenes immediately decreased below 100 µg/L (fig. 22A). At well KBA-11-13A,

(A)

(B)
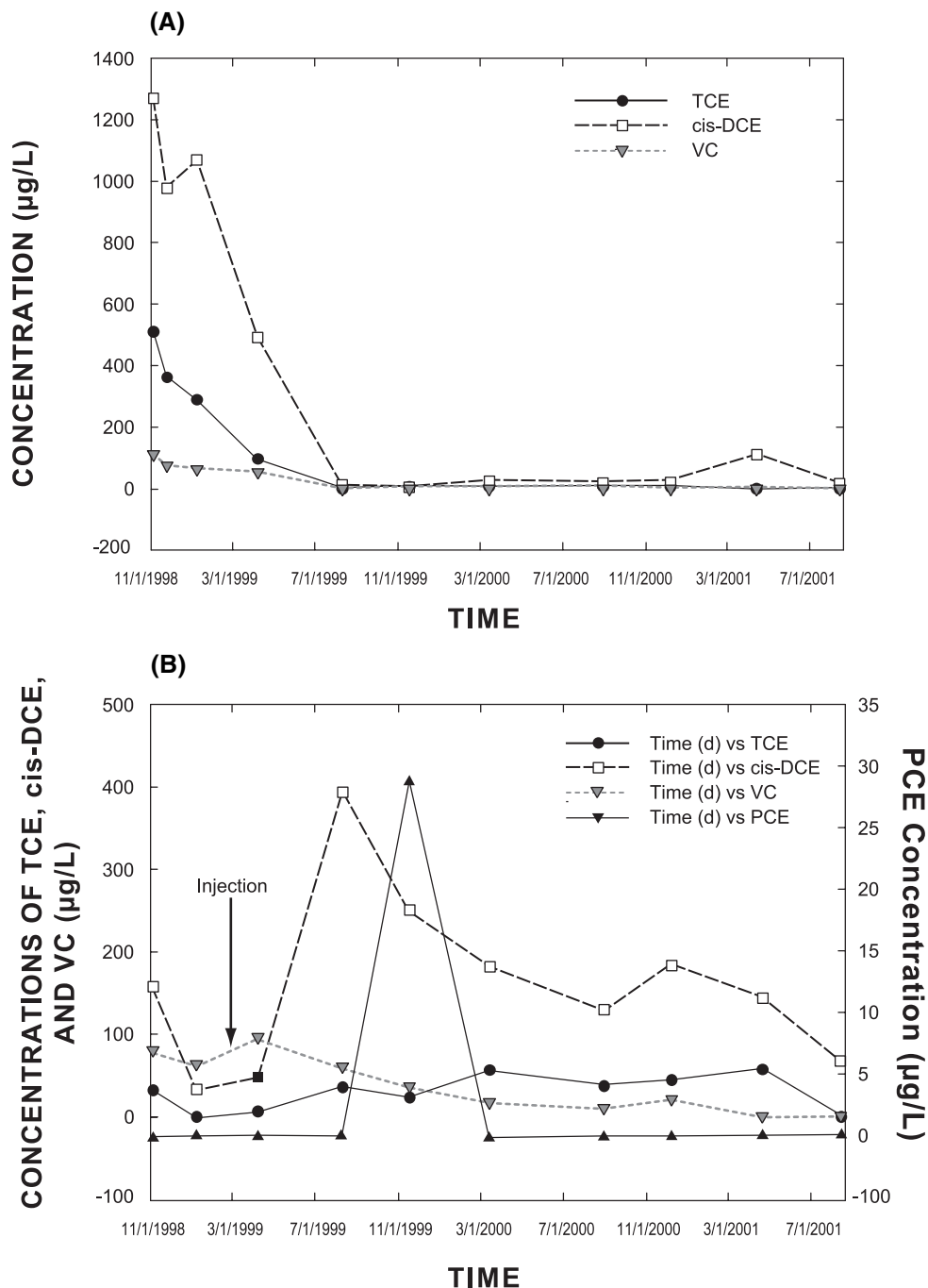
Figure 22. Observed concentration changes at (A) well USGS-3 in the zone of Fenton's reagent injection, and (B) well