EPA United States
Environmental Protection
Agency

Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration

Workshop Summary

Dallas, Texas - April 25-27, 2000

Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration

Workshop Summary
Dallas, Texas
April 25-27, 2000

Edited by

Richard T. Wilkin
Ralph D. Ludwig
Robert G. Ford
Subsurface Protection and Remediation Division
National Risk Management Research Laboratory
Ada, OK 74820

Notice

The preparation of this report has been funded wholly by the U.S. Environmental Protection Agency's Office of Research and Development. The views expressed in this Workshop Summary are those of the individual authors and do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency (EPA). This document has been reviewed in accordance with EPA's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients. Monitoring oxidation-reduction processes has direct application to performance assessments of remedial measures and to risk management approaches that reduce risk through minimizing exposure. Understanding the complexities associated with oxidation-reduction processes for remediating contaminated ground water is a major priority of research and technology transfer for the U.S. Environmental Protection Agency's Office of Research and Development and the National Risk Management Research Laboratory. This report summarizes the findings of a workshop held to discuss and summarize the current state-of-the-science with respect to methods of redox monitoring, data interpretation, and their applications to ground-water remediation.

Stephen G. Schmelling, Acting Director
Subsurface Protection and Remediation Division
National Risk Management Research Laboratory

Contents

Introduction

Redox conditions are among the most important factors controlling contaminant transport and fate in ground-water systems. Oxidation-reduction (redox) reactions, that is, reactions involving electron transfer, mediate the chemical behavior of both inorganic and organic chemical constituents by affecting solubility, reactivity, and bioavailability. In recent years, innovative technologies have emerged to meet ground water clean-up goals that take advantage of the redox behavior of contaminant species. Remedial technologies that strategically manipulate or capitalize upon subsurface redox conditions to achieve treatment may emphasize reductive processes (e.g., subsurface permeable reactive barriers, monitored natural attenuation) or oxidative processes (e.g., air sparging). In this context, there is an obvious need to provide stakeholders with a current survey of the scientific basis for understanding redox behavior in subsurface systems within the framework of site characterization, selection of remedial technologies, performance monitoring of remediation efforts, and site closure.

Many elements can exist in nature in more than one valence or oxidation state. Nine of the sixteen inorganic species for which EPA has set specified maximum contaminant levels (MCLs) in drinking water exhibit multiple oxidation states. These include antimony, arsenic, chromium, copper, lead, mercury, selenium, and nitrogen (nitrate and nitrite). Consequently, the reactivity, solubility, and mobility in the environment of these and other redox-sensitive elements depend, in part, on redox conditions. For example, uranium and chromium are insoluble (immobile) under reducing (anaerobic) conditions. In contrast, iron and manganese are relatively insoluble under oxidizing (aerobic) conditions but are quite soluble (mobile) under anaerobic conditions. Environmental mobility of other potentially hazardous metals, such as cadmium, nickel, and zinc, is indirectly related to redox conditions because these metals form ionic complexes and solid precipitates with redox-sensitive elements (e.g., sulfur). Carbon may exist in several oxidation states, from +4 (most oxidized) to –4 (most reduced). Therefore, organic contaminants in ground water can also be strongly influenced by redox conditions, especially through the metabolic activity of microorganisms. For example, BTEX compounds are generally more biodegradable in oxidizing (aerobic) ground water than in reducing (anaerobic) ground water. In contrast, chlorinated solvents such as trichloroethylene and tetrachloroethylene are more biodegradable under more reducing conditions. Examples are abundant in each of the major ground-water contaminant classes: inorganics, petroleum-derived hydrocarbons, and chlorinated solvents, where redox processes have important implications in environmental risk assessment and risk management.

Despite the importance of redox processes for understanding contaminant transport and fate, these processes present recurring sources of confusion. Part of the confusion regarding redox processes no doubt relates to the unfortunate fact that there is no single measurable quantity that uniquely defines the redox state of natural systems. Unlike pH measurements, which correlate with the concentration (activity) of hydronium ions in aqueous solution, there is no equivalent single measurable parameter that correlates well with redox speciation in aquifer systems. At one point there was promise that Eh measurements (referenced potential of a platinum electrode) could fulfill the equivalent for redox characterization that pH measurements serve for evaluating acid-base determinations (see, for example, Garrels and Christ, 1965, *Solutions, Minerals, and Equilibria*, Harper and Row, New York). Subsequent research has shown that the Eh-pH framework, while correct within the rigid constraints of thermodynamic equilibrium, is likely to give an inaccurate model of the redox state of ground-water systems. This is primarily because ground-water systems are rarely, if ever, in thermodynamic equilibrium. The modern view that has emerged over the past several decades is that proper redox characterization involves a more complete assessment of the concentrations of potential electron donors and electron acceptors, that is, species that can participate in redox or electron transfer reactions. Standard electrode (Eh) measurements may still play a useful role in redox characterization, but such measurements need to be interpreted within the context of other geochemical and biochemical data.

Monitoring oxidation-reduction processes in ground-water systems can be viewed as an integrated assessment of hydrogeochemical processes, microbiological diversity, and aquifer characteristics. A complete assessment of redox processes will involve developing a system inventory of the most important redox species. This may include measurement of dissolved oxygen, nitrogen species, iron species, manganese species, sulfur species, carbon species, and dissolved hydrogen. The fact that redox processes in