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Natural Attenuation of Groundwater Contamination — A Workshop Summary

Denver, Colorado

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Denver, Colorado August 19-21, 1997

EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) sponsored a *Workshop on Natural Attenuation of Groundwater Contamination*, which was held from August 19 - 21, 1997 at the EPA Region 8 office in Denver, Colorado. With few exceptions, the 88 workshop participants were representatives of EPA and state environmental agencies implementing groundwater clean-up programs.

A plenary session consisting of presentations was held on the first day of the workshop. Among other topics, speakers discussed the state-of-the-science of natural attenuation and the ongoing efforts by ORD to develop guidance for evaluating natural attenuation. Many of the speakers discussed material covered in greater detail in documents prepared for or co-authored by researchers at ORD's National Risk Management Research Laboratory, Subsurface Processes and Remediation Division in Ada, Oklahoma. These documents were distributed to the participants prior to the commencement of the workshop.

The second day of the workshop consisted of breakout sessions on the following four topics: (1) Analytical Methods for Evaluating Natural Attenuation; (2) Site Characterization for Natural Attenuation Assessments: Hydrogeologic Considerations; (3) Data Quantity and Quality Issues; (4) and Interpretation and Use of Site Characterization Data. A plenary session to discuss the breakout session findings and summarize the workshop accomplishments was held on the last day of the workshop.

The nature of breakout session discussions and recommendations reflected, in large part, the content of the reference documents distributed prior to the workshop. For example, the reference documents provided a great level of detail regarding the analytical methods needed to evaluate natural attenuation. As a result, the analytical methods breakout session offered some very specific comments. While there was general acceptance of the analytical approaches contained in the reference documents, there were several areas of concern. Consensus comments included a recommended alternative preservative for samples analyzed for methane; there is a need for a greater emphasis on quality assurance and quality control measures (*e.g.*, the use of independent standards to check accuracy) in the standard operating procedures (SOPs); and there is a need to correct and finalize the draft SOP for analysis of dissolved molecular hydrogen. A general concern was that field analytical methods should not be so complex as to discourage their use. Since field analysis for dissolved hydrogen was viewed as difficult, the workshop participants were very encouraged by new results of a multi-laboratory study showing that samples can be successfully preserved and shipped to fixed-base laboratories for hydrogen analysis.

In contrast to analytical methods, the reference documents provided few details on hydrogeologic methods for site characterization. Participants in the breakout sessions addressing this topic wanted to see a greater level of detail because they believed that natural attenuation remedies require better site characterization than do most active remedial approaches for groundwater. This belief is due to the fact that site characteristics determine whether natural attenuation will meet remedial objectives. Many participants in these breakout sessions wanted to see additional guidance addressing approaches to the three-dimensional delineation of plumes, including identification of any highly contaminated plume core areas; the appropriate scale of site characterization; and the use of tools such as geophysical methods, direct push sampling technologies, tracer tests to determine groundwater flow paths and velocities, and modeling during the site characterization process.

The breakout sessions on data quantity and quality issues addressed not only the subject of analytical data quality (which was also addressed in the analytical methods breakout), but also the broader issue of the necessary quality of site characterization data sets for making decisions on use of natural attenuation. The

adequacy of a data set for decision-making is affected not only by analytical data quality, but by many other factors including the cleanup goals, number of samples, representativeness of sampling locations, bias and imprecision associated with sampling and sample handling prior to analysis, methods used for data interpretation, and cost of making a wrong decision. Many participants in these breakout sessions wanted to see guidance addressing greater attention to determining spatial variability; greater attention to assessing and controlling sampling error; greater use of statistics in data analysis; greater use of field methods versus off-site laboratory methods; analysis of more samples with methods that are less precise, less accurate, and cost less versus fewer samples using methods that are more precise, accurate, but cost more; and use of EPA's current data quality objectives process.

Participants in the breakout sessions on interpretation and use of site characterization data generally did not question that natural attenuation of groundwater contaminants can be demonstrated to be protective for some sites. However, they had many questions about the amount and type of characterization data needed, and about the time and effort needed to make such a demonstration. There was much discussion about the reliability of predictive models for simulating future groundwater restoration. There was a consensus that if source areas will remain uncontrolled, predictive models are not suited to estimating restoration time frames. Historical data trends were given much more weight than modeling results by the participants. These breakout participants also discussed the role that ORD can play in the development of guidance. The ORD representative serving as the breakout topic leader stated that ORD can prepare "protocols" or "best practice documents" on data collection, data interpretation, and data use for evaluating natural attenuation, but ORD does not issue program-specific guidance. The need for technical documents with greater emphasis on groundwater sampling methods and groundwater sampling network design were among the consensus recommendations.

The breakout session findings were presented and further refined during plenary session discussions on the last day of the workshop. This report provides a more detailed summary of the workshop proceedings.

CONTENTS

ACRONYMS

ACL	alternate concentration limit
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ALARA	as low as reasonably achievable
ASTM	American Society for Testing and Materials
BART	biological activity/reactivity test
BTEX	benzene, toluene, ethylbenzene, and xylenes
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DEM	Department of Environmental Management
DEQ	Department of Environmental Quality
DCE	dichloroethene
DIC	dissolved inorganic carbon
DNA	deoxyribonucleic acid
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
GC	gas chromatograph
HCl	hydrochloric acid
HSSM	Hydrocarbon Spill Screening Model
IC	ion chromatograph
ICP-AES	inductively coupled plasma and atomic emission spectroscopy
L/min	liters per minute
M	molar
MCL	maximum contaminant level
mL	milliliter
MTBE	methyl tertiary butyl ether
NAS	Naval Air Station
NAPL	non-aqueous phase liquid
NEIC	National Enforcement Investigations Center
NERL/ERD	National Exposure Research Laboratory, Ecological Research Division
NERL/CRD	National Exposure Research Laboratory, Characterization Research Division
NRMRL/LRPCD	National Risk Management Research Laboratory, Land Remediation and Pollution Control Division
NRMRL/SPRD	National Risk Management Research Laboratory, Subsurface Protection and Remediation Division

ORD	Office of Research and Development
ORP	oxidation/reduction potential
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCE	tetrachloroethene
PRP	potentially responsible party
PVC	polyvinyl chloride
QA/QC	quality assurance and quality control
RCRA	Resource Conservation and Recovery Act
RI	remedial investigation
RNA	remediation by natural attenuation
RPM	remedial project manager
ROD	record of decision
RSD	relative standard deviation
RSKSOP	Robert S. Kerr Research Center Standard Operating Procedure
SOP	standard operating procedure
TCA	trichloroethane
TCE	trichloroethene
TMB	trimethylbenzene
TOC	total organic carbon
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
UST	underground storage tank
VOA	volatile organic analyte
VOC	volatile organic compound

INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) sponsored the *Workshop on Natural Attenuation of Groundwater Contamination*, which was held from August 19 - 21, 1997 at the EPA Region 8 Office in Denver, Colorado. With few exceptions, participation in the workshop was limited to representatives of EPA and state environmental agencies implementing groundwater cleanup programs.

EPA's Office of Solid Waste and Emergency Response (OSWER) had prepared a draft policy directive regarding the use of monitored natural attenuation for the remediation of contaminated soil and groundwater at sites regulated under OSWER programs. It was noted in the draft OSWER directive that ORD is developing detailed technical guidance for evaluating remedial alternatives that involve the use of monitored natural attenuation. While the workshop provided a forum for participants to learn about the state-of-the-science for evaluating natural attenuation and about ORD's efforts to develop technical guidance, the chief objective of the workshop was to further refine approaches to site characterization, sampling and analytical methods, and data quality and quantity specific to natural attenuation in groundwater. This effort will contribute to ORD's development of the technical guidance for natural attenuation. Through active contributions from EPA and state agency participants, the workshop was designed to help in integrating the state-of-the science with practical considerations in evaluating and implementing natural attenuation.

The evaluation of natural attenuation of groundwater contamination in OSWER programs requires a team effort involving project managers, hydrogeologists, chemists, and others. Therefore, the workshop attendees were selected to provide participants from a variety of disciplines and backgrounds (see Appendix A for the Workshop Participants List).

An important focus of the ORD workshop was on the analytical methods needed to evaluate natural attenuation of contaminants in groundwater. Some of these methods have been used chiefly for research purposes. It was especially important that ORD receive feedback on these analytical methods in regard to their potential use at fixed-base and on-site laboratories that perform analysis for OSWER programs. Therefore, participation of laboratory chemists and quality assurance and quality control (QA/QC) specialists was a key element of the workshop.

Two weeks prior to commencement of the workshop, prospective participants were mailed documents (refer to the transmittal letter in Appendix B for further details) intended to serve as a point of departure for discussion purposes at the workshop. It was noted that a number of the documents are labeled "draft" and do not represent EPA policy.

A plenary session consisting of presentations was held on the first day of the workshop. The second day consisted of breakout sessions on the following four topics: (1) Analytical Methods for Evaluating Natural Attenuation; (2) Site Characterization for Natural Attenuation Assessments: Hydrogeologic Considerations; (3) Data Quantity and Quality Issues; and (4) Interpretation and Use of Site Characterization Data. A plenary session to discuss the breakout session findings and summarize the workshop accomplishments was held on the last day of the workshop.

The following sections of this report summarize the workshop proceedings. Styles and formats of the sections may differ somewhat due to the preferences of the workshop speakers and breakout topic leaders who assisted in preparing this document.

PLENARY SESSION (Workshop Day 1)

Welcoming Remarks

Jack McGraw, Acting Regional Administrator for EPA Region 8, welcomed participants to the *Workshop on Natural Attenuation of Groundwater Contamination*. He said that natural attenuation is an emerging topic that has generated a lot of debate within EPA. While he was Assistant Administrator for Solid Waste and Emergency Response during the early- to mid-1980s, natural attenuation was selected as part of the remedy at only about 3 percent of contaminated sites. It is now a part of 28 percent of Superfund remedies and an even higher percentage for underground storage tank sites. One of the biggest obstacles to the use of natural attenuation is opposition from local communities who often have a difficult time understanding that natural attenuation can be protective. McGraw said that good science needs to be incorporated into policy and regulation decisions.

Jon Josephs of EPA's Office of Science Policy and Superfund Technical Liaison for EPA/Region 2 facilitated the workshop and introduced the presenters.

State-of-the-Science on Natural Attenuation
John Wilson, EPA National Risk Management Research Laboratory, Subsurface Protection and Remediation Division (NRMRL/SPRD)–Ada, OK

Wilson said that scientific understanding of natural attenuation has come a long way in recent years. He attributed this progress to a recognition that previous assumptions have been proven wrong. For example, natural petroleum seeps were long known to degrade naturally. Yet, many scientists did not make the connection to petroleum spills, choosing instead to assume that refined hydrocarbons would last forever in the environment.

A quantitative assessment of natural attenuation is needed to satisfy the risk management process. Elements of a quantitative assessment include delineating the extent of contamination, delineating the movement of contaminants in groundwater, installing monitoring wells along plume centerlines, determining attenuation rates, using mathematical models to estimate whether cleanup goals will be met at the points of compliance, and confirming the protectiveness of natural attenuation through long-term monitoring.

There are a number of patterns that can be used to recognize natural bioattenuation. If oxygen or nitrate is available, microbes can grow rapidly and exhaust their resources within days. As a result, the groundwater may contain contaminants and no oxygen or nitrate, or oxygen and nitrate and no contaminants. Furthermore, biodegradation of groundwater contaminants often will result in the accumulation of metabolic by-products, including sulfide, ferrous iron [Fe(II)], and methane. Many contaminant plumes are in a dynamic steady state where the input of contaminants dissolving from a non-aqueous phase liquid (NAPL) source area is balanced by the rate of biodegradation in the groundwater. This results in a contaminant plume that does not spread, even though groundwater flow rates dictate that it should.

Wilson said that the spatial distribution of oxidation/reduction (redox) zones at a site needs to be delineated. As an example of this need, Wilson described an assessment of contaminant plume behavior at Hill Air Force Base (AFB) in Utah. The source of the plume was on the side of a hill with groundwater flow rates of 800-1000 feet per year. An ambitious assessment effort began in August 1993 with the analysis of more than 50 samples. The plume was reassessed in 1994 and 1995. Background dissolved oxygen (DO) concentrations of about 5 mg/L decreased to zero within the plume core. The plume did not appear to be

growing as rapidly as expected from contaminant mass transfer considerations, providing evidence of the occurrence of natural bioattenuation.

Near the source, the concentration of soluble electron acceptors was low, while benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations were high. At the toe of the plume, which represented about one year of travel time at groundwater flow rates, the BTEX concentrations were found to be much lower, but 1,2,4-trimethylbenzene (TMB) remained high. This suggested that BTEX was being removed, but it was not possible from BTEX data alone to differentiate natural removal due to biodegradation verses sorption and dilution effects. Consequently, TMB was used as a conservative tracer to determine actual biological attenuation. To differentiate natural bioattenuation from dilution and sorption, Wilson divided the BTEX concentrations by the concentration of the tracer at upgradient and downgradient wells. He defined a "good" tracer as one that is present at concentrations at least one hundred times its detection limit and that will be adsorbed and desorbed as readily as the contaminant. He cautioned, however, that TMB will degrade if oxygen is present, and may not be a good tracer in oxygenated plumes.

Wilson stressed that monitoring is one of the most essential components of the credible use of natural attenuation. Monitoring well data are critical to answering the two most basic questions for any remedy: when to start and when to stop. OSWER policy clearly stresses the remediation of source areas. Wilson suggested that proactive remediation can be discontinued when it is no faster than natural attenuation. If the remedial goals can be met in a reasonable time frame, then the transition to natural attenuation can be justified. He added that natural processes can biodegrade groundwater contaminants, but may not directly biodegrade the source material. Because the dissolution of source material can be a very long slow process, groundwater restoration within a reasonable time frame is unlikely without active remediation for source materials.

Wilson said that there is an additional problem with chlorinated solvent plumes. Often the contaminant source cannot be observed, but evidence of biological activity can. This makes it difficult to estimate the contaminant mass in the source area, which is necessary to estimate the attenuation of the source.

Tetrachloroethene (PCE), trichloroethene (TCE), and trichloroethane (TCA) cannot serve as food sources for microorganisms. However, they are metabolized as electron acceptors. Wilson made the analogy of microbes using electron acceptors as humans breathe air. This biochemical process ("reductive dehalogenation") involves electron transfer from the donor "food" to the chlorinated solvent acting as an electron receptor. To occur, there must be a primary substrate (native organic carbon, BTEX, or some other source) and strongly reducing conditions.

Wilson described three chlorinated solvent plume behaviors: Type 1, in which the primary substrate consists of anthropogenic organic compounds; Type 2, in which native organic carbon provides an alternate food source; and Type 3, in which there is little native organic carbon, little anthropogenic organic carbon, and the presence of DO and nitrate at concentrations that inhibit reductive dechlorination. For the first two plume types, the characteristic behavior involves some degree of chlorinated solvent biodegradation. In the third type, there is not enough organic carbon to fuel biodegradation. He pointed out that a plume can transition between all three types of behavior along its flowpath. Where the conditions match the first two types, the scientific questions to be addressed include: Does the electron donor (organic carbon) supply exceed the demand? Is the rate of biodegradation adequate? Is vinyl chloride being oxidized? Do PCE, TCE, and dichloroethene (DCE) dechlorinate?

In conclusion, Wilson said that the science behind natural attenuation is progressing rapidly. There is now a common vocabulary; scientists are looking at contaminant behavior, not only at concentrations; they are

beginning to predict the impacts of various remediation options; and defensible decisions on natural attenuation can be made.

Questions and Answers: Diane Easley (EPA/Region 7) asked whether there are guidelines on using natural attenuation versus traditional technologies like pump-and-treat. For example, are there concentration levels unsuited for natural bioattenuation? Wilson said that no guidelines exist and that decisions must be made within the regulatory and geological context of the site. Frank Chapelle (USGS) added that it would be a mistake to make a decision based solely on concentration levels. He agreed that the hydrology and geological context are crucial.

Draft OSWER Policy on Monitored Natural Attenuation
Bill Brandon, EPA/Region 1

Brandon discussed OSWER's policies regarding natural attenuation. A policy document on natural attenuation is in its second draft and an interim final document is expected in September. Natural attenuation refers to naturally occurring processes (physical, chemical, and biological) that act to reduce the mass, toxicity, mobility, volume, or concentration of contaminants. Natural processes include biodegradation, dispersion, dilution, adsorption, volatilization, and the chemical or biological stabilization and destruction of contaminants. The biological and hydrological aspects are key considerations that need to be separated. Brandon noted that there are a lot of synonyms for natural attenuation, including intrinsic remediation, passive bioremediation, natural recovery, and natural assimilation. EPA is using the term "monitored natural attenuation" in order to stress the need for a long-term commitment to monitoring. Natural attenuation is not a "select-and-forget" concept.

Brandon stressed that the use of natural attenuation must be consistent with the regulatory framework under applicable cleanup authorities (*e.g.*, underground storage tank [UST], RCRA, Superfund, state and local authorities). The selection of monitored natural attenuation as a remedial action by EPA does not mean that the groundwater has been "written off" and will not be cleaned up. Rather, if monitored natural attenuation is selected, the expectation is that natural processes *will* effectively reduce contaminants in the groundwater to concentrations protective of human health in a time frame comparable to that which could be achieved through active restoration. OSWER's policy is to consider monitored natural attenuation as potentially appropriate for remedial actions at UST, RCRA and Superfund sites; it is not considered a presumptive remedy. Monitored natural attenuation should not be the only remedial approach evaluated; active remedial technologies must be considered as well. Principal threats must be addressed, and contaminated soil and groundwater cleaned up within a reasonable time frame.

The advantages of monitored natural attenuation include:
* less remediation waste is generated or transferred;
* it is less intrusive;
* it may be applied to all or part of a site;
* it may be used with or as follow-up to other active remediation methods; and
* it may be cost-effective.