KBA-11-13A, which are 160 feet downgradient of the injection zone.
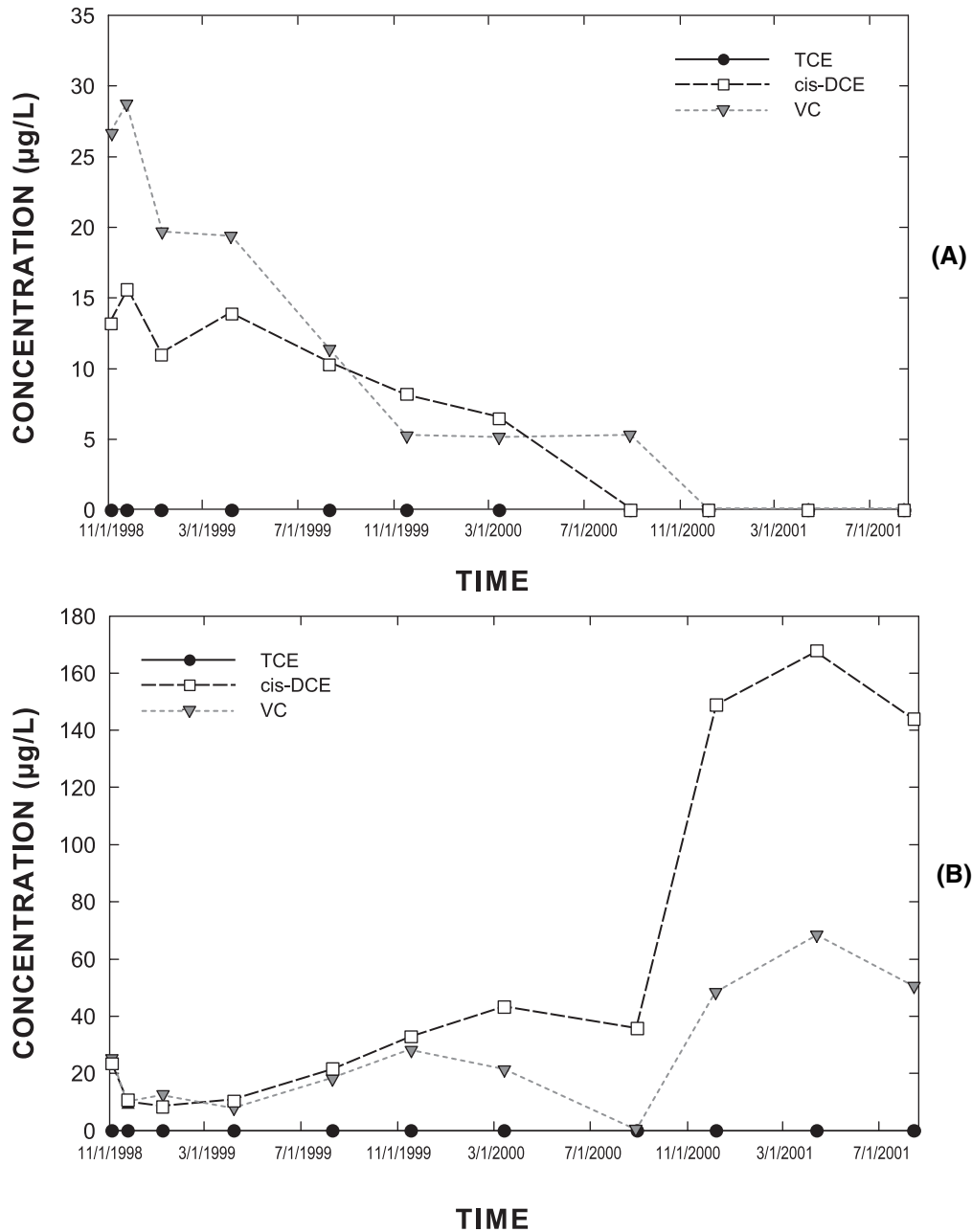
Figure 23. Observed concentration changes at wells (A) USGS-9 and (B) USGS-11, which are 380 feet downgradient of the injection zone.