The disadvantages of monitored natural attenuation include:
* it generally takes longer than active remediation to achieve remedial goals;
* it may be more complex and more costly to characterize sites in the detail required to support natural attenuation evaluations;
* the resulting daughter compounds may be more toxic than the parent compounds;

- longer monitoring periods may be required;
- there is a potential for continued contaminant migration;
- changes in hydrogeochemical conditions could mobilize contaminants; and
- more community education and outreach is often needed.

In most cases, monitored natural attenuation will be a component of a remedy. Evaluation of source control measures is critical if monitored natural attenuation is being considered.

One goal of an evaluation of monitored natural attenuation is to demonstrate that natural contaminant degradation processes will reduce contaminant concentrations in groundwater to below risk-based or regulatory levels before potential receptor pathways are completed. A proponent must provide sufficient site-specific characterization and analysis to support the use of monitored natural attenuation. A conceptual model should be developed to integrate site data and assess the potential for natural attenuation. The conceptual model should be refined as new information is collected. If preliminary information indicates that monitored natural attenuation is promising, then fate and transport models should be developed to evaluate the effectiveness of natural attenuation.

Monitored natural attenuation can be appropriate where:
- it will be protective of human health and the environment;
- it can achieve site-specific remediation objectives; and
- it will be completed within a reasonable time frame compared to other methods.

Monitored natural attenuation is not appropriate where:
- unacceptable risk is posed to human and environmental receptors; or
- it can't achieve site-specific remediation objectives.

Monitored natural attenuation is generally not considered to be a viable remedy in cases where plumes are expanding in size or migrating into clean areas. A critical issue is the "reasonableness" of the remediation time frame. Time frames should be evaluated on a site-specific basis, estimated for all remedial alternatives under consideration, and compatible with land and groundwater use. If available, Comprehensive State Groundwater Protection Program Plans should be consulted.

Performance monitoring must be conducted to demonstrate that natural attenuation is occurring as expected. To help in evaluating the effectiveness of monitored natural attenuation, historical data should be presented as a time series, and contaminant and daughter product contour maps should be prepared. Mass reductions of parent and daughter products should be evaluated over time.

Monitored natural attenuation may not be working when:
- there is an increase in contaminant concentrations with time;
- there is plume expansion;
- the rate of contaminant reduction is slower than expected; or
- changes in land use or groundwater use result in increased risk levels through additional potential receptor pathways.

Contingency remedies should be seriously considered in conjunction with monitored natural attenuation remedies. Contingency remedies should be documented in the record of decision (ROD) in case the selected remedy fails to perform as expected. The contingency may specify a different technology or call for a modification of the originally selected remedy. Current research indicates that monitored natural attenuation

could work at approximately 80 percent of petroleum sites and approximately 20 percent of chlorinated solvent sites where it is the only implemented remedy.

In summary, Brandon said that EPA is fully committed to the regulatory framework that governs the selection of any remedial or corrective action approach, including monitored natural attenuation. Monitored natural attenuation is considered a "passive" approach for soil and groundwater remediation, but not a "do nothing" approach. Monitored natural attenuation is not considered a presumptive remedy for any type of site. The burden of proving that monitored natural attenuation will be a protective remedy and that it can be achieved in a reasonable time frame is on its proponent. Long-term monitoring and contingency planning are essential.

Editorial comment: Following the *Workshop on Natural Attenuation of Groundwater Contamination* but prior to issuance of this report in November 1997, OSWER issued Directive #9200.4-17 on "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites." The directive can be accessed by the public at the following EPA website address: http://www.epa.gov.swerust1/directiv/d9200417.htm

Overview of Draft Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater
    John Wilson, EPA, NRMRL/SPRD–Ada, OK

Wilson noted that the draft Air Force Center for Environmental Excellence (AFCEE) *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, or "AFCEE protocol," evolved from his research at a number of sites and from negotiations between responsible parties, States and EPA Regions. He emphasized that the protocol was tested only for large plumes (greater than one-half mile long) and requires detailed site characterization and extensive monitoring. He added that it is not a low-cost solution and would be overkill for small plumes. Wilson said that Revision 2 of the draft protocol is now in review to determine if it meets EPA's requirements for an ORD publication. The major changes from the original draft involved deletion of language with policy implications.

Wilson described the initial site screening process in six steps, citing steps (1), (2), and (4) as ones that the protocol covers in particular detail:

1) Determine if natural bioattenuation is occurring based on the geochemical data (*e.g.*, Are bacteria destroying hydrocarbons?).

2) Determine groundwater flow paths and solute transport paths and rates.

3) Locate sources and receptors within the hydrologic setting.

4) Estimate the rate of natural attenuation.

5) Compare the rate of contaminant transport to the rate of contaminant degradation.

6) Compare the conditions at potential points of exposure to the remedial goals and cleanup criteria.

Referring to a candle-flame analogy, Wilson said that the protocol would allow one to recognize the extent of the "flame," whether it is stable, and how rapidly the "flame" would be extinguished after the source was

removed. He stressed that, in the absence of source control, the protocol should not be used to predict remediation time frames or address restoration to beneficial use. The protocol's screening process encourages use of data from existing remedial investigation (RI) wells to determine whether a basis exists for further investment in natural attenuation. Wilson said that he and Todd Wiedemeier of Parsons Engineering Science, Inc., developed a weighting scheme (Table 1) that uses commonly available geochemical parameters to qualitatively determine the strength of the evidence that natural attenuation is occurring. He added that the screening criteria were designed for chlorinated solvents and cannot be used for hydrocarbons.

Wilson presented parameters from two hypothetical sites to illustrate the interpretation of results. If the total "score" is 0-5 from summing the weights attributed to the parameters, there is inadequate evidence of biodegradation. A score of 6-15 is limited evidence; 16-20 is adequate evidence, while a score more than 20 presents strong evidence of biodegradation.

Wilson noted that reductive dechlorination may sometimes proceed relatively rapidly, resulting in a plume that is small and difficult to locate by monitoring groundwater alone. Examination of core samples can provide a useful indicator. Sometimes one can tell from visual examination of a core (*e.g.*, from the presence of reduced iron) where biodegradation is occurring. Monitoring for contaminants of concern at locations identified by core sample examination can help in defining the plume and providing evidence of reductive dechlorination.

One workshop participant asked whether Fe(II) data or DO data are more reliable when the two conflict. Wilson suggested that if the quality of the results were good, he would give more credence to the iron data. Frank Chapelle (USGS) added that if samples contained both Fe(II) and DO, it may be an indication of mixing across aerobic and anaerobic horizons in the placement of the well screens. He said that the data will nullify each other in terms of the screening computation. Mark Filippini (EPA/Region 10) noted that the example emphasizes the need to consider how the wells are screened in order to interpret aquifer heterogeneity.

Wilson said that it is necessary to determine rate constants for natural attenuation, and listed four important reasons: (1) to determine whether the plume is contained (at a dynamic steady state) or shrinking, and that concentrations are protective of potential receptors; (2) to compare the rate of biodegradation at the site to rates published in the literature in order to provide a "reality check"; (3) to predict plume alteration caused by changes in flow rates; and (4) to determine how fast the groundwater plume will disappear after source control is achieved. Rate constants can be used for each of these objectives. Wilson noted that determination of rate constants for natural attenuation requires accurate estimates of plume velocity and flow paths.

Table 1. Initial Screening Steps

Parameter	Screening Value	Weight	Comments
Dissolved oxygen	<0.5 mg/L >5.0 mg/L	+3 -3	Assumes that reductive dechlorination is necessary for natural bioattenuation; O_2 poisons reductive dechlorination
Nitrate	<1 mg/L	+2	Nitrate inhibits reductive dechlorination
Fe(II)	>1 mg/L	+3	Fe(II) is an efficient O_2 scavenger, which prevents O_2 from poisoning reductive dechlorination
Sulfate	<20 mg/L	+2	Competes with reductive dechlorination
Sulfite	>1 mg/L	+3	Metabolic product and O_2 scavenger
Methane	>0.1 mg/L >1.0 mg/L	+2 +3	Metabolic product
Redox potential	<+50 mV <-100 mV	+1 +2	Indicates whether groundwater is in the right redox zone
Total organic carbon	>20 mg/L	+2	Measures humic material which may serve as electron donor to drive reductive dechlorination
Temperature	>20°C	+1	Process favored by warm conditions
Carbon dioxide	>2 times background	+1	Evidence of respiration
Alkalinity	>2 times background	+1	Evidence of respiration
Chloride	>2 times background	+2	Metabolic product
Hydrogen	>1 nanomolar (nM)	+3	Indicator of reductive dechlorination (field sampling and analysis must be done with extreme care)
Volatile fatty acids	>0.1 mg/L	+2	Sources of carbon and reducing power
BTEX	>0.1 mg/L	+2	
Reductive daughter products	Detectable	+2	Look at NAPL in source area, not just groundwater. To score, the daughter products in groundwater must not be present in the source material.
Ethane/ ethene	>0.01 mg/L >0.1 mg/L	+2 +3	Daughter products of vinyl chloride/ethene

8

To estimate the rate of natural attenuation, three techniques can be used: (1) measuring attenuation along the flow path through comparisons between transects; (2) microcosm studies (particularly useful where well locations cannot be optimized or where the aquifer is extremely complex); and (3) extrapolation from the literature, coupled with sensitivity analyses to determine protectiveness. Wilson noted that microcosm studies are potentially valuable for landfill leachate plumes, even though the U.S. Air Force does not use them because of their cost. Wilson summarized both mathematical and model-fitting methods to calculate rate constants.

Using readily available screening data from the St. Joseph (Michigan) site, Wilson demonstrated the calculation of a first-order biodegradation rate of about 0.6 yr^{-1} with a high degree of confidence. The average rate determined at St. Joseph from microcosm studies was 1.38 yr^{-1}, which compared favorably to the calculated rate. He pointed out that a first-order rate of 1 yr^{-1} represents a 2 percent reduction per week, or a half-life of about 8.3 months. Even minor variations in rate constants were shown to have significant effect upon the extent of a plume. He said that use of microcosm studies to estimate rates could take 18-24 months and cost $300,000. Nevertheless, microcosm studies provide a useful boundary on rates. Agreement between computed and microcosm rates implies greater confidence in the results. He noted that microcosm rate constants are generally faster than *in situ* rates, due to the acceleration caused by mixing and homogenizing core samples. For biodegradation occurring under methanogenic or sulfur-reducing conditions, rates reported in the literature generally fall within a relatively narrow range. (First order rate constants for TCE and benzene typically range from about 0.3 to 3 yr^{-1}, with a cluster of rates around 1 yr^{-1}.)

Status of Draft Technical Guidance for Evaluating Natural Attenuation in Soil and Sediment
    D. Fred Bishop, EPA, National Risk Management Research Laboratory, Land Remediation and Pollution Control Division (NRMRL/LRPCD–Cincinnati, OH)

Bishop noted that natural attenuation occurs not only in groundwater, but also in soil, sediment, landfills, and surface water. His laboratory division (NRMRL/LRPCD) is investigating the background information needed to develop technical guidance for natural attenuation of soil, sediment, and landfills. He explained that the programmatic approach involves four broad phases:

1) Review and evaluate the literature to investigate pertinent science, contaminant fate and transport models, monitoring and sampling protocols, risk assessment methods, and overall definition of critical issues and limits to natural attenuation.

2) Prepare interim technical guidance as the science and engineering permits.

3) Conduct further laboratory and field research to validate assumptions in the guidance.

4) Prepare technical guidance protocols as the science and engineering evolves, incorporating feedback from field application of the interim guidance.

Bishop noted that his presentation will address the status of work on surface soil, subsurface soil (*e.g.*, at UST sites) and sediment.

Soil: At present, the work on surface and subsurface soil is complete on the identification of critical science and engineering issues. Ongoing work includes revising draft interim guidance and conducting critical research and field studies. The critical research needs include substantial work on modeling fate and transport.

Bishop indicated that a major problem is the presence of NAPLs in the soil. Without NAPL source control, NAPL contaminants are continuously leached into groundwater as a result of rainfall percolation and vapor transport. He indicated that in evaluating natural attenuation of soil, as compared to active remediation, impacts on other media must be considered (*e.g.*, effects on attenuation of any associated groundwater plume). Bishop noted that weathering is also a major research issue. NRMRL is looking at aging through diffusion and sorption/desorption in soil micropores; humification (chemical sequestering in soil pores); toxicity and bioavailability changes with aging and humification; and the effects of asphaltene films on free-product surfaces. The films retard diffusion of the more volatile fractions and hence prolong the existence of the more mobile components.

The critical issues associated with evaluating natural attenuation in soil include:

- Predicting vapor migration into surrounding structures. Because some of the volatile organic compounds (VOCs) are combustible, vapor migration may create explosive hazards, as is the case with methane and fuel chemicals;

- Understanding precipitation impacts on rates of transport and degradation;

- Source longevity in soil;

- Developing predictive tools to estimate remediation time frames; and

- Developing guidance on erosion issues, which would address 1) the erodible material (*i.e.*, what is transported from the area) and 2) the underlying soil in the area. For the former, the impact of the erodible material needs to be evaluated (*e.g.*, if there are high molecular weight contaminants sorbed to soils, the impact to potential receptors would need to be assessed). For the latter, the depth and extent of erosion will impact oxygen concentrations in the soil profile. Where erosion is significant, portions of the soil which were previously under low oxygen concentrations can be exposed to higher concentrations. Bishop added that the redox conditions in the soil are very important; if oxygen content in the bound-soil-moisture is below 2 mg/L, degradation rates decrease quickly and the process can become anaerobic at depth.

Bishop said that NRMRL's programmatic research and field studies include evaluation of natural attenuation rates in surface soil, evaluation of rates in the subsurface (concentrating on polycyclic aromatic hydrocarbon [PAH] sites, such as creosote sites and town gas works), and work at UST sites, which will begin next year. They have examined the available literature, and have correlated observed rates by a structural activity modeling approach. They have estimated typical upper bounds on degradation rates, in soils that generally have been exposed to annual tillage and fertilization.

Bishop described a mesocosm experiment on creosote-contaminated soil (mainly sand, with about 8.5 percent organics). Mesocosms were ran with ambient soil moisture (5.5 percent) and with an increase to 6.9 percent moisture. Natural attenuation rates of PAHs were documented over time, with the highest rates obtained for 3- and 4-ring compounds, followed by 2-ring compounds, and the lowest rates for 5- and 6-ring compounds. First-order rate constants were also derived for environments with DO concentrations of the bound-soil-moisture above and below 2 mg/L. Bishop reported that the rate constant decreased with DO concentrations below 2 mg/L. Moisture content above 2 mg/L also resulted in a maximum biodegradation rate, which may permit manipulation of rates by controlling soil moisture.

Sediment: Bishop said that ORD has completed literature reviews and evaluations of sediment, delineated critical issues, and peer-reviewed an interim technical guidance document. The interim guidance has been sent to OSWER for review, and will be subsequently sent to EPA's Office of Water and to the regional offices.

ORD has begun coordinating attenuation studies with the U.S. Army Corps of Engineers (USACE). Bishop explained that sediment resuspension and transport is an important component of this research, and the USACE has models for storm events and resuspension that will be very useful for assessing risk. Emphasis of the studies will be on cohesive sediment (clays and organic matter) contaminated with metals (mainly mercury) and high molecular weight organics, such as polychlorinated biphenyls (PCBs), PAHs, dioxins, dibenzofurans.

Bishop identified the key mechanisms affecting natural attenuation in sediment: biodegradation, biotransformation, burial, sediment resuspension, adsorption, bioturbation, dispersion, dilution, chemical stabilization or destruction, and volatilization. He noted that bioturbation and burial work against each other. Monitoring trends in the literature have documented declines in tissue concentrations of contaminants in fish and shellfish. These trends have been attributed to the regulation of aquatic discharges, but contrary to expectation, the decline in the fish/shellfish body burden has stabilized instead of continuing to decline. Bishop attributed this to transportation mechanisms that wash contaminated sediment from land into water bodies or are resuspending and remobilizing sediment contaminants back into the water column. This has been documented following storms in the Great Lakes, and he acknowledged that this is of concern. Ninety-five percent of sites in a National Sediment Quality Survey have shown PCB cancer risks in excess of 10^{-5}. There are lower but still important risks from mercury. He noted that methylation of mercury increases its mobility.

Bishop summarized findings thus far:

- Anaerobic conditions limit aerobic biodegradation (*e.g.*, some PAHs and lightly chlorinated ortho-substituted PCBs will not degrade anaerobically).

- Contaminant mobilization due to storm events and resuspension is a significant concern.

- There is variability in the extent and rate of attenuation—reductive dehalogenation occurs in laboratory studies and microcosms, but is variable in the field. This will require additional research.

- Atmospheric concentrations of contaminants are a complication. Over Lake Michigan, airborne PCBs may actually be contributed by the water column.

- Bioaccumulation and biomagnification of contaminants in aquatic organisms can increase concentration levels by factors of as much as 20,000.

- Bioturbation increases the bioavailability of contaminants to bioaccumulation.

- The recent leveling off in the decline of aquatic body burdens, presumably due to the remobilization of contaminants washed in from the land during storm events, is a concern that needs further research.

- Risks associated with bioaccumulation in aquatic organisms are affecting predators.

- Fish consumption advisories are often ineffective, especially for subpopulations that depend upon fish and shellfish for subsistence.

Questions and Answers: Tom Stafford (Louisiana DEQ) asked whether there was any upper bound to the maximum biodegradation rate measured in the mesocosm experiments with increased moisture content. Bishop replied that the literature reveals an optimal range, which will be addressed in the protocol.
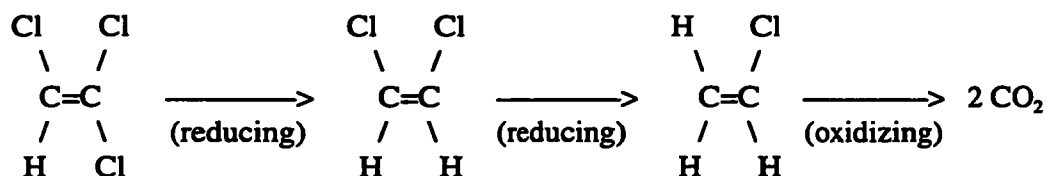
Identifying Redox Conditions that Favor the Natural Attenuation of Chlorinated Ethenes
    Frank Chapelle, U.S. Geological Survey, Columbia, SC

Chapelle put today's understanding of the degradation of chlorinated ethenes into context with the understanding held just two to three years ago. At that time, it was known that some systems existed in which TCE degraded efficiently, but it was not known why. The varying behavior of chlorinated ethenes has since been explained scientifically and is no longer a mystery.

Chlorinated ethenes do not behave uniformly in groundwater systems. Chapelle explained that there are three types of systems that affect the behavior of chlorinated ethenes: (1) Type 1, in which degradation of TCE is rapid and complete; (2) Type 2, in which degradation of TCE is slower and incomplete; and (3) Type 3, in which TCE does not degrade. He noted that chlorinated ethenes are subject to a variety of microbially-mediated redox processes including reductive dechlorination (an electron-accepting process), direct oxidation (an electron-donating process), and co-metabolism (most often an electron-accepting process).

The rate and extent of biodegradation processes depend on the sequence of redox conditions. For example, a sequence of reducing conditions followed by oxidizing conditions must exist to degrade TCE to vinyl chloride and then to carbon dioxide:

$$
\begin{array}{ccccccc}
\mathrm{Cl} \quad \mathrm{Cl} & & \mathrm{Cl} \quad \mathrm{Cl} & & \mathrm{H} \quad \mathrm{Cl} & & \\
\backslash \quad / & & \backslash \quad / & & \backslash \quad / & & \\
\mathrm{C{=}C} & \xrightarrow{\text{(reducing)}} & \mathrm{C{=}C} & \xrightarrow{\text{(reducing)}} & \mathrm{C{=}C} & \xrightarrow{\text{(oxidizing)}} & 2\,\mathrm{CO_2} \\
/ \quad \backslash & & / \quad \backslash & & / \quad \backslash & & \\
\mathrm{H} \quad \mathrm{Cl} & & \mathrm{H} \quad \mathrm{H} & & \mathrm{H} \quad \mathrm{H} & &
\end{array}
$$

For reductive dechlorination of PCE (PCE→TCE→cis-DCE→vinyl chloride) to occur, methanogenic, sulfate-reducing and/or ferric iron [Fe(III)]-reducing processes must take place at one or more stages of dechlorination. These processes affect and are affected by the concentration of dissolved hydrogen gas in the groundwater because molecular hydrogen is the key electron donor in the reductive dechlorination process.

Chapelle indicated that because the hydrogen concentration in the groundwater reflects the redox condition, it will be indicative of the biodegradation pathway. A high hydrogen concentration will favor reducing processes, and a low hydrogen concentration will favor oxidizing processes. In contrast, a high oxygen concentration indicates oxidizing conditions, and a low oxygen concentration indicates reducing conditions. Chapelle explained that it is important to distinguish oxidizing from reducing conditions, and to distinguish between methanogenesis, sulfate reduction, ferric iron reduction, and nitrate reduction. By monitoring redox conditions, one can predict whether effective natural bioattenuation is likely to occur.

Brandon asked Chapelle if there is a problem with measuring methane as an indicator of conditions favorable to reductive dechlorination. Chapelle replied that the presence of methane is not necessarily

indicative of reducing conditions at the sampling point; the methane may have been produced elsewhere and migrated to the sampling location. Compared to methane, hydrogen reacts rapidly and is closer to equilibrium with its surroundings. In light of this information, measurement of hydrogen is needed to identify redox conditions.

Chapelle explained that when sampling groundwater for hydrogen, hydrogen partitions into the headspace bubble of the bubble-strip sampler. Over time, the gas-phase hydrogen concentration in the bubble asymptotically approaches equilibrium with the aqueous phase. The bubble gas can then be sampled and analyzed with a gas chromatograph.

Chapelle discussed a site at the Naval Air Station (NAS), Cecil Field, as an example of where a desirable sequence of methanogenic and iron-reducing conditions was encountered. These conditions resulted in concentrations of chlorinated ethenes that approached "zero." He also mentioned a second site at NAS, Cecil Field, in which the measured hydrogen concentration indicated that conditions were insufficient to reduce concentrations of *cis*-DCE in the groundwater plume prior to its reaching a stream. He said that diffusion samplers were subsequently used to measure the concentrations of chlorinated ethenes within depths of 50 cm and 5 cm of the stream bed. Chlorinated ethenes were detected within 50 cm of the stream bed, but not within 5 cm. The difference was attributed to the presence of iron-reducing conditions within the 50-cm interval and oxidizing conditions within the 5-cm interval. Chapelle indicated that natural attenuation in the stream bed sediments was an order of magnitude faster than in the deeper sediments. Brandon asked whether dilution was considered as a factor in the reduction of chlorinated ethenes. Chapelle explained that although dilution was not evaluated, the argument could be made that natural bioattenuation was occurring. He added that a tracer study was needed to distinguish between reduction due to dilution versus biodegradation.

Chapelle cited conditions at the Marine Corps Logistics Base in Albany, Georgia, as an example where natural bioattenuation of TCE would *not* occur. This site is underlain by a carbonate aquifer with virtually no organic matter. There is a high concentration of dissolved oxygen and low concentrations of methane and hydrogen.

Chapelle noted that the rate and extent of biodegradation processes depend on the sequence of redox conditions. He said that this concept was built into the draft AFCEE protocol for determining the efficiency of natural attenuation. He proposed that the protocol's information must now be made available for the regulatory community and its use translated into a regulatory reality.

Questions and Answers: In response to a question asking whether a succession of reducing to oxidizing conditions is always necessary for the degradation of chlorinated ethenes, Chapelle replied that complete dechlorination is possible when reduction of vinyl chloride to ethene occurs under highly reducing conditions. As to why *cis*-DCE is produced in reductive dechlorination, rather than *trans*-DCE, Chapelle said that, due to the structure of the TCE molecule, it is easiest for microbes to remove the chlorine that yields the *cis*-DCE degradation product.

In response to a question regarding the status of modifying site conditions to obtain the required reducing and oxidizing environments, Bishop said that he came up with the idea of using hydrogen gas in bioventing to easily destroy PCE and TCE; oxygen is subsequently injected into the ground to degrade vinyl chloride to carbon dioxide and chloride. Bishop added that it may prove a cheap and effective treatment method and will soon be tested in the field.

Chapelle was asked to comment on the limitations of collecting hydrogen samples from different types of wells and using different collection methods. He noted that hydrogen is produced by the iron in steel and

by direct current, so as a result, stainless steel wells and Grundfos pumps can interfere with accurate hydrogen measurements. He cited an example of hydrogen measurements made at adjacent polyvinyl chloride (PVC) and stainless steel wells; hydrogen concentrations of 0.5 nM and 500 nM were measured at the wells, respectively. He added that the drilling of wells can upset microbial metabolism. Therefore, conditions should be allowed to equilibrate for about two months after well installation prior to sampling for hydrogen.

Chapelle recommended sampling for hydrogen using a peristaltic pump or a Bennet positive displacement pump. He clarified that although the Bennet pump is constructed of stainless steel, it is driven by gas and should not affect hydrogen measurements. Chapelle cautioned against the use of direct current electric pumps because they can produce hydrogen gas.

Initial Steps in Evaluating Natural Attenuation (Site Conceptual Model and Site Screening Analysis)
Steven D. Acree, EPA, NRMRL/SPRD–Ada, OK

The initial phases in the site-specific evaluation of natural attenuation involve development of a conceptual model for contaminant sources, transport, and fate at the site and performance of a screening-level evaluation of the potential effects of natural attenuation processes. The conceptual model is not a "data dump." It is a coherent interpretation of characterization data that results in a three-dimensional representation of contaminant source areas, groundwater flow conditions, and solute transport based on all available information, including hydrogeologic, geochemical, biological, contaminant, and climatological data. In this sense, the conceptual model should be viewed as a living document that is continually revised as new information is obtained. The model serves as a focus for evaluating the potential role of natural attenuation processes in site remediation and identifying data gaps for further study. An initial screening approach is devised based on the site-specific conceptual model.

The elements of the conceptual model include a description of the source (the nature, extent, and magnitude of contamination); interpretation of migration controls (geologic, hydrogeologic, biologic, and geochemical); and identification of potential receptors. Receptors in this sense may include any point, area, or resource to be protected and may not necessarily be limited to single points, such as existing drinking-water wells. The development of a conceptual model involves the definition of the problem; the interpretation, integration, and presentation of the data; and an assessment of whether additional data are needed. If additional data are needed to complete the screening-level analysis, the information should be collected.

The objective of the initial evaluation steps, development of a site conceptual model and performance of the site screening analysis, is to determine whether natural attenuation may be occurring in the subsurface at sufficient rates to cost effectively meet remedial goals and warrant detailed characterization. The screening information required to make this determination includes source and receptor locations, geologic and chemical data, and groundwater flow parameters. The first step in the process, as outlined in the draft AFCEE protocol, is to determine whether biological transformation of the contaminants is occurring. This is accomplished through evaluation of geochemical and contaminant indicators of biological transformations. The number of monitoring wells or points required to characterize plume behavior will depend on the size and complexity of the plume. Next, groundwater flow and solute transport parameters, including source and receptor locations, must be determined.

The potential range of biodegradation rates is then estimated, and used to assess whether natural attenuation processes may be occurring at rates sufficient to be protective of human health and the environment, meet remedial objectives, and warrant further investigation for incorporation into potential remedial alternatives.

This screening-level assessment may be performed using simple analytical models of contaminant transport, such as BIOSCREEN. Such evaluations should always include analyses of sensitive model parameters and estimates of the effects of uncertainty in the values of these parameters. If these analyses indicate natural attenuation processes may be occurring at sufficient rates to warrant consideration in potential remedial alternatives and reliance on these processes is acceptable from a regulatory standpoint, then detailed characterization to support these screening-level analyses is indicated.

General Principles of Site Characterization
Jeff van Ee, EPA, National Exposure Research Laboratory, Characterization Research Division (NERL/CRD)–Las Vegas, NV

van Ee described site characterization as being necessarily based on data needs for the entire decision-making process (including risk assessment, remedial technology evaluation, fate and transport modeling, etc.). The primary goals of site characterization are to complete the process as efficiently as possible and to make the best decisions (considering risks and costs) with the best available information. He added that the decisions involve a number of disciplines, media, and risks; a variety of costs; data of different quality and from a number of sources; data on different spatial and temporal scales; and different information sources.

van Ee mentioned that often those who characterize sites tend to focus on the data, but not on what the data represent. Decisions are made on large volumes of media, based on small volumes of samples. For example, contaminated soil at a site may be excavated with backhoes based on analytical results of a few teaspoon-sized samples. Therefore, spatial scales must be considered. van Ee added that the cost of characterization versus the number of samples collected also must be considered. The point where just enough samples are collected to make an appropriate decision, can be estimated from a cost optimization curve. This curve can be constructed by plotting the total cost (the estimated sampling cost plus the estimated cost of decision errors) as a function of the number of samples collected.

van Ee noted that quality assurance has previously focused on analytical error, but the error from the sample collection process is more significant. The sampling error is the sum of measurement error and network design error; the measurement error, in turn, is the sum of the collection error, handling error, and analytical error.

There is bias and imprecision in both the data collection effort and the interpretation of the data. van Ee listed several sources of bias:

- Measurement bias introduced in sample collection and not caused by contamination;

- Measurement bias introduced in sample collection caused by contamination;

- Measurement bias introduced in handling and preparation not caused by contamination;

- Measurement bias introduced in handling and preparation caused by contamination;

- Measurement bias introduced in subsampling not caused by contamination;

- Measurement bias introduced in subsampling caused by contamination;

- Measurement bias introduced in the laboratory analytical process not caused by contamination;

- Measurement bias introduced in the laboratory analytical process caused by contamination; and

- Total measurement bias.

van Ee pointed out the variability in data interpretation by citing an example in which the same data set was provided to 12 contractors, who were asked to identify where the contaminants were located. Each contractor provided very different results, which in turn, varied from the actual contaminant locations.

van Ee noted that the typical approach to site characterization involves budgeting the resources for sampling and analyses, followed by the actual sample collection and analysis. The data are then analyzed, evaluating spatial distributions, temporal trends and data gaps. Additional resources are subsequently allocated for additional sampling and analyses, and the investigation deadlines are extended. van Ee recommended that a number of options for a site be considered before conducting extensive sampling. Conceptual models should be developed and used as a guide as to what samples are needed to make appropriate decisions. He cited the data quality objectives (DQO) process as a better, more efficient process for optimizing site characterization.

Goals of the DQO process may be to answer questions such as "How clean is clean?" and to determine the probability that the correct decision is being made. The areal extent of contamination, the concentration of contaminants, and the exposure routes must be defined. van Ee said that the objectives (data use, data quality requirements, acceptable spatial and temporal scales, and permissible errors) must be clearly defined before data collection begins.

The DQO process is as follows:
- State the problem;
- Identify the decision;
- Identify inputs to the decision;
- Define the study boundaries;
- Develop a decision rule;
- Specify limits on decision errors; and
- Optimize the design for obtaining data.

van Ee said that one of the typical basic questions to be answered during site characterization is whether or not a standard is exceeded currently, and whether or not a standard will be exceeded. He said that an action level by itself is meaningless; a corresponding level of support is required. He added that "support" refers to the size, shape, and orientation of the physical sample taken at a sampling point. van Ee indicated that definitions are important when planning a sampling program. As an example, he pointed out that the CERCLA and RCRA programs use different grain size criteria in defining the term "soil."

NERL/CRD has produced three papers to evaluate data interpolation methods and three papers to evaluate sampling design options. van Ee concluded his presentation by listing several "rules of thumb" identified from these studies.

On interpolation:
- If 12 people interpolate the same data, 12 different answers are obtained;
- The best answer depends on the method of score-keeping;
- Ordinary kriging is hard to beat; and
- Interpolation with transformed data is risky.

On sampling design, in general:

- Grid sampling is better than random sampling, but not much better;
- Precise data are better than imprecise data, but not much better;
- Unbiased data are better than biased data, but not much better; and
- Many data are much better than few data.

On site-specific sampling design:
- If enough preliminary data points are available (50 to 100 points), a conditional simulation of a site can be used to accurately optimize site-specific designs.

Chemical Characterization Methods for Natural Attenuation Evaluations
William Lyon, ManTech Environmental Research Services, Corp., and Dan McInnes, EPA, NRMRL/SPRD–Ada, OK

John Wilson noted that his laboratory has developed and continues to develop standard operating procedures (SOPs) for analytical methods needed to evaluate natural attenuation. He introduced William Lyon of ManTech Environmental Research Services Corporation and Dan McInnes of NRMRL/SPRD to present information about two of these SOPs.

HCl Extraction of Soil and Sediment to Screen for Microbially Available Iron: Lyon explained that it is important to determine the amount of microbially available Fe(III) in soil and sediment in order to assess whether there is sufficient reducible iron present at a site to support the anaerobic biodegradation of various pollutants such as BTEX compounds. He said that it is difficult to develop a straight-forward method of determining the amount of microbially available iron, due to the varying extractability of iron minerals. The hydrochloric acid (HCl)-extraction of minerals should be viewed as an alternative, easier-to-apply surrogate method of extraction, which is thought to be highly correlated with microbial extraction. The extent of this correlation remains to be established by laboratory microcosm experiments with various iron-reducing bacteria.

Soils and sediments may contain a complex mixture of HCl-resistant minerals (*e.g.*, inert iron in silicates, pyrite, marcasite, FeS_2, and crystalline iron oxide-hydroxide minerals) and HCl-extractable minerals (*e.g.*, ferric gel, protoferrihydrite, ferrihydrite, ferrous carbonate, ferrous phosphate, "green rusts," acid-volatilized sulfides, and crystalline iron oxide minerals such as maghemite and magnetite). The extent of reduction in the $Fe(II)/Fe_{total}$ ratio seen in HCl extracts of such mineral mixtures reflects, to some extent, the intensity of microbial iron-reducing activity. However, that portion of Fe(II) iron in non-extractable minerals such as pyrite will *not* be seen by this method.

The extraction method developed at the R.S. Kerr Laboratory is described in RSKSOP-193 and involves a 24-hour acid extraction using 0.5 molar (M) HCl. The extract can be analyzed for both Fe(II) and Fe(III) iron using ion chromatography. Fe_{total} by ion chromatography has been routinely checked for accuracy by running duplicate samples by inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

The extraction method provides a measure of the fairly active portion of the sample's Fe(III), which is used to predict how long a site can support the biodegradation. While the iron minerals attacked by the dilute HCl are somewhat uncertain, the results of the extraction provide an operationally stable value of the extent of reduction useful for stratigraphic comparisons and a conservative estimate of available Fe(III).

The redox condition of the soil or sediment sample must be preserved during sample collection. The samples should be quickly placed under nitrogen in an airtight container. Ideally, soil cores should be collected in a protective sleeve and transferred to a nitrogen-sparged field glovebox for splitting and sampling. Experiments show that samples prepared for extraction inside a glovebox can show substantially higher values of the reduction ratio. Wet samples to be used for HCl extraction should be maintained under cool conditions, protected from light, but should not be frozen.

Questions and Answers: Jon Josephs pointed out that both the quantity of bioavailable iron and its rate of leaching from soil to groundwater can limit iron-reducing processes. In response, Lyon indicated that he has not investigated methods to determine the rates at which iron is leached from soils. However, he noted that leaching rates will depend on the variety of iron-bearing minerals present, groundwater pH, and other factors. Another workshop participant commented that currently, bioavailable Fe(III) is rarely considered in deciding on whether a monitored natural attenuation remedy will be implemented. However, it may be considered more frequently in future for natural attenuation evaluations and in reevaluating the performance of selected natural attenuation remedies.

Bubble Strip Method for Sampling Dissolved Hydrogen in Groundwater: McInnes demonstrated the use of the bubble strip method, which is used by and under continued development at the R.S. Kerr Environmental Research Center, for the collection of groundwater samples for dissolved hydrogen analysis. A peristaltic pump is used to draw a water sample into a sampling bulb connected to the outflow end of the pump hose. The outlet end of the sampling bulb is held upright to remove the gas bubbles as water passes through. Nitrogen gas is injected into the bulb via a sampling port, and the gas and water are allowed to equilibrate for 20-30 minutes. During this time, the sampling bulb is oriented at a 45-degree angle to increase the surface area of the gas-water interface. A gas-tight syringe inserted through the gas sampling port of the bulb is then used to extract a gas sample. Henry's Law is used to determine the concentrations of dissolved hydrogen in the groundwater phase, based on the concentration measured in the gas phase.

McInnes described research he has done in order to estimate the accuracy of measurements and the needed equilibration time. He indicated that in the future, the laboratory plans to do similar experiments at temperatures other than 20°C and with gases other than hydrogen gas. Josephs noted that the pump was installed between the sampling bulb and the pump discharge point, which was at atmospheric pressure. He said that, since pressure is a factor in Henry's Law, it may be necessary to measure the pressure in the bulb, which can be less than atmospheric pressure due to the partial vacuum created by locating the pump downstream of the sampling bulb. McInnes agreed that a partial vacuum can form. Chapelle noted that the Henry's Law coefficient is not affected by changes in pressure as much as by temperature changes. Further discussion of this matter was deferred to stay on schedule.

Site Characterization for Natural Attenuation Assessments: Hydrogeologic Considerations
Steven D. Acree, EPA, NRMRL/SPRD–Ada, OK

Traditional hydrogeologic characterization methods, such as large-scale aquifer pumping tests, grew from techniques used to assess aquifers for water-supply purposes. Such methods often result in characterization of bulk or average aquifer properties. However, most subsurface formations are highly heterogeneous. Heterogeneity results in complexity in the groundwater flow system and, ultimately, contaminant distribution and transport. Contaminants may be preferentially transported through more conductive zones. Similarly, sources for groundwater contamination, such as dense nonaqueous phase liquids (DNAPLS), are often complex and heterogeneously distributed in the subsurface. This often results in plumes with small zones of very high contaminant concentrations and larger areas with lower concentrations. Characterization

of average aquifer properties and limited contaminant characterization without regard for the effects of subsurface heterogeneity may result in inaccurate or highly uncertain assessments of natural attenuation processes.

Hydrogeologic information obtained during natural attenuation assessments is often used to constrain sampling locations, calculate biodegradation rates, and predict contaminant migration. Calculation of biodegradation rates and prediction of contaminant migration using average aquifer properties and plume descriptions are of particular concern in these evaluations. In current field studies, biodegradation rates are often calculated based on one of three techniques.

1) Apparent loss of contaminants along a flowpath or between transects. This technique incorporates retardation, dispersivity, and estimates of groundwater seepage velocity. Use of the method assumes that differences in contaminant concentrations between monitoring points are representative of actual contaminant mass loss from the system and not artifacts of sampling locations, methods, or source history.

2) Normalization of the apparent contaminant loss relative to conservative tracer data. This method incorporates retardation and groundwater seepage velocity and assumes that relative reductions in concentrations are a result of mass removal and are not artifacts of changes in source history.

3) Estimates derived during calibration of a mathematical model. Use of this technique incorporates information on hydraulic conductivity distribution, hydraulic gradients, and other potentially sensitive parameters. Much of the information used for these assessments is often based on average parameter values and may not be representative of zones in which contaminants are migrating.

In order to reduce the uncertainty in these calculations to acceptable levels, all of these techniques must incorporate estimates of hydraulic parameters representative of conditions within the portions of the aquifer in which contaminants are migrating. These zones may often be of higher hydraulic conductivity than average conditions due to the heterogeneity of the subsurface. Evaluations of natural attenuation processes using values for average conditions may result in ambiguous or misleading conclusions at many sites. For example, a well screen may bracket geologic units of varying hydraulic conductivity and chemistry, resulting in a mixture of waters during sampling, and misleading sampling results. In addition, estimation of natural attenuation rates using lines of wells positioned along assumed groundwater flowpaths implies contaminant distribution and flowpaths for groundwater contamination are well defined. The level of effort necessary to adequately accomplish this task is relatively large at many sites.

Hydraulic conductivity and contaminant distributions vary three-dimensionally in the subsurface due to differences in geologic materials and complexity in contaminant sources. Spatial and temporal variations in hydraulic gradients also may be significant effects on contaminant transport at many sites. Various tools are available for characterization of groundwater flow and contaminant transport in porous media at multiple scales of investigation. Examples of hydrogeologic characterization tools include:

- Geologic tools (*e.g.*, continuous geologic logs, grain size analyses, and cone penetrometer logs);

- Hydrologic tools (*e.g.*, potentiometric information, tracer tests, borehole flowmeters, laboratory permeameters, slug tests, and pumping tests); and

- Geophysical tools (*e.g.*, surface geophysical surveys and borehole geophysics).

Economical techniques, such as direct push technologies, are now available for discrete sampling of subsurface materials allowing better definition of the three-dimensional distribution of contaminants, geochemical conditions, and biological processes. Similarly, hydrogeologic parameters may be economically defined in detail using tools such as borehole flowmeters and variations on traditional slug and pumping tests. Tracer tests may also be designed at many sites to obtain multi-level hydrogeologic information.

Hydrogeologic characterizations must be conducted on an appropriate spatial scale. Contaminant transport largely depends on hydrogeologic controls on groundwater flow. The most significant controls at many sites are hydraulic conductivity distribution and hydraulic gradients. Without adequate characterization, decreases in contaminant concentrations at monitoring wells may incorrectly be attributed to reductions in contaminant mass, rather than to the effects of monitoring point locations and system designs. Temporal variations in hydraulic gradients must also be considered on several scales. Variations may be due to short-term influences, such as nearby production wells or tidal effects; intermediate-term influences, such as seasonal differences in recharge; and long-term influences, such as multi-year weather patterns.

In summary, uncertainty in hydrogeologic characterization will always exist. The degree of uncertainty will be a function of site complexity and availability of funds to conduct the characterization. However, tools and approaches are available to better define contaminant migration in the subsurface and evaluate the effects of various natural attenuation processes, such as degradation, dilution, and dispersion. The focus of hydrogeologic characterization for natural attenuation studies should be on the geologic units through which contaminants are migrating and the dominant controls on migration. This level of characterization generally will require more detail than bulk aquifer tests can offer. Three-dimensional information regarding parameters such as hydraulic conductivity distribution, hydraulic gradients, and contaminant distribution allows hydrostratigraphic controls to be defined and contaminant transport to be assessed with less uncertainty. This level of detail is needed to support projections of contaminant transport and the role of natural attenuation processes in remedial decisions.

Using Natural Attenuation Data for Groundwater Contamination Modeling and Exposure Assessment

Jim Weaver, EPA, National Exposure Research Laboratory, Ecological Research Division (NERL/ ERD)— Athens, GA

Weaver described how a groundwater plume forms, and discussed the interpretation and use of site characterization data. He depicted DNAPL contamination of a water table aquifer where the DNAPL release followed a complex pathway through groundwater and pooled atop a stratigraphic layer of low permeability.

Weaver emphasized that an observed plume reflects a balance between the release of mass from the source, transport in the aquifer (advection, dispersion and retardation) and losses (including biodegradation). He noted that it is necessary to understand the role of each of the factors. Plumes may also tend to flow downward into aquifers because recharge to the aquifer may generate a layer of clean water above the contaminant plume. Thus, care should be taken in determining the vertical extent of contamination. Wells screened only near the water table could miss the contamination due to the downward motion of the plume.

Because the source of contamination generates the plume, critical initial and boundary conditions for modeling are usually unknown. Referring to the description of plume formation, Weaver pointed out that the mass of the source, the timing of the release, and the dissolution rate of the DNAPL are rarely known. As a result, scientists and engineers are faced with difficulties in establishing realistic boundary conditions for contaminant transport models.

As an example, Weaver discussed a gasoline spill that occurred on Long Island, New York. The timing and mass of the release are unknown, but aqueous phase concentration data from the site span 2½ years of a total event duration estimated at 15 years. Thus, the data only represent a small fraction of the entire contamination event. The data were collected years after the release occurred, so they do not represent the initial stages of plume formation.

Weaver showed how recharge depressed the plume as it moved from the source area and the changes in the length of the benzene plume at the site. The benzene plume appeared to increase in length during the early sampling event, but possibly retracted during later ones. Thus, the plume had not reached steady-state, but reflected transients in the factors influencing plume formation (source release, transport, and degradation).

Weaver also showed similar data from the St. Joseph, Michigan TCE site, noting a similar vertical distribution of contaminants. He emphasized the strong vertical variability of contaminant concentrations noting that the concentrations varied by orders of magnitude between different sample locations in the vertical. The concentration variations were attributed to variation in hydraulic conductivities, lithologies, and recharge. The well screen length at the St. Joseph site was 5 feet; at the gasoline site, the screen length was less than one foot.

Weaver pointed out that historical monitoring well data often reflect fluctuations in concentration. At St. Joseph these were attributed to changes in analytical procedures over time, analytical and sampling errors, rainfall events, variations in hydraulic gradient, and other factors. Trends in the data due to biodegradation thus need to be separated from fluctuations due to these factors.

Weaver generalized that there are two quantitative routes to environmental decisions: (1) analyzing site-specific data; and (2) simulation modeling. The two approaches are not mutually exclusive and may be used together. Simulation modeling, depends upon site-specific data analysis, but can permit extrapolation of current conditions or investigation of various scenarios.

Demonstrating natural attenuation includes documenting reduction in contaminant concentrations in the plume, reduction in the mass of the contaminant in the aquifer, or shrinkage of the plume. There are various techniques to estimate the contaminant mass in the aquifer, based on contouring, or nearest-neighbor polygons. Shrinkage of a plume can be quantified by estimating the change in position of its center of mass and the spatial variance of its distribution.

Using the Long Island gasoline spill example, Weaver indicated that estimated masses of BTEX declined over the study. Because of their spatial distribution, each of these chemicals is still being released from the gasoline source to the aquifer, so the decline in aquifer mass suggested biodegradation. Methyl tertiary butyl ether (MTBE), which moved through the aquifer as a pulse and is generally resistant to degradation, would be expected to have constant mass if no degradation occurred. The data showed, however, an initial increase in mass that was not due to release from the source, then a decline in mass. The pattern of the MTBE data suggested that there could be inaccuracy introduced by the sampling network and by temporal fluctuation of the chemical data. (In response to a question, Weaver rejected the possibility that the MTBE increase could have been caused by a non-point source, because of the distribution of the MTBE plume at depth in the aquifer). For some of the contaminants, there were retreats of the centers of mass over time, suggesting shrinkage of those plumes.

Weaver noted that another measure of mass transport is the mass flux of contaminants at each point along the plume. This was estimated at St. Joseph by measuring concentrations and groundwater velocities at transects of samplers set perpendicular to the assumed flow path. The decrease in mass between transects

can be used to estimate the natural attenuation. To estimate degradation rates, inferences can be made from observed concentrations. Weaver described a number of methods used to estimate rate constants, each based upon different transport principles and associated field data: one-dimensional steady flow, two-dimensional steady flow, mass flux, mass conservation and simulation modeling, and simulation-model parameter fitting. He pointed out that rate constants represent observations and summarize (but do not predict) contaminant behavior, and that all of the methods of estimating rate constants are based on idealized situations.

NERL/ERD and Region 4 are developing microcomputer software that will enable regional personnel to estimate the mass, center of mass, mass flux, and degradation rates, and to pre-process data to be used in simulation models. The software will account for sparse data and will compare data from two or more methods for each computation, in order to provide a sensitivity check on the data. However, Weaver pointed out that there are still questions that only simulation modeling can answer:

- What mass of released TCE matches the observed concentration?

- What is the lifetime of the source?

- What is the lifetime of the plume?

- How long will reductive dechlorination continue?

Two types of models have been developed. The simpler approach uses first order rate constants and field estimated rate constants as previously described. These models include simple analytical solutions of the transport equation, codes developed for analysis of natural attenuation (BIOSCREEN), codes that include the NAPL source (the Hydrocarbon Spill Screening Model, HSSM) and conventional numerical codes (MODFLOW coupled with MT3D). The second type of model essentially includes a prediction of the biodegradation rates by including more of the fundamental biological phenomena. Examples of this type of model include an option in BIOSCREEN and models currently being completed (Rice University's BIOPLUME III, Batelle's RT3D, and the University of Texas's UTCHEM).

There are tradeoffs between the different kinds of models, and the model selected depends upon data availability and the purpose of the modeling. Complex models require a large number of parameter estimates, and some codes (Weaver cited UTCHEM) contain parameters that cannot be measured onsite. In those cases, a default or literature values must be used, and the model results become hypothetical. One advantage of simpler models is that, if rate constants are estimated from field data, then the model results will be strongly tied to field observation. However, the limitations of site investigations often result in situations where it is necessary to make assumptions in describing the contaminant source, mass and timing of the release, rate of source dissolution, etc.

Questions and Answers: Bill Brandon (EPA/Region 1) asked Weaver to comment on the appropriateness of complex models, given data variability. Weaver acknowledged that despite the extensive data set, there still were uncertainties in understanding and thus simulating the observed plume at the Long Island site. He said that, generally, parameters might be unavailable for complex models. This renders these models impractical or less useful for some sites. He said that he chose to use less complex models because he could supply a greater proportion of their parameters from field data. Weaver indicated that using complex models with a high percentage of default parameters will result in hypothetical solutions. Wilson agreed, noting that some complex models that have more parameters than data become little more than video games unconstrained by field data. Weaver added that assumptions underlying the mathematical model need to fit the site conceptual model. Chapelle asked Weaver what weight he would place on modeling, microcosms,

mass data, geochemical parameters, and other types of remedy-decision support information. Weaver felt that he would place half his effort on documenting mass loss, and one-quarter each on modeling and on geochemical conditions. Jack Guswa (HSI GeoTrans) pointed out that the data are not independent and would all be required to some extent. Weaver agreed that it was important to obtain as much data as possible and to have confidence in those data.

Diane Easley (EPA/Region 7) said that she distrusts modeling simulations because of her experience with questionable results submitted by consultants for potentially responsible parties (PRPs). When she suggested that the simulations be compared to field observations, the consultants usually balked. Wilson pointed out that models are not reality; he recommended that remedial project managers (RPMs) place their trust in the modelers, not the models. Weaver agreed that if you can verify the models with field observations, you will increase confidence in the results; however, this is seldom achieved. Typically, the groundwater flow portion of the model is field-calibrated, but not the transport model. Wilson said he attempted to observe short-term model predictions in the field, but the results were usually not as the model predicted. Predictions are affected as much by assumptions as by the data. He pointed out that models are better for predicting ranges rather than predicting exact values. Debbie Goldblum (EPA/Region 3) argued that few PRPs will accept regulatory decisions based solely upon modeling results, especially if the simulations do not support the PRPs' position or result in more expensive solutions. For example, if a simulation model predicts that the available electron acceptors are insufficient to drive natural attenuation beyond 10 years, PRPs would prefer to proceed anyway and reconsider the effectiveness of natural attenuation after 10 years, rather than drop natural attenuation as a remedy. Easley pointed out that CERCLA mandates a 5-year review anyway, but she remained skeptical about the costs associated with collecting high-quality data. Before authorizing such costs, she would like ORD to provide guidance for justifying the expense.

PLENARY SESSION SUMMARIES (Workshop Day 3)

Plenary Session Summary for Topic 1: Analytical Methods for Evaluating Natural Attenuation

Steve Vandegrift (ManTech Environmental Services) presented a summary of the *Analytical Methods* breakout session (see Appendix C for additional details of that session).

The natural attenuation of BTEX compounds and chlorinated solvents can be assessed quantitatively using measurements of particular analytes in groundwater. These analytes include: (1) primary contaminants such as PCE, TCE, and BTEX and daughter compounds such as *cis*-DCE and vinyl chloride; (2) redox-sensitive parameters such as DO, Fe(II), sulfate, sulfide, methane, and molecular hydrogen; and (3) inorganic daughter products of contaminant degradation such as chloride and dissolved inorganic carbon. A significant problem for EPA and state regulatory personnel is that standard methods for many of these analytes are either available, but not widely known; not currently available; or not adequately documented.

The session participants concluded that:

1) Methods for analyzing primary drinking water contaminant VOCs and daughter products are currently available (EPA's SW-846, methods 8260 and 8021).

2) Methods for analyzing redox-sensitive parameters include field methods that need documented SOPs, including colorimetric methods (such as Hach and Chemetrics™) that need QA/QC procedures to assure data quality.

3) Methods for analyzing inorganic daughter products are currently available.

4) John Wilson's method of preserving molecular hydrogen for laboratory analysis, rather than using time-consuming and fragile field analyzers, has the potential to save considerable time and cost.

In addition, the following issues and recommendations were identified:

1) Field parameters (Fe(II), sulfide, and DO) need to have independent standards to check calibration and identify potential systematic bias.

2) ORD's SOP for methane (RSKSOP-147) may be improved by preserving samples with hydrochloric acid instead of sulfuric acid.

3) ORD's SOP for methane should be proposed for adoption as an SW-846 method.

4) ORD's SOP for methane needs to include criteria for analytical precision.

5) ORD's analytical procedures for Fe(III) in soil, which were presented to the workshop participants, are sufficient to form basis of SOP (Ye, *et al.*, *Analysis of Ferric and Ferrous Ions in Soil Extracts by Ion Chromatography*).

6) SOPs should recognize emergence of new technologies and should not be written to preclude improved methods and techniques (*e.g.*, portable CO_2 analyzers and fiber optics).

Table 2 summarizes the group's consensus on key analytes and methods:

Table 2. Analytes and Methods Significant to Natural Attenuation

Analyte	Method	Comment
(1) Primary contaminants (VOCs)		
parent compounds (TCE, PCE) and daughter products (*cis*-DCE, vinyl chloride)	SW-846, Methods 8260, 8021 Methods exist for BTEX, chlorinated compounds, ethane.	SW-846 packed-column methods have been deleted and replaced by capillary methods.
(2) Redox-sensitive parameters		
Dissolved oxygen	Probes, Hach or Chemetrics™ colorimetric kits	Each has pros and cons.
Nitrate	EPA Method 300	
Fe(II)	Hach field kit	Colorimetric technique
Manganese	Hach field kit	Colorimetric technique
Sulfate	EPA Method 300	
Sulfide	Hach field kit	
Methane	Proposed SOP	
Ethane	Proposed SOP	
Molecular hydrogen	Proposed SOP (new storage technique)	Issues of temperature and pressure dependence of aqueous partitioning need to be addressed in SOP.
(3) Inorganic daughter products		
Chloride	EPA Method 300	
Total dissolved inorganic carbon (carbon dioxide+ carbonate+bicarbonate)	Standard methods	acidify sample with GC analysis of off-gas CO_2
Bromide	EPA Method 300	
Nitrite	EPA Method 300	Dissolved nitrite triggers EPA's 48-hr holding time.

Questions and Answers: One workshop participant indicated that he works at a site where sampling is conducted using West Bay multi-port piezometers that have a 300 mL/min flow rate, and asked how enough sample volume could be obtained for H_2 analysis. Vandegrift acknowledged that sufficient sample volume could not be obtained with such a low flow.

John Bradley (Michigan DEQ) said that he believes that people have no confidence in probes for measuring DO, and therefore may not be measuring DO at all. Wilson asked for a show of hands from participants, and about 3/4 felt that DO measurements were important, while 1/4 felt that they were not.

Bradley also asked what types of carbon compounds contribute to the measured total organic carbon (TOC). Wilson replied that the way TOC analysis is usually done, the sample is first acidified to drive off inorganic carbon. In this step, most of the VOCs (*e.g.*, BTEX and volatile fatty acids) are lost. As a result, TOC

measures chiefly non-volatile organics (*e.g.*, native organic carbon [humic material]). However, there is an alternative TOC method that can measure much of the carbon present as VOCs.

Bill Brandon (EPA/Region 1) asked about the minimum number of TOC samples needed, and Wilson suggested at least one per lithologic unit plus one per 1-2,000 feet of plume length, to understand the variability. Diane Easley (EPA/Region 7) pointed out that if the strata were largely comprised of sand with little organic carbon, as was the case in many of her sites, organic carbon was not necessary at all. Jack Guswa (HSI GeoTrans) added that it was important to correlate TOC with stratigraphy, because it would provide necessary understanding for retardation effects and timing.

Plenary Session Summary for Topic 2: Site Characterization for Natural Attenuation Assessments: Hydrogeologic Considerations

Steven Acree summarized the findings of the breakout sessions on *Hydrogeologic Considerations* (see Appendix D for additional details about those sessions). The following conclusions on plume distribution, hydrogeologic characterization, source characterization, modeling, and the need for additional guidance were summarized from the breakout session discussions:

<u>Hydrogeologic Characterization</u>

1) The development of a conceptual model for hydrogeologic setting is paramount. The appropriate level of detail in the model varies with the hydrogeologic setting.

2) Increased complexity in hydrogeologic setting results in increased expenditures for characterization. In spite of this factor, complex hydrogeologic settings should not be categorically excluded from consideration of the effects of natural attenuation on contaminant transport.

3) Hydrogeologic characterization should be objective-oriented, and expenditures to characterize hydrogeology should be justified by the value of the data. Perfection in hydraulic conductivity estimates may be cost-prohibitive and unnecessary at some sites, depending on characterization objectives.

4) The degree to which a site should be characterized is related to the consequences (in dollars and risks) of missing data. The cost of remedial decisions and the information needed to make remedial decisions are related to the value of resources, risk, and hydrogeologic complexity.

5) Knowledge of hydrostratigraphic controls, hydraulic gradient (both horizontal and vertical), stratigraphy, contaminant distribution (both horizontal and vertical), and groundwater discharges (*e.g.*, pumping wells) is important. Hydraulic conductivity information should be obtained from contaminated zones. Estimates of contaminant transport rates derived from such information are important.

6) The use of surface geophysics to better understand the geologic context is helpful, as is information from continuous geologic cores.

7) Information from transects should be used to site wells for the evaluation of temporal trends and hydraulic gradients.

8) Compounds such as chloride, TMBs, and MTBE in contaminant mixes may be useful tracers for normalization of apparent contaminant losses and deserve evaluation. However, experience in this area is very limited.

9) Information on dispersivity is viewed as helpful but, currently, is seldom obtained from field studies.

Plume Distribution

1) Many data of lower precision are preferred to fewer data points of higher precision.

2) The definition of a plume (both horizontally and vertically) in two-dimensional transects perpendicular to groundwater flow direction is important. This information also gives qualitative insights into hydrogeologic controls.

3) Knowledge of plume stability is important.

4) Direct push technologies such as Geoprobe should be used to obtain samples to the extent practicable.

5) Field analysis of organic and inorganic parameters, together with a representative percentage of samples analyzed by fixed-based laboratories, should be used.

6) The definition of contaminant loss using monitoring wells located along downgradient flowpaths is uncertain, unless the wells were sited using information from transects. Wells with long screens result in misleading chemistry and contaminant data, due to mixing of water in the well.

7) Contaminant concentration data should be used to position permanent wells.

Source Characterization

1) Some source characterization is essential.

2) Information on the lateral and vertical extent of sources is important.

3) The inability to accurately estimate the total contamination mass leads to uncertain time estimates for mass removal.

4) Spatial location of sources is used as the starting point for characterizing plume trajectory.

Modeling

1) Solute transport models are of value in natural attenuation evaluations.

2) There should be a strong reliance on field data and a healthy degree of skepticism regarding the use of complex simulations.

The need for the following additional guidance was expressed:

1) Objective-oriented guidance, especially with respect to hydrogeologic characterization for natural attenuation evaluations.

2) Guidance regarding work plan and report development and contents, including the priority of items to include in a work plan, the minimum level of characterization needed prior to evaluating natural attenuation, and the minimum information required for reports (as well as guidance regarding report formats).

3) Groundwater sampling protocols, including filtering of samples, frequency of sampling, and the order of sample collection during each sampling episode.

4) Discussion of potential pitfalls in characterizations, including monitoring network design.

5) Guidance regarding the relative roles of field data and laboratory data in making these evaluations.

6) Guidance concerning situations where ecosystems are potential receptors.

7) Guidance regarding assessment of background geochemical conditions.

8) Rules of thumb for determining the existence of bad data, including improbable and impossible data.

9) Educational seminars.

Plenary Session Summary for Topic 3: Data Quantity and Quality Issues

Jeff van Ee presented a preliminary report of the breakout session discussions of *Data Quantity and Data Quality Issues* (see Appendix E for additional details of those sessions). He noted that there was some overlap between the sessions and that the numbering of the following summary issues do not reflect a ranking.

1) Decisions for the selection of site characterization methods and remediation measures will necessarily vary and depend on site-specific factors, programs, and state regulations.

2) A protocol for the evaluation of natural attenuation as a remediation measure is desirable, but it must allow for the factors in the decision-making process enumerated in summary item No.1.

3) The draft AFCEE protocol is useful and a good beginning point. The protocol could be renamed to "Best Practices" or other alternatives to ensure that the valuable information in the protocol is used properly. In particular, workshop participants liked the tables included in the protocol.

4) Characterization of a site is important to assess a variety of remediation measures, but scripting of the characterization process will be difficult. It also is difficult to identify when enough or too much data for the money (concept of data worth) have been collected.

5) Initial steps in responding to a release of contaminants to the environment should focus on the protection of existing critical receptors. Such steps would include monitoring well installation and the identification, containment, and/or removal of the source.

6) The American Society for Testing and Materials (ASTM) "Remediation by Natural Attenuation" draft protocol may be promising. Circulation of this draft to the workshop participants would be beneficial.

7) If possible, a performance protocol, rather than a prescriptive protocol, should be developed. A performance approach would allow for flexibility and innovation in dealing with a complicated data gathering decision-making process. Equal attention should be given to the development of procedures, methods, and standards to assess the performance of the various sample collection and analytical methods. The performance of any protocol should be assessed.

8) Demonstrating that natural attenuation is occurring and able to meet a variety of performance criteria also will require long-term monitoring.

9) Greater use of statistics in analyzing the collected data is important, and more assistance is needed in this area.

10) Using a cone penetrometer to obtaining more data at a relatively low cost is desirable in many cases. Field methods appear to be preferable to laboratory-based methods in most cases. Data need to be collected as quickly and inexpensively as possible.

11) Whether the protocol has more detail on QA/QC methodologies or not, guidance, standard procedures, and standards need to be developed to assess variability and bias throughout the measurement process. QA/QC should not be neglected, and QA/QC procedures are needed to evaluate contractor data.

12) There is an increased appreciation for the importance of spatial variability in the site characterization process, and more attention needs to be devoted to this issue. Sampling algorithms for soils may be adapted for groundwater.

13) National guidance and SOPs are desirable and need to be further developed. For example, guidance could be developed for low-flow, small-volume systems.

14) EPA training requirements are desirable for people using natural attenuation guidance and SOPs.

15) Different DQOs are involved in the site characterization and remediation selection processes. The DQO process and the status of existing QA guidance are misunderstood. A meeting is being held on August 20, 1997, in Kansas City to educate people on new DQO procedures.

16) Guidance is needed on the frequency of monitoring.

Questions and Answers: One workshop participant suggested that because the amount of money available for site characterization varies by program and state, guidance is needed on what monitoring is essential and what monitoring would be good. van Ee replied that the new DQO process accounts for these factors, but guidance is needed on what constitutes critical data and how much it costs to collect it. A participant noted that all monitoring data in Superfund is for compliance monitoring, and monitoring for natural attenuation goes beyond compliance monitoring. Another participant suggested that, because understanding spatial variability is more important for natural attenuation analyses than for standard analyses, it may be more important to collect more data of lower quality rather than fewer data of higher quality.

A number of workshop participants discussed whether natural attenuation should be considered to be a remedial technology. Several participants stated that natural attenuation should be considered in the same manner as other engineered remedies, even though it is a natural process. Others added that, since natural attenuation occurs in some form at every site, it should be addressed in all remedial investigations and feasibility studies. van Ee noted that there will be a requirement for long-term monitoring of any remedy.

With natural attenuation, it is a question of the degree of monitoring required and what will be measured. Information is also needed on when to stop an engineered process and start monitored natural attenuation. Jon Josephs explained that natural attenuation is viewed by OSWER as a remedial alternative, as are incineration and "no action," for example. He noted that natural attenuation can be distinguished from no action in that natural attenuation can be selected to attain cleanup objectives, while no action is selected when cleanup objectives are already being met. He added that he does not consider natural attenuation to be a technology.

Plenary Session Summary Topic 4: Interpretation and Use of Site Characterization Data

Participants were provided with copies of a written summary of the discussions at the breakout sessions on *Interpretation and Use of Site Characterization Data* (see Appendix F for a summary of those breakout sessions). John Wilson then offered his thoughts that EPA can develop and publish generic SOP recommendations for:

- Field sampling of groundwater that builds on Region 4's procedures. Wilson noted that breakout group participants preferred, where possible, to filter and fix samples in the field and then send them to the laboratory for analysis. In addition, they agreed that bailers should be replaced with inertial samplers with an inner diameter less than 2 inches. If low-flow pumping still purges wells dry, diffusion cell samplers should be used. He added that EPA may be able to develop a manual or training course for sampling technicians, since there was concern that sampling technicians do not have the proper training or education to collect samples correctly in the field.

- Field measurement of oxygen.

- Field measurement of redox potential

- Field procedures to compute a site-specific estimate of the dispersion coefficient for sites where dispersion and dilution dominate natural attenuation. This could include tracer tests.

Wilson said that EPA can develop a logic for determining the spacing of long-term monitoring wells, the frequency of sampling and the duration of sampling needed before natural attenuation can be recognized to be protective with some level of confidence. This could include the following recommendations:

- Well spacing could be sized with respect to the reduction in concentration between the hot spot and acceptable concentrations.

- The rule of thumb could include spacing corresponding to tenfold reductions in concentration (at a minimum) along the plume core.

- Spacing should reflect the dynamics of the plume.

- The long-term sampling frequency could be a function of the time for groundwater to travel between upgradient and downgradient monitoring wells (*i.e.*, the plume length). How that travel time is divided into increments could reflect the proximity and vulnerability of receptors.

- The expected behavior of the plume based on initial site characterization sampling data and mathematical modeling could be used to ensure a sampling frequency that is protective of receptors.

John Bradley (Michigan DEQ) noted that, when considering the duration of monitoring to verify a groundwater fate and transport model, one must consider that most plumes are dynamic, rather than continuously stable or shrinking. Wilson agreed that the behavior of most plumes is dynamic and that the duration of verification monitoring must be sufficient to distinguish long-term trends from transient ones. Jeff Moody (Indiana DEM) posed a question about the duration of verification monitoring following implementation of source control measures. In response, Wilson said that, he would like to see at least a tenfold reduction of contaminants in wells once source control is achieved prior to beginning long-term monitoring. However, he noted that there may be alternative approaches for determining how long to continue verification monitoring after source control is implemented.

Wilson noted that ORD cannot develop a generic philosophical approach for judging the adequacy of proposals for natural attenuation. Specific requirements in the CERCLA, RCRA, and the UST programs, as well as specific state requirements, will result in important differences in the implementation of natural attenuation from site to site.

Wilson closed by stating that ORD will continue to develop approaches to site characterization and data evaluation that will allow evaluation of natural attenuation as a process. He added that the use of those approaches will only be one component of the complex regulatory process of selecting or rejecting natural attenuation as a remedy or part of remedy.

APPENDIX A
Workshop Participants

Steve Acree
U.S. EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74820
(405) 436-8609
acree.steven@epamail.epa.gov

David Ariail
Environmental Engineer
U.S. EPA, Region 4
UST Section, 61 Forsyth Street, SW
61 Forsyth Street, SW
Atlanta, GA 30303-3104
404-562-9464
ariail.david@epamail.epa.gov

Jeffery Babb
Principal Environmental Engineer
Georgia UST Management Program
4244 International Pkwy., Suite 104
Atlanta, GA 30354
404-362-2594
land.jeff_babb@mail.dnr.state.ga.us

James Barnett
Environmental Program Analyst
Virginia Department of Environmental Quality
P.O. Box 10009
Richmond, VA 23240
804-698-4289
jsbarnett@deq.state.va.us

Katherine Baylor
RCRA Corrective Action
U.S. EPA, Region 9
75 Hawthorne Street (WST-5)
San Francisco, CA 94105
415-744-2028
baylor.katherine@epamail.epa.gov

Robert Becker
Program Assistant
U.S. EPA, Region 8 (MC 8P2-W-GW)
999 18th St., Suite 500
Denver, CO 80122-2466
303-312-6127
becker.robert@epamail.epa.gov

Rob Beierle
Environmental Protection Specialist
Colorado Dept. of Public Health and Environment
Hazardous Material Waste Management
4300 Cherry Creek Dr. South
Denver, CO 20222
303-692-3360
robert.beierle@state.co.us

Bob Bianchi
Hydrogeologist
U.S. EPA, Region 8
Office of Ecosystem Protection and Remediation
999 18th Street, Suite 500
Denver, CO 80202-2466
303-312-6560
bianchi.bob@epamail.epa.gov

D. Fred Bishop
Research Chemical Engineer
U.S. EPA, NRMRL
26 West Martin Luther King Drive
Cincinnati, OH 45268
513-569-7629
bishop.dolloff@epamail.epa.gov

Jim Borovich
Geologist
Nebraska Department of Environmental Quality
P.O. Box 98922
Lincoln, NE 68509-8922
402-471-4230

John Bradley
Geologist
Michigan Department of Environmental Quality
P.O. Box 30426
Lansing, MI 48909
517-335-3146

Bill Brandon
BRAC Hydrologist
U. S. EPA, Region 1
JFK Federal Bldg.
Boston, MA 02203
617-573-9629
brandon.bill@epamail.epa.gov

Lynne Cayting
Environmental Specialist
Maine Department of Environmental Protection
#17 State House Station
Augusta, ME 04333-0017
207-287-4862
lynne.a.cayting@state.me.us

Frank Chapelle
Hydrologist
U.S. Geological Survey
720 Gracern Rd., Suite 129
Columbia, SC 29210
803-750-6116
chapelle@usgs.gov

Kent Coleman
Program Manager
South Carolina DHEC
Bureau of Land & Waste Management
2600 Bull Street
Columbia, SC 29201
803-896-4040
wpo{dhec4005.columb34.colemankent}@gmo.state.
sc.us

Jack Cunningham
Hydraulic Engineer
U.S. Bureau of Reclamation, Groundwater and
Drainage
Denver Federal Center, Box 25007
Denver, CO 80225-0007
303-236-8066 ext. 243
cunning@teton.earthsci.do.usbr.gov

James Cutler
Senior Geologist
Virginia Department of Environmental Quality
Piedmont Regional Office
4949-A Cox Rd.
Glen Allen, VA 23060
804-527-5068
jlcutler@deq.state.va.us

Maggie Davison
Biologist, Program Principle
Wyoming Department of Environmental Quality
Water Quality Division
122 West 25th Street, 4th Floor West
Herschler Building
Cheyenne, WY 82001
307-777-7092
mdavis@missc.state.wy.us

Diane Easley
Remedial Project Manager
U.S. EPA, Region 7
726 Minnesota Avenue
Kansas City, KS 66101
913-557-7797

Andrew English, P.E.
Section Chief, Bureau of Western Remedial Action
New York State Department of Environmental
Conservation
50 Wolf Road
Albany, NY 12233-7010
518-457-0315

Edgar Ethington
Environmental Protection Specialist
Colorado Dept. of Public Health and Environment
4300 Cherry Creek Dr. South
Denver, CO 20222
303-692-3438
edgar.ethington@state.co.us

Mark Ferrey
Soil Scientist
Minnesota Pollution Control Agency, Site Response
Program
520 Lafayette Road
St. Paul, MN 55155-4194
612-296-7775
mark.ferrey@pca.state.mn.us

Mark Filippini
Hydrogeologist
U.S. EPA, Region 9
Superfund Division
75 Hawthorne St, SFD-8-B
San Francisco, CA 94105
(415) 744-2395
filippini.mark@epamail.epa.gov

Renee Gelblat
Environmental Scientist/Project Manager
U.S. EPA, Region 3 (3HW80)
841 Chestnut Street
Philadelphia, PA 19107
215-566-3421
gelblat.renee@epamail.epa.gov

Mary Goldade
Chemist
U.S. Bureau of Reclamation
Geophysics & Seismotechtonics
Mail Code D-8330
P.O. Box 25007
Denver, CO 80225
303-236-4196 ext. 294
mgoldade@do.usbr.gov

Debbie Goldblum
Geologist/ Project Manager
U.S. EPA Region 3
841 Chestnut Building
Philadelphia, PA 19107
215-566-3432
goldblum.deborah@epamail.epa.gov

Art Gravenstein
Environmental Management Specialist
Nevada Division of Environmental Protection
333 West Nye Lane
Carson City, NV 89706-0851
702-687-4670 ext. 3032

ChiFeng Gu
Advanced Geologist
Georgia UST Management Program
4244 International Parkway, Suite 104
Atlanta, GA 30354
404-362-2589
land.chifeng_gu@mail.dnr.state.ga.us

John H. Guswa
HSI Geotrans
6 Lancastar County Road
Harvard , MA 01451
508-772-7557

Jim Harris
Environmental Specialist
Missouri Department of Natural Resources
P.O. Box 176
Jefferson City, MO 65101
573-751-6822

Neal Heil
Geologist
Nebraska Department of Environmental Quality
P.O. Box 98922
Lincoln, NE 68503
402-471-4230

Steve Hirsh
Regional Project Manager
U.S. EPA, Region 3 (3HW50)
841 Chestnut Building
Philadelphia, PA 19107
215-566-3352
hirsh.steven@epamail.epa.gov

Steven Huddleson
Manager, Remedial Action Program
New Mexico Environment Department
P.O. Box 26110
Sante Fe, NM 87501
505-827-0173
steven_huddleson@NMENV.state.nm.us

Walter Huff
Branch Chief
Mississippi Department of Environmental Quality
P.O. Box 10385
Jackson, MS 39289
601-961-5142
walter_huff@deq.state.ms.us

Kelly Hurt
NRC Research Associate
U.S. EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74820
405-436-8987
hurt@ad3100.ada.epa.gov

Jack Hwang
Hydrologist
U.S. EPA, Region 3
841 Chestnut Street
Philadelphia, PA 19107
215-566-3387
hwang.jack@epamail.epa.gov

Dawn Ioven
Toxicologist
U.S. EPA, Region 3 (3HW41)
841 Chestnut Street
Philadelphia, PA 19107
215-566-3320
ioven.dawn@epamail.epa.gov

Charles Johnson
Environmental Protection Specialist
Colorado Dept. of Public Health and the Environment
4300 Cherry Creek Dr. South
Denver, CO 80222-1530
303-692-3348

Jon Josephs
Superfund Technical Liaison
U.S. EPA, Region 2
290 Broadway
New York, NY 10007-1866
212-637-4317
josephs.jon@epamail.epa.gov

Gary Kleeman
Remedial Project Manager
U.S. EPA, Region 8
999 18th Street, Suite 500
Denver, CO 80202
303-312-6246
kleeman.gary@epamail.epa.gov

David Kruchek
Geologist
Colorado Department of Public Health and Environment
4300 Cherry Creek Drive, South
Denver, CO 80222-1530
303-692-3328
303-692-3328
david.kruchek@state.co.us

Russ Leclerc
Chemist
U.S. EPA, Region 8
999 18th Street, Suite 500
Denver, CO 80202-2405
303-312-6693
leclerc.russell@epamail.epa.mail

Herbert Levine
Hydrogeologist
U.S. EPA, Region 9
75 Hawthorne Street
San Francisco, CA 94105
415-744-2312
levine.herb@epamail.epa.gov

David Lown
Environmental Engineer
North Carolina DEHNR, Superfund Section
P.O. Box 29603
Raleigh, NC 27611
919-733-2801 ext. 278
lowndj@wastenot.ehnr.state.nc.us

William Lyon
Research Scientist
ManTech Environmental Research Services
U.S. EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74821-1198
405-436-8666
lyon.william@epamail.epa.gov

Sharon Matthews
Hydrogeologist
U.S. EPA, Region 4
980 College Station Road
Athens, GA 30605
706-355-8608
matthews.sharon@epamail.epa.gov

Dan McInnes
U.S.EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74821-1198
McInnes.daniel@epamail.epa.gov

Richard McMillin
Organic Lab Team Leader
U.S. EPA, Region 6
10625 Fallstone Road
Houston, TX 77099
281-983-2107
mcmillin.rick@epamail.epa.gov

Read Miner
Hydrogeologist III
South Carolina DHEC
Bureau of UST Management
2600 Bull Street
Columbia, SC 29201
803-734-5327
minerrs@colunb26.dhec.state.sc.us

Douglas Minter
UIC, Class V Team Leader
U.S. EPA, Region 8
999 18th St., Suite 500
Denver, CO 80202
303-312-6079
minter.douglas@epamail.epa.gov

Randy Minyen
Environmental Program Administrator
Oklahoma Corporation Commission
P.O. Box 52000-2000
Oklahoma City, OK 73152-2000
(405) 522-5266
r.minyen@occmail.occ.state.ok.us

William Monheiser
Environmental Scientist
U.S. EPA, Region 8 (8P2-W-GW)
999 18th Street, Suite 500
Denver, CO 80202
303-312-6271
monheiser.william@epamail.epa.gov

Jeff Moody
Environmental Engineer
Indiana Department of Environmental Management
Office of Solid and Hazardous Waste Management
100 North Senate
P.O. Box 6015
Indianapolis, IN 46206
317-232-8842
jmood@opn.dem.state.in.us

Khwaja Murshed
Remediation Coordinator
Texas Natural Resource Conservation Commission
P.O. Box 13087, MC 137
Austin, TX 76711-3087
512-239-5769
kmurshed@tnrcc.state.tx.us

Rich Muza
Hydrologist
U.S. EPA, Region 8
999 18th Street, Suite 500
Denver, Co 80202-2466
303-312-6595
muza.richard@epamail.epa.gov

Wendy Naugle
Professional Engineer/Project Manager
Colorado Department of Public Health and Environment
4300 Cherry Creek Drive South
Denver, CO 80222
303-692-3394

Bruce Nicholson
Head, Special Remediation Branch
North Carolina DEHNR, Superfund Section
401 Oberlin Road, Suite 150
Raleigh, NC 27605
919-733-2801 ext. 353
nicholsonbi@wastenot.ehnr.state.nc.us

Steve Noel
Environmental Protection Specialist
Department of Labor and Employment
Oil Inspection Section, Tower 3
1515 Arapahoe Street, Suite 610
Denver, CO 80202
303-620-4014
steve.noel@state.co.us

Emil Onuschak Jr.
Hydrologist
Delaware DNREC/UST
715 Grantham Lane
New Castle, DE 19720
302-323-4588
eonuschak@dnrec.state.de.us

Greg Pashia
Enforcement Officer
U.S. EPA, Region 6
1445 Ross Avenue
Dallas, TX 75202-2733
214-665-2287

Joachim Pleil
U.S. EPA, NERL
MD-44
Research Triangle Park, NC 27711
919-541-4680
pleil.joachim@epamail.epa.gov

Victor Puckett
Environmental Engineer
Mississippi Department of Environmental Quality
P.O. Box 10385
Jackson, MS 39289
601-961-5288
victor_puckett@deq.state.ms.us

Ray Roberts
Senior Hydrologist
Oklahoma Department of Environmental Quality
1000 NE Tenth Street
Oklahoma City, OK 73117-1212
405-271-1345

Randall Ross
Hydrologist
U.S. EPA, NRMRL/SPRD/TATT
P.O. Box 1198
Ada, OK 74820
405-436-8611
ross.randall@epamail.epa.gov

Bruce Rundell
Senior Geologist
U.S. EPA, Region 3
Hazardous Waste Division
841 Chestnut Building
Philadelphia, PA 19107
215-566-3317
rundell.bruce@epamail.epa.gov

Theresa Santangelo-Dreiling
Planning/Grants Specialist II
Colorado Department of Transportation
4201 East Arkansas, Room 284
Denver, CO 80222
303-757-9793

Mary Ellen Schultz
Environmental Scientist
U.S. EPA, Region 3
201 Defense Highway, Suite 200
Annapolis, MD 21401
410-573-2746
schultz.maryellen@epamail.epa.gov

Thomas Stafford
Environmental Quality Specialist
Louisiana Department of Environmental Quality
P.O. Box 82282
Baton Rouge, LA 70884-2282
504-765-0487
tstafford@deg.state.la.us

Phil Stoffey
Environmental Protection Specialist
Colorado Dept. of Public Health and Environment
4300 Cherry Creek Drive
Denver, CO 80220-1530
303-692-3067
philip.stoffey@state.co.us

Charles Stone
Project Manager
Texas Natural Resource Conservation Commission
P.O. Box 13087, MC 136
Austin, Texas 78711-3087
512-239-2120, 512-239-5825
cstone@tnrcc.state.tx.us

Laurence Strattan
Chemist
U.S. EPA-NEIC
P.O. Box 25227
Denver Federal Center
Denver, CO 80225
303-236-5132 ext. 278
strattan.larry@epamail.epa.gov

Lisa Taber
Hydrogeologist II, Federal Trust Fund
North Carolina DEHNR, Division of Water Quality
P.O. Box 29578
Raleigh, NC 27626-0578
919-733-1325
lisa_taber@mail.ehnr.state.nc.us

Robert Talbot
Geologist
U.S. Bureau of Reclamation, Groundwater and Drainage
Box 25007, DFC Bldg. 67
Lakewood, CO 80225-0007
303-236-8066 ext. 233
talbot@earthsci.do.usbr.gov

Eric Taxer
Petroleum Fund Administrator
Nevada Division of Environmental Protection
333 West Nye Lane, Suite 138
Carson City, NV 89706-0851
702-687-4670

Derval Thomas
Environmental Engineer
U.S. EPA, Region 2
Ground Water Compliance Section
290 Broadway
New York, NY 10007-1866
212-637-4236
thomas.derval@epamail.epa.gov

J. Robert Tinsley
Hydrogeologist
U.S. Nuclear Regulatory Commission
Mail stop: T7-J9
Washington, DC 20555
301-415-6251
jrt1@nrc.gov

Jeff van Ee
U.S. EPA, NERL-ESD
P.O. Box 93478
Las Vegas, NV 89193-3478
702-798-2367
vanee.jeff@epamail.epa.gov

Steve Vandegrift
ManTech Environmental
U.S. EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74820
405-436-8684
vandegrift.steve@epamail.epa.gov

Matt Varney
Senior Geologist
Kentucky Division of Waste Management
14 Reilly Road
Frankfort, KY 40601
502-564-6716
varney@nrdep.nr.state.ky.us

Brian Wakelyn
Senior Geologist
Arkansas Department of Pollution Control
8001 National Drive
Little Rock, AR 72219-8913
501-682-0845

Jim Weaver
Hydrologist
U.S. EPA, NERL
960 College Station Road
Athens, GA 30622
706-355-8329
weaver.jim@epamail.epa.gov

Bruce Wicherski
Environmental Hydrogeologist
Idaho Department of Environmental Quality
1410 North Hilton
Boise, ID 83706
208-373-0246
bwichers@deq.state.id.us

Richard Willey
Hydrologist
U.S. EPA, Region 1
JFK Federal Building (HSS)
Boston, MA 02203
617-573-9639
willey.dick@epamail.epa.gov

John Wilson
Research Microbiologist
U.S. EPA, NRMRL-SPRD
P.O. Box 1198
Ada, OK 74820
405-436-8534
wilson.johnt@epamail.epa.gov

Ming Ye
Project Scientist
ManTech Environmental
U.S. EPA, NRMRL-SPRD
P.O. Box1198
Ada, OK 74820
405-436-8674

Ronald Zdyb
Program Assistant
U.S. EPA, Region 8
MC 8P2-W-GW
Denver, CO 80122-2466
(303)312-6250
zdyb.ronald@epamail.epa.gov

Manjiang Zhang
Hydrogeologist
Delaware Department of Natural Resources
715 Grantham Lane
New Castle, DE 19720
302-323-4540
mzhang@dnrec.state.de.us

Harry Zinn
Environmental Engineer, Special Remediation
North Carolina DEHNR, Superfund Section
401 Oberlin Road
Raleigh, NC 27605
919-733-2801 ext. 313
zinnhj@wastenot.ehnr.state.nc.us

APPENDIX B
Letter Sent to Prospective Workshop Participants

ENVIRONMENTAL MANAGEMENT SUPPORT *Inc.*

August 6, 1997

Mr. Fname Lname
U.S. EPA, Region 4
UST Section
61 Forsyth Street, SW
Atlanta, GA 30303-3104

Dear Mr. Lname:

In anticipation of your attendance at the U.S. Environmental Protection Agency's *Workshop on Natural Attenuation of Groundwater Contamination* to be held August 19-21, 1997 in Denver, Colorado, I have enclosed several documents that will be used at the workshop for discussion purposes. The enclosures are:

--Draft Revision 2 of the "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater." (Please note that this draft document was developed by the Air Force Center for Environmental Excellence in cooperation with U.S. Environmental Protection Agency researchers, but was not issued by EPA and does not represent EPA guidance.);

--draft standard operating procedure for dissolved hydrogen analysis;

--RSKSOP-147, describing analysis of headspace samples for nitrous oxide, methane, ethene, and ethane;

--RSKSOP-175, describing sample preparation for headspace sampling for nitrous oxide, methane, ethene, and ethane analysis; and

--RSKSOP-193, describing analysis of soil and sediment samples for microbially available iron.

Please note that the Robert S. Kerr Environmental Research Center (RSKERC) Standard Operating Procedures (RSKSOPs) are intended only for use at RSKERC and may be inappropriate for use by other laboratories. In addition, some of the documents are labeled "draft" and are subject to revision. The documents are provided only to serve as a point of departure for workshop discussions.

We look forward to your participation in the workshop. If you have any questions, feel free to call me at (301)589-5318, send an E-mail message to ddopkin@emsus.com, or call Jon Josephs, EPA Region 2 Superfund Technical Liaison, at (212)637-4317.

Sincerely,

Diane Dopkin

Enclosures

8601 GEORGIA AVE., SUITE 500 • SILVER SPRING, MD 20910 • (301) 589-5318 • FAX (301) 589-8487

APPENDIX C
Breakout Session for Topic 1: Analytical Methods for Evaluating Natural Attenuation

Topic Leader: Frank Chapelle, USGS

Discussions from the one breakout session on the topic of analytical methods for evaluating natural attenuation are summarized below.

Chapelle pointed out that "EPA-approved" analytical methods do not exist for a number of key chemicals whose analyses are important to natural attenuation. Chapelle presented a list of analytes, and the group participated in identifying whether available methods exist or whether NRMRL/SPRD's proposed methods would be satisfactory. Josephs added that, regardless of whether the proposed methods become EPA-approved methods, EPA's regional laboratories will need to use some methods and will benefit from recommendations and limitations identified by the group.

Mary Ellen Schultz (EPA/Region 3) cautioned that EPA's packed-column methods (8240-Volatile Organic Analytes [VOAs] and 8080-Pesticides) have been deleted from SW-846 and replaced by capillary-column methods (8260-VOAs, 8081-Pesticides). Diane Easley (EPA/Region7) pointed out that methods exist for the analysis of ethane, methane, and ethene, although there are no "EPA-approved" methods.

Of the redox-sensitive parameters, Chapelle said that DO is critical since neither PCE nor TCE will bioattenuate in the presence of DO. He said that USGS uses the Hach colorimetric technique, which is based on the traditional Winkler titration. He added that the biggest drawback to the technique is that it requires some expertise and experience, and that the technician must be meticulous with the apparatus (*e.g.*, use no silicon tubing). Chapelle also described the Chemetrics™ kit, which is easier to use. The Hach kit method has a detection limit of about 0.02 mg/L, while the Chemetrics kit has a limit of about 0.1 mg/L. Schultz asked Chapelle about USGS's methods for analytical controls to avoid analytical bias. Chapelle acknowledged that there is no standard method that invokes in-field calibration and QC using samples from other sources. The group concluded that this QC issue needs to be resolved.

Chapelle expressed skepticism about the DO probe method, because it uses a semi-permeable membrane that can become clogged with VOCs, if present. He acknowledged, however, that if VOCs are not present, the probe is convenient, cheap, and fast. Chapelle said that he thinks that EPA will need to sanction some DO method.

Chapelle said that USGS uses a version of the Hach method for field analysis of Fe(II), manganese, and sulfide. He noted that precision is not critical for sulfide; a concentration of 0.1 or 0.5 mg/L is adequate for purposes of documenting natural attenuation potential. Laurence Strattan (EPA/National Enforcement Investigations Center) asked whether manganese or iron data should be believed if they were not in agreement. Chapelle pointed out that, while manganese can be reduced abiotically, iron cannot. Therefore, a finding of reduced manganese in the absence of reduced iron is not necessarily a lack of agreement in the data, but may result from a lack of iron-reducing microbes. He also noted that manganese is currently limited as a secondary drinking water contaminant, but may be elevated to primary contaminant status.

USGS does not analyze methane in the field, and Chapelle introduced Steve Vandegrift (ManTech Environmental Services) to present NRMRL/SPRD's SOP, *Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique* (RSKSOP-175).

Concentrations of dissolved methane and ethylene in aquifers contaminated with petroleum and solvents are important in evaluating microbial degradation activity. Mixed fuel and chlorinated solvent breakdown products frequently can include methane and ethylene. Henry's Law states that the mole fraction of a gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface. Solubility data for different gases related to temperature can be obtained from technical handbooks. Sample preparation, headspace analysis, and calculations are described for a routine technique to analyze water samples for methane and ethylene. The technique has not been subjected to EPA's review process, so official endorsement should not be inferred.

A water sample from a field site monitoring well is collected to completely fill a 60-mL glass serum bottle. Several drops of a 1:1 mixture of sulfuric acid and water are added as a preservative to maintain a pH less than 2. The filled bottle is capped with a Teflon-lined butyl rubber septa. The samples are kept cool and stored away from direct sunlight for shipment to the analytical laboratory.

A headspace is prepared by replacing 10% (6 mL) of the bottled sample with helium. A syringe containing helium is injected into the inverted bottle, while a second needle without a syringe is placed through the septum to emit the replaced sample. The bottle is then shaken for five minutes. Aliquots of headspace (usually 300 μL) are injected into a gas chromatograph (GC) with a flame ionization detector and a 6 ft x 1/8 in Porapak Q stainless steel column, and the temperature of the remaining sample is recorded. The sampling syringe should be purged by air vacuum between samples to remove residual contamination. Using GC conditions of a helium carrier gas flow of 20 mL/min at 55°C for one minute, then 20°C per minute to 140°C, the chromatograph retention times for methane and ethylene have been near 0.6 and 1.8 minutes, respectively. Peak area counts generated for each sample are compared to a calibration standard curve generated daily. The analytical method is also applicable for ethane, carbon dioxide, nitrous oxide, and vinyl chloride. The detection limits for methane and ethylene are 0.001 and 0.003 mg/L, respectively. Typical dissolved methane and ethylene concentrations at natural attenuation field sites have been <1 and <0.1 mg/L, respectively. Methane levels have always been higher.

Field trip blanks and sample duplicates collected at a rate of 10% or less are also submitted for analysis. Calibration of the GC is checked each day of use. Syringe barrel tightness and cleanliness are checked frequently. Precision and accuracy for six replicates of a prepared 19.8 mg methane per liter sample was a standard deviation of 0.6 mg/L, relative standard deviation (RSD) = 3.2%, and average recovery of 87%. Similar statistics for 118 mg/L ethylene using three replicates was a standard deviation of 8.8 mg/L, RSD = 7.5%, and an average recovery of 90%.

Easley (EPA/Region 7) and Schultz said that HCl is preferable to sulfuric acid because the former does not degrade organics; most EPA standard methods specify HCl for this reason. Joachim Pleil (EPA/NERL-Research Triangle Park, NC) asked how well the sealed samples stored, and Vandegrift indicated that rubber seals work well, while Teflon seals are not good barriers to gas exchange. Similarly, Vandegrift said that there is no problem with water vapor in the samples; the baking process for BTEX or TCE drives off any water (although it decreases the throughput). Strattan asked about the interchangeability of the columns, and Vandegrift said that the columns were uniquely machined to the brand of GC used. Schultz expressed doubt about subtracting blanks and wanted the SOP to address quantitatively criteria and standards for sample calibration.

Richard McMillin (EPA/Region 6) noted that commercial headspace methods exist (as does an SW-846 method) and asked why these are not suitable. Vandegrift said that these are capillary methods, and he questioned how calibration would be performed with gaseous standards.

Easley noted that the purpose is to identify methanogenesis, not to quantify the precise concentration of methane; she asked if order-of-magnitude differences would be acceptable for this. Chapelle agreed. He said that some methane will always exist, but it is only necessary to detect methane at mg/L concentrations. Easley said that there needs to be some indication of necessary precision in the technique, and the group agreed.

Josephs asked if microbial DNA (deoxyribonucleic acid) or phospholipid fatty acid measurements are as useful as hydrogen to identify biodegradation processes. Chapelle said that identifying microbial populations using those measurements will not necessarily define the dominant biodegradation process. For example, iron reduction and sulfate reduction can both be carried out by the same microbes. Therefore, hydrogen measurements are crucial for determining the dominant electron accepting process.

Chapelle noted that methane analysis is critical for natural attenuation purposes because one needs to determine whether methanogenesis is occurring. He asked if the group would recommend that the ORD SOP go through EPA's process for listing as an SW-846 method. There was general agreement that ORD should initiate the process to get the SOP adopted formally.

Chapelle said that USGS takes samples for anion analysis in the field, but sends them to a laboratory for analysis. An approved EPA Method 300, established by the Office of Water, exists for nitrate, sulfate, chloride, bromide, and nitrite.

Josephs asked whether RSKSOP-147 addresses the calculation of aqueous concentrations of methane and other dissolved gases. Vandegrift noted that, while RSKSOP-147 does not, the laboratory's RSKSOP-175 addresses conversion of measured gas concentrations to aqueous concentrations.

Chapelle recommended determining carbon dioxide as part of the dissolved inorganic carbon (DIC) (carbon dioxide+carbonate+bicarbonate). He said USGS measures DIC in the laboratory by acidifying the sample and using GC methods for analysis of off-gas CO_2. No EPA-approved method was identified. Carbon dioxide concentrations can be calculated from DIC data, utilizing carbonate alkalinity and pH measurements. (As noted previously by Vandegrift, RSKSOP-175 can also be used for CO_2 analysis.) Elevated DIC and carbon dioxide concentrations (compared to background levels) are indicative of oxidative biodegradation. In response to a question, Chapelle indicated that typical groundwater concentration ranges for DIC are $1-10^3$ mg/L. Pleil said that field-portable instruments exist for measuring gas phase carbon dioxide concentrations. They have fast response times are accurate at the 0-10% (volume percent) concentration range.

Chapelle described a method developed by John Wilson at NRMRL/SPRD for field preservation of gas samples for molecular hydrogen. Chapelle distributed a chart documenting the results of multi-laboratory analyses of standard H_2 samples that were stored for five days prior to analysis. Standard errors were less than 1 nanomole/liter (nM/L). (Chapelle said that H_2 concentrations less than 1 nM/L will not support reductive dechlorination.) Chapelle mentioned Wilson's interest in including this preservation technique in an SOP to provide an alternative to analysis in the field. Since GC analysis for hydrogen in the laboratory is much more convenient than field analysis, Chapelle urged the group to endorse this suggestion. The group agreed with Chapelle as to the need for a reliable preservation method, without necessarily endorsing Wilson's new method.

Josephs noted that a potential source of error in analysis for molecular hydrogen is the use of sampling configurations that cause the pressure in the sampling bulb to differ significantly from atmospheric pressure. He pointed out that, although pressure is a variable in the calculation of the aqueous concentration of

hydrogen, pressure isn't usually measured in the sampling bulb, which is assumed to be at atmospheric pressure. He noted that during Dr. McInnes' demonstration of the sampling technique, the pump was placed between the sampling bulb and a discharge point at atmospheric pressure. In that configuration, the sampling bulb will be under a partial vacuum. Unless the pressure in the sampling bulb is measured and accounted for in the calculations, a significant error may occur. Josephs also noted that the draft SOP for hydrogen analysis contains a formula that erroneously substitutes the total pressure for the partial pressure of hydrogen. Vandegrift said that this SOP is a draft, has not undergone full review by the R.S. Kerr Laboratory and can be easily changed. Chapelle noted that he does not use the sampling configuration demonstrated by McInnes. Others agreed that the formula described in the draft SOP for hydrogen needs correction and there was general agreement that issues involving temperature and pressure dependence of aqueous partitioning need to be better addressed in the final version of the SOP.

Chapelle said that Fe(III) represents the most abundant oxidant in most aquifer systems. In a typical BTEX spill, the microbial oxidation of contaminants will first consume free oxygen, then nitrate, and then ferric oxyhydroxide minerals. Nitrate is usually not present in high enough concentrations to be a significant electron acceptor for BTEX degradation in most aquifer systems. The presence of ferric oxyhydroxide minerals can result in rapid biodegradation of BTEX. He added that for this reason, Wilson recommended development of an SOP for microbially available iron analysis.

William Lyon (ManTech Environmental Research Services Corporation) summarized NRMRL/SPRD's SOP, *Anaerobic HCl Extraction of Soils or Sediments: Rapid Sample Preparation Prior to a Screening Test for Microbially Available Iron* (RSKSOP-193). Lyon noted that this SOP considers sample handling and preparation of extracts. He said that the goal was to identify that present-day Fe(III) in the sediment, which is microbially available as a terminal electron acceptor. Determination of total extractable iron is an inadequate measure of available Fe(III) because a significant fraction of the iron may reside in ferrous iron minerals. There is currently no "approved" analytical method for determining microbially available ferric gel (amorphous iron oxyhydroxides) that is both selective and redox-neutral. Lyon described a provisional surrogate procedure using a 24-hour extraction with 0.5M HCl, which seems practical and simple. Speeding up the process by utilizing elevated temperatures, or ultrasonic agitation tends to decrease the selectivity of the analysis. He felt that the 24-hour extraction was a reasonable compromise between selectivity and speed. Ultimately, the correlation between HCl-extractable Fe(III) and microbially available Fe(III) remains to be established by laboratory microcosm experiments with various iron-reducing bacteria.

Lyon showed a plot of extractable iron versus sample depth from a well at George AFB. It was readily apparent from the plot that iron concentrations were highly variable and that peaks in Fe(II) and Fe$_{total}$ on occurred at depths that presumably correlated with certain geologic layers. He noted that dried samples typically become less extractable than samples kept moist, and that freezing also was thought to reduce extractability of ferric gels.

Sample extracts stored for 30 days in ambient light seem to have exhibited some photochemical reduction. He cautioned that sample extracts should, therefore, be wrapped in foil for storage as well as during the extraction itself. The greatest discrepancies in extent of reduction appeared for those samples highest in Fe(III). In contrast, high ferrous iron extract samples showed little tendency to oxidize during storage at pH < 2.

Lyon showed an anomalous QC plot of the extent of reduction for extracts of crystalline γ-Fe$_2$O$_3$ (maghemite). This plot exhibited an as-yet unexplained high variability in the amount of reduction. (Note: This apparent reduction seen in HCl extracts from an essentially pure ferric iron mineral is now thought to

be an artifact caused by stainless plumbing in the ion chromatograph (IC). Use of an IC equipped with all-polymer plumbing seems to have eliminated this problem.)

Lyon said that use of a glovebox in the field is recommended, especially for the most anoxic samples (ratios of Fe(II)/Fe$_{total}$ >0.2). He indicated that these most highly-reduced samples can be susceptible to significant oxidation during sample splitting and preparation.

Finally, he compared Fe$_{total}$ analyses by ICP-AES against analyses by the new IC technique developed at the laboratory. There were some extreme outliers in the data, which are still under investigation. Lyon then introduced Ming Ye of ManTech to summarize the new protocol, *Analysis of Ferric and Ferrous Iron in Soil Extracts by Ion Chromatography* (RSKSOP-195).

Ye described his IC method for the simultaneous analysis of Fe(II) and Fe(III). He uses an ion exchange column to separate the two species, using an anionic chelating agent to form anionic complexes. The soil extractions carried out with both 0.5 M HCl and 0.36 M oxalate under anaerobic conditions were compared. The detectable limits are 3-4 parts per billion (ppb) for Fe(III) and Fe(II). Ferric and ferrous ions were stable in either HCl solution or deionized water when stored outside of a glove box. Traditional techniques use a complexing agent to measure Fe(II) then a reducing agent to convert Fe(III) to Fe(II). Total iron is then measured and Fe(II) is subtracted to obtain Fe(III). This complicated process takes more time and has more opportunity for analytical error. Ye said that the main limitation of the new method is that the analysis must be at or below a pH of 2. Above a pH of 3.1, there is wide variability. He pointed out that oxalate digestion has been reported in the literature for Fe$_{total}$, but he presented data that showed that oxalate was not suitable because ferrous ions are converted to Fe(III) in a non-predictable way. Chapelle added that even the original authors of the oxalate method have abandoned it. Ye also reported that calcium, magnesium, and aluminum compounds commonly found in minerals do not interfere with the iron analyses.

Chapelle asked the group whether the technique could form the basis for an SOP for iron, and there was no disagreement. Josephs pointed out that Lyon had mentioned future microcosm experiments with iron-reducing microbes to test the bioavailability of Fe(III) and noted that the results could affect the SOP. Lyon indicated that those microcosm tests will take a long time to design and complete, but he agreed that he wanted to see how well those experimental results correlate with measurements using the SOP.

Easley pointed out that the iron analyses could be expensive and suggested that screening criteria be developed to help decide when the analyses should be conducted. Chapelle agreed that the tests could be expensive; if a soil core is taken, one can often tell by inspection whether reducible iron is present, but concentration is unknown. He felt that iron analysis is probably unnecessary for chlorinated sites, but very valuable for BTEX sites because Fe(III) is often the most abundant of the electron acceptors needed for biodegradation. He pointed out that in either case, there is no harm in developing an approved SOP. However, guidance on when to use the SOP could be helpful.

Josephs pointed out that PRPs may prefer to use their own methods and asked about the need for performance evaluation standards or other checks on their methods. Schultz also pointed out that only the drinking water program has laboratory certifications. Mary Goldade (U.S. Bureau of Mines) argued against laboratory certifications because one major objective in developing the field SOPs is to have easy, fast, and "ballpark" methods that do not discourage use because of complicated bureaucratic procedures. There was general agreement that certification would be overkill for field screening methods. Chapelle asked if there should be a recommendation for ORD to develop a systematic evaluation of the advantages and disadvantages of the various methods. Goldade agreed that it would be useful.

Vandegrift pointed out that EPA requires that nitrite analyzed alone has a 48-hour maximum holding time, but if one analyzes for nitrite plus nitrate (without distinguishing between them), then holding time isn't critical. However, nitrite is of microbiological significance (indicating that nitrate is biologically reduced to nitrite), so the two compounds should be distinguished.

Josephs asked Pleil how his laboratory ships gas samples to the laboratory. Pleil said that the NERL Research Triangle Park laboratory uses stainless steel canisters equipped with bellows valves. The gas is shipped under positive or negative pressure, so there can be no question of leakage. Also, the canisters can be lined with vapor-deposited silica or chromium oxide if there could be any question of surface reactivity to the iron in the stainless steel. He said he much prefers this technique to the glass-vial-and-stopper method.

Easley pointed out that analytical techniques are advancing constantly and urged that SOPs may discourage the development or implementation of technological innovations. She urged that, wherever possible, EPA's protocols should encourage the adoption of innovations and emerging technologies. Examples noted by the group included the field-portable CO_2 analyzer mentioned by Pleil, analyzers developed by the Navy for munitions chemicals, and fiber optics downhole sensors being investigated by ORD's Las Vegas laboratory.

APPENDIX D
Breakout Sessions for Topic 2: Site Characterization for Natural Attenuation Assessments:
Hydrogeologic Considerations

Topic Leaders: Steven D. Acree, EPA, NRMRL/SPRD–Ada, OK, and Richard E Willey, EPA/Region 1

Discussions from the three Topic 2 breakout sessions are summarized below.

Current studies performed to determine processes and rates of contaminant transport and fate in the subsurface often rely on apparent changes in contaminant concentrations along the assumed center line of a plume and estimates of groundwater seepage velocities. These in turn are used to evaluate biological transformation rates and predict contaminant migration. However, significant uncertainties in key physical parameters such as hydraulic conductivity distribution and temporal variations in hydraulic gradients exist at most sites. In addition, contaminant distribution is usually poorly defined due to such factors as heterogeneity in geologic materials and subsurface distribution of NAPLs. To the degree that these factors are not given adequate consideration, attempts to properly assess natural attenuation at a site are likely to fail.

Traditional methods for hydrogeologic characterization, such as large-scale aquifer pumping tests, are useful to define bulk hydraulic properties, but they often do not provide sufficient detail regarding the hydrostratigraphic controls on contaminant migration. Recent developments in tools and approaches for more detailed characterization of hydrogeologic parameters and contaminant distribution can improve this definition. These breakout groups discussed approaches to hydrogeologic characterization for purposes of defining natural attenuation processes and whether new approaches should be recommended. Group discussions also addressed topics related to characterization of groundwater flowpaths and use of detailed characterization strategies.

The general consensus was that the definition of contaminant distribution in three-dimensional space was preferred to a one-dimensional approach to flowpath analysis. Characterization of geologic controls on contaminant migration and estimates of hydrogeologic parameters within zones of contaminant migration were also viewed as important to these investigations.