which is located in the central part of the plume about 160 ft downgradient of the source area, chlorinated ethene concentrations were observed to "spike" following the Fenton's reagent injection, possibly reflecting contaminants being pushed downgradient (fig. 22B). Since that time, however, concentrations of chlorinated ethenes have steadily decreased. Of the eight downgradient wells at the site, all but one showed a trend of decreasing contaminant concentrations as illustrated by well USGS-9 (fig. 23A). Conversely,

well USGS-11 showed an increasing trend of chlorinated ethene concentrations over time.

The concentration trends shown by the monitoring wells can be compared to TOR estimates provided by NAS. A comparison of the NAS-simulated concentration trends to monitoring data collected from well KBA-11-13A is shown in figure 24. The NAS simulation predicts that concentrations of chlorinated ethenes would remain constant for the first 2 years following in situ oxidation (before remediated water

Figure 24. Observed concentration changes compared to NAS-simulated changes at well KBA-11-13A.

reaches KBA-11-13A), and then decrease gradually over the next 3 years. Actual monitoring data, however, show more complex behavior. Concentrations of chlorinated ethenes were observed to be relatively variable. Part of this observed variability can be attributed to hydrologic disturbance follow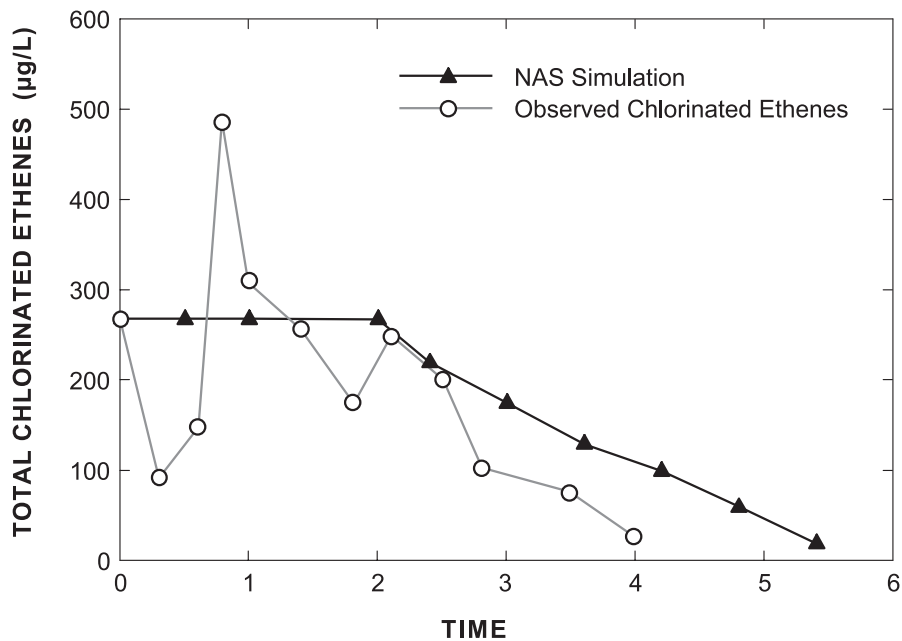ing in situ oxidation. Much of the variability, however, probably reflects the more complex flow and chlorinated ethene transport in the aquifer than can be simulated by the relatively simple analytical model imbedded in NAS.

Comparison of the NAS predictions with chlorinated ethene concentrations observed in the more downgradient wells also shows considerable variability. In well USGS-9, for example, concentrations of chlorinated ethenes have decreased much more rapidly than predicted by the NAS simulation (fig. 25A). The pattern shown by well

USGS-9 is observed in all but one of the downgradient wells. The exception to this pattern is well USGS-11, which shows that concentrations of chlorinated ethenes have actually increased over time. This pattern of behavior is actually more consistent with the NAS predictions (fig. 25B) than that observed at well USGS-9 (fig. 25A). In all cases, the differences between the NAS estimates and the observed behaviors can be attributed to hydrologic complexities of the site that NAS cannot simulate. These include head changes caused by Fenton's reagent injection, ground-water flow direction changes caused by precipitation events, and the cessation of the pump-and-treat system in 1998. All of these processes affect directions and rates of ground-water flow as well as the transport of contaminants in the system.
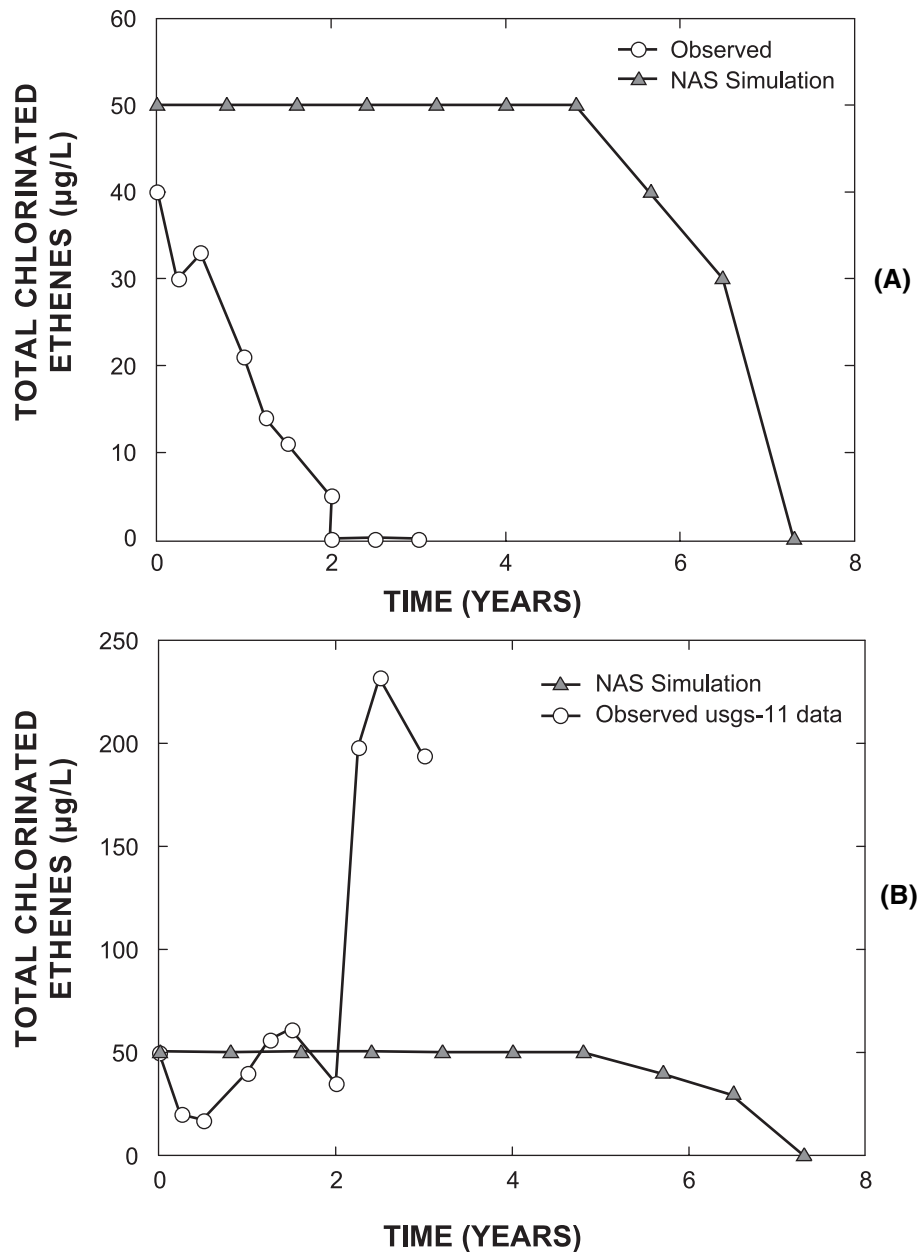
Figure 25. Observed concentration changes compared to NAS-simulated changes at wells (A) USGS-9 and (B) USGS-11.

SUMMARY

The time-of-remediation (TOR) problem can be divided into three interrelated components including (1) the distance of stabilization (DOS) of a plume from a constant contaminant source of known concentration, (2) the time of stabilization (TOS) for a plume to shrink following a source-removal action, and (3) the time it takes for a NAPL of given composition to dissolve and disperse. A combination of analytical solutions (DOS and TOS) and numerical solutions (NAPL dissolution) to the solute-transport equation can be used to evaluate TOR questions, and are imbedded in the Natural Attenuation Software (NAS) described in this report.

Comparison of the NAS-generated TOR estimates with actual long-term monitoring data at the Laurel Bay, S.C., (petroleum hydrocarbons) and Kings Bay, Ga., (chlorinated ethene) sites illustrates the uncertainties involved in making TOR estimates and

suggests how such estimates can be used appropriately in practical applications. One observation is that over a timescale of 1 to 3 years, the NAS predictions often differ substantially from observed monitoring data. In the Laurel Bay and Kings Bay examples, observed contaminant concentrations tended to decrease much faster at most monitoring wells than was predicted by the TOR analysis. In other cases, such as at well USGS-11 at Kings Bay, contaminant concentrations were observed to increase over time when the TOR analysis indicated that contaminant concentrations would remain steady over time. These observations clearly show that the actual behavior of contaminated sites can differ from the predicted behavior. These differences can be traced to the simplifications needed to model aquifer systems in NAS, as well as show that this procedure introduces uncertainty into each analysis. Thus, using TOR estimates as precise predictions of system behavior is not appropriate.

On the other hand, the comparison of simulated and observed behavior suggests that over longer periods of time, the precision of TOR estimates becomes somewhat better. Over a timescale of about 10 years, for which monitoring data are available at the Laurel Bay site, predicted and observed contaminant concentrations were largely in accord. Part of this concordance can be attributed to the fact that, in general, contaminant concentrations in ground-water systems tend to decrease because of natural attenuation processes. Nevertheless, these observations suggest that TOR estimates derived from NAS are likely to be more in accordance with observed behavior over periods of 5 to 10 years than with shorter periods of time.

These observations emphasize that TOR estimates should not be regarded as precise predictions of future contaminant behavior. Rather, it is more appropriate for TOR estimates to focus on the effects of NAPL removal on long-term remediation goals, or on how different hydrologic factors affect time and DOS estimates.

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Methodology for Estimating Times of Remediation Associated with Monitored Natural Attenuation

CHAPELLE