Objectives of Characterization

Contaminant distribution information is often acquired on a finer scale than information on hydraulic parameters. Sufficient hydrogeologic information to define controls on groundwater flow and contaminant migration is often not obtained. Hydrogeologic characterization should be oriented to objectives such as the co-characterization of contaminant distribution and hydraulic conductivity, as this approach focusses attention on the value of data to be obtained from these studies. Highly detailed definition of hydraulic parameters may not be necessary at all sites and may be cost-prohibitive at many sites. However, the level of detail required in these investigations is a function of many factors including hydrogeologic setting, subsurface heterogeneity, contaminant distribution, and other site-specific complexities. Toward this end, the development of a conceptual model for site hydrogeology is of paramount importance in all natural attenuation evaluations.

The appropriate level of detail needed for a site characterization varies with the complexity of the site as determined by the contaminant distribution and hydrogeologic setting. There was general recognition that the degree to which a site should be characterized should be related to the consequences, in dollars and risks, of missing data. The cost of remedial decisions and the information needed to make remedial decisions are

related to such factors as risks to human health and the environment and hydrogeologic complexity. Increased complexity often necessitates increased expenditures for characterization. However, complex hydrogeologic settings should not be categorically excluded from consideration when assessing the role of natural attenuation in site remediation.

The objectives of these investigations should include estimation of contaminant transport rates and a determination of plume stability. This requires estimation of dominant transport and fate processes as well as the existing controls on those processes. There was general agreement that many data of lower precision were preferable to few data points of higher precision in evaluating these processes. It was acknowledged that most of the uncertainty in subsurface contaminant distribution was related more to heterogeneity in hydrogeologic parameter distributions than to such factors as laboratory variability in chemical analyses. Thus, estimation of hydraulic parameters in zones where contaminants are migrating was generally seen as more useful than traditional estimates of bulk aquifer properties. Other objectives include more detailed evaluation of temporal variations in hydraulic gradients and the resulting effects on directions and rates of contaminant migration. These factors are often not defined in detail and may have significant impact on evaluation of contaminant fate processes such as the estimation of biodegradation rates.

Some degree of source characterization was generally viewed as essential for natural attenuation studies. At a minimum, information regarding the lateral and vertical extent of sources was considered to be important. However, it was recognized that routine characterization tools are often inadequate to define contaminant sources, such as subsurface distributions of DNAPLs, in detail.

Methods of Characterization

It was generally agreed that characterization of contaminant distribution in greater detail will be important at many sites. However, this needed detail may not be practicable to achieve using traditional monitoring wells. Techniques such as vertical profiling using direct push technologies with onsite analytical support, coupled with a representative percentage of samples analyzed by fixed-based laboratories, often offer cost-effective methods for acquiring this information. Similarly, tools such as the cone penetrometer for detailed reporting of site lithology and borehole flowmeters, mini-slug tests, and small-scale pumping tests for defining relative differences in hydraulic conductivity allow detailed evaluations of hydrostratigraphic controls on contaminant migration and better estimates of migration rates.

Much discussion focussed on difficulties in characterizing one-dimensional groundwater flowpaths using conventional monitoring wells. Apparent decreases in contaminant concentrations along flowpaths are often used to estimate contaminant mass reduction due to processes such as biodegradation. This approach often leads to inaccurate estimates of actual mass loss due to insufficient information on subsurface heterogeneity and poor understanding of contaminant distribution. The definition of a plume using two-dimensional (horizontal and vertical) transects perpendicular to groundwater flow direction was viewed as a best-available-technology alternative to characterization of one-dimensional flowpaths, especially where sampling using push technologies is possible. This information also gives qualitative insights into the nature of hydrogeologic controls on contaminant migration. Information from transects should be used to site wells for the evaluation of temporal trends and hydraulic gradients. Long well screens are to be avoided because they often provide misleading geochemical and contaminant data due to mixing of waters from different zones in the well. Appropriate screen placement is highly site-specific and will depend on hydrostratigraphic controls on contaminant migration and on the distribution of contaminants and other geochemical parameters.

47

Solute transport models were seen as effective site characterization tools applicable to many of these investigations. Models may be used to better understand dominant transport and fate processes and the potential effect of hydrogeologic controls on those processes. Simulations offer means to cost-effectively test hypotheses developed during characterization. However, simulation of site conditions is not a substitute for characterization performed in the field. There should be a strong reliance on field data in these assessments and a healthy degree of skepticism regarding results of simulations.

Other tools and techniques for evaluating contaminant migration and fate which were discussed included tracer tests. Chloride, TMBs, MTBE, and other relatively conservative constituents already in contaminant mixes may function as useful tracers for normalization of apparent contaminant losses and deserve further evaluation. Studies using injected tracers, particularly longer-term tests, may also provide vital information regarding hydraulic parameters including dispersivity, three-dimensional contaminant transport, temporal variability in hydraulic gradients, and contaminant fate processes.

Technical Guidance Needs

Many workshop participants expressed the need for additional guidance on evaluating studies designed to characterize natural attenuation processes. The need for focussed, objective-oriented technical guidance was identified in the following areas:

- hydrogeologic information that is necessary for evaluations of natural attenuation processes;

- identification of the minimum level of site characterization needed prior to evaluation of natural attenuation processes, including ranking of parameters as essential, important, or useful with discussion of the utility of these parameters. In a similar manner, guidance regarding workplan development and contents, including the priority of items to include in a workplan, is needed. Such guidance should include "rules of thumb" for determining the existence of "bad data," including improbable and impossible data values, and the relative roles of field parameters and laboratory parameters in making these evaluations;

- groundwater sampling protocols, including guidance concerning filtering of samples, frequency of sampling, and the order of sample collection during each sampling episode;

- potential pitfalls in characterizations, including monitoring network design and determination of background geochemical conditions; and

- improved guidance for assessment of situations where ecosystems are potential receptors.

APPENDIX E
Breakout Sessions for Topic 3: Data Quantity and Quality Issues

Topic Leader: Jeff van Ee, EPA, National Exposure Research Laboratory–Las Vegas, NV

van Ee facilitated the three breakout sessions on *Data Quantity and Quality Issues*. The discussion highlights were recorded on flip charts for each session. With some minor editing, the charts read as follows:

Topic 3, Session 1

- Do not scrimp on characterization. Cannot use scripted characterization for site "types."

- Natural attenuation can be appropriate in areas with low population density.

- Consider remedial alternatives before collecting data.

- Aquifer quality is an important consideration.

- Criteria for considering natural attenuation as an option include:
  - age of the spill
  - variability in federal programs and state policies
  - legislative mandates
  - trust fund availability
  - potential use of surrounding properties (risk to potential receptors)
  - protection of the receptors (existing wells)
  - point of compliance
  - source control
  - aquifer quality
  - ability to remediation to maximum contaminant levels (MCLs) (scientific questions)
  - ability to monitor plume
  - remediation time frame
  - penalties for sloppy work
  - level of comfort with natural attenuation

- Approaches to handling errors in selecting (or not selecting) natural attenuation at a site include:
  - remedies can be revisited (Superfund five-year review, RCRA review points)
  - send letters to residents by certified mail
  - place conditions in agreements to reopen the selected remedy when land use at the site changes
  - depends on the consequences of making an error in selecting natural attenuation
  - use deed restrictions
  - base decisions on scientific evidence

- Current data requirements for selecting natural attenuation include:
  - depends on flexibility allowed to contractor or the potentially responsible party
  - ASTM "Remediation by Natural Attenuation" (RNA) draft protocol approach (lines of evidence)
  - performance (goal-based) protocol approach versus design (prescriptive) protocol approach
  - property transactions are a driver
  - depends on contaminant (petroleum hydrocarbons versus solvents)
  - demonstrate that natural attenuation is occurring (for example, in South Carolina)

    - monitor contaminant levels (for example, in North Carolina)
    - natural attenuation ability to achieve MCLs in a reasonable time frame
    - MTBE monitoring requirements vary by state
    - AFCEE protocol a good place to start; most complete "cookbook" available; needs to include more diverse environments; never intended to be all encompassing

- Criteria for attaining remediation levels include:
    - MCLs (may not be available or may be lower than detection limit)
    - As Low as Reasonably Achievable (ALARA) approach
    - Alternate Concentrations Limits (ACLs)
    - depends on program and state

- Criteria for determining the frequency of monitoring include:
    - function of money, risk, hydraulic conductivity, compound, historical data, etc.
    - as frequently as needed to make regulators comfortable
    - depends on site and program
    - need more data when you start and when you stop

- When not to use natural attenuation:
    - when you cannot monitor the plume
    - in karst terrain
    - when the plume is expanding?
    - main question is what is an adequate monitoring system?

- Driving factors in decision making include:
    - assimilative capacity
    - contaminant concentrations
    - source material
    - presence of free DNAPL

- Rules of thumb include:
    - If the concentration of BTEX compounds in groundwater is above 50 ppm, then remove residuals.
    - If the concentration of BTEX compounds in groundwater is below 50 ppm, then natural attenuation may be appropriate.
    - If TCE and _cis_-DCE are present in groundwater at concentrations above 300 ppb, and vinyl chloride is above 20 ppb, then bioremediation is occurring.
    - If the concentration of contaminants in groundwater plume is not reduced in two years, then impose contingency plans (RCRA, EPA/Region 3).

- We should be using more statistical analysis on our datasets.

- EPA/Region 9 has a variety of RODs with 10^{-4} risk within the plume area.

Topic 3, Session 2

Referring to a hypothetical dry cleaning facility, Jeff van Ee asked breakout session participants how they would approach site characterization leading to a decision to select, or not select, natural attenuation.
    - Preliminary risk assessment.
    - sample existing wells

- drill down with one well to do a quick look at how bad the site is
- remove the source and excavate to water table
- conduct a preliminary site characterization (for a RCRA Part A assessment, there should be one hole downgradient, one hole to the side, and one hole further downgradient.)
- conduct a utility survey, soil map analysis, and fence line monitoring
- using direct push methods and field GC collect soil samples and water samples, look for PCE and daughter products down to vinyl chloride (cost $1,000/day for equipment and $1,500 for analyses).

- If groundwater contaminant concentrations are large near the source, then return to the office and consider remediation options.
  - natural attenuation (cost=$200,000)
  - engineering methods (costs do not include pilot tests of the technology)
  - pump and treat using half dozen wells (cost=$1 million over 10 years)
  - soil vapor extraction (cost=$7,000/month)
  - excavation and off-site disposal (cost=$75/hour for equipment, $250/ ton for disposal if a landfill is within 100 miles of the site)

- Main site characterization
  - determine the groundwater flow rate (conventional wells, nested wells with 10-foot screen, slug tests, pump tests)
  - direct push technologies can be used for unconfined aquifers; cone penetrometers can be used to map the plume and characterize lithology.

Breakout session #2 ended before a decision could be made about using natural attenuation or an engineered remedy at this hypothetical site.

Topic 3. Session 3

- When do you have enough data?
  - depends on the data quality; data quality for a new suite of parameters needs to be established
  - need more samples of lower quality rather than fewer samples of higher quality
  - use iron and methane data to qualitatively determine redox conditions across the site
  - what DQO level should the data achieve? (EPA is moving away from DQO levels.)
  - when applying natural attenuation, spatial aspects must be considered in more detail than in standard settings; there are no standard methods to evaluate spatial error
  - there will be resistance to increasing the density of spatial sampling
  - a portion of a site can be intensely sampled and the data used to determine variability and the number of samples needed for the rest of the site.

- The goal is to have SOPs that expand upon existing procedures. They need to be on a national guidance level (for example, low-flow guidance).
  - Standards are needed to assess data quality (beyond instrument calibration).
  - EPA should have a training requirement for data quality assessments.
  - SOPs for field testing of natural attenuation are needed (state consistency)
  - Guidances in five to six subject areas are needed. They should be developed in consultation with QA/QC specialists. Standards, duplicates should be advocated.
  - Methods are needed for determining sources of variability in measurements.
  - Consistency in sampling and consistency in data quality are needed for field methods to reduce uncertainty.

APPENDIX F
Breakout Sessions for Topic 4: Interpretation and Use of Site Characterization Data

Topic Leader: John Wilson, EPA, NRMRL/SPRD–Ada, OK

Wilson presented each breakout group with a list of items to discuss during the breakout sessions on *Interpretation and Use of Site Characterization Data*. The following is a summary of the discussions which took place during the three breakout sessions on this topic:

<u>Dilution vs. Bioremediation</u>

To determine if biodegradation of a plume is occurring, changes in plume characteristics should be modeled using a transport and fate model that accounts for non-destructive attenuation mechanisms (e.g., through dilution, dispersion, sorption), but not degradation. The modeling results should be compared to field data. If the field results indicate that the plume is attenuating along the flowpath at a faster rate than expected from the model, biodegradation can be assumed and testing for natural attenuation parameters initiated. In addition, biodegradation rate constants should be determined.

If it is determined up front that biodegradation is *not* occurring at a site, less monitoring may be required to evaluate dilution and dispersion as primary mechanisms of natural attenuation. Such monitoring should include tracer tests (*e.g.*, the use of soluble salts to determine groundwater flow velocities and concentration changes due to dilution and dispersion).

<u>Models</u>

The participants noted that they trust monitoring results more than modeling results, and that they more frequently use models to verify decisions, not make them. Models can be used as tools to:

- find data gaps and plan monitoring strategies;
- confirm and communicate conceptual models;
- identify where to place monitoring wells;
- select remedies among options;
- design and optimize a remedy;
- set clean-up levels;
- perform cost/benefit analyses;
- determine when groundwater plumes will intercept surface water;
- verify site characterization results; and
- forecast future behavior of contaminants in groundwater.

Problems with data use in models include:

- deficiencies in code;
- selection of inappropriate code;
- improper calibration;
- inadequate documentation of implementation, which makes it difficult or impossible to review; and
- input data that is too sparse, not representative, in error, or missing critical parameters.

Duration of Monitoring

Wilson noted that there are several kinds of monitoring:

- site characterization monitoring to build a conceptual and mathematical of a plume and allow a risk assessment to determine whether natural attenuation may be appropriate at a site;
- verification monitoring to determine that the conceptual and mathematical models realistically describe the site; and
- long-term monitoring to make sure the behavior of the plume does not change.

In some cases, different methods are appropriate for different types of monitoring.

Bill Brandon (EPA/Region 1) noted that University of Utah's natural attenuation course stresses that natural attenuation needs to be monitored until cleanup objectives are shown to have been attained. Since costs need to be compared with other remedial alternatives before a remedy is selected, the remedial time frame and duration of monitoring must be estimated as part of the remedy selection process. Effective time and cost comparisons, such as are appropriate to the feasibility study stage, require that the various remedial options under consideration, including monitored natural attenuation, are quantified in absolute terms, (*i.e.*, years and dollars), not just on a relative basis. Many participants commented that EPA guidance for natural attenuation should not include any inflexible rules about monitoring frequency and duration. However, some said that a minimum requirement of quarterly sampling should be implemented. Wilson suggested that, at a minimum, monitoring should take place during the time it takes groundwater to flow through the plume from an upgradient monitoring well to a downgradient one. This may help distinguish significant from non-significant trends in the data. For example, if the rate of groundwater flow is slow, a short period of monitoring may fail to recognize an expanding plume over statistical noise in sampling results. As a result, the length of monitoring before accepting natural attenuation should be scaled to the rate of attenuation of the contaminants at the site. Wilson added that at least one monitoring well should be installed for each order of magnitude of contaminant reduction; this will help to identify significant spatial trends in the data. For example, if a tenfold reduction in concentration is the criterion, the wells should be spaced at the distance groundwater would move in the time required for a tenfold reduction in contaminant concentration.

One participant noted that sentinel wells should be installed at natural attenuation sites to ensure that the plume is not moving into clean areas. Another participant suggested that these wells be placed in previously contaminated areas that are known to be clean. It was noted that heterogeneous flow fields should require tighter spacing between monitoring wells.

Use of Bailers

It was noted by the participants that Geoprobe check valves are better than bailers, but not as good as peristaltic pumps for collecting samples. If low-flow pumping still purge wells dry, diffusion cell samplers should be used instead.

Contamination Interferences with Hach Field Methods

It was agreed that Hach kits and other field screening methods are most appropriate for initial site characterization monitoring purposes. There was agreement among participants that, for verification monitoring and long-term monitoring, it is better to send samples to an off-site laboratory for analysis, whenever possible. For analytes that are unstable (*e.g.*, ferrous iron, sulfide), off-site laboratory analysis is not possible.

Biological Activity/Reactivity Test (BART) for Bacteria in Water Samples

Participants familiar with Hach's BART kits agreed that there is little evidence that these kits can identify whether microorganisms are active in the subsurface.

Calibration and Cleaning of Oxidation/Reduction Potential (ORP) Probes

Wilson noted that good quality ORP probes are preferred by the Robert S. Kerr Environmental Research Center and that cheaper versions may not be as effective. He added that ORP probes should be calibrated with two buffer solutions prior to sampling. He added that the preferred method for calibrating ORP probes is to use the manufacturer's solution that comes with the test kit. ORP probes should be cleaned regularly to remove hydrocarbon buildup.

Filtration of Sulfate, Nitrate, and Oxygen Samples

Participants agreed that sulfate and nitrate samples should be filtered. DO samples, on the other hand, do not need to be filtered.

Best Method to Measure Oxygen

Some participants agreed that DO cannot be accurately measured and therefore, should not be a required parameter. One participant suggested monitoring for Fe(II) as an indicator since the presence of Fe(II) indicates absence of DO. Wilson said that he prefers DO reporting to include information on how the DO samples were collected and how the equipment was calibrated for each sample or well. He added that test kits are available that are inexpensive, effective for measuring DO, do not require maintenance, and do not need to be calibrated.

Well Purging/Well Sampling

Wilson said that it is a myth that peristaltic pumps cause loss of volatile compounds because they create vacuums. If no gas phase is present (*i.e.*, no headspace or bubbles) volatiles won't be lost. He added that he prefers to purge wells from the top of water column before sampling and then lower the pump to sample from the middle of the screen.

Pump Preferences

Most participants agreed that peristaltic pumps are preferable to bailers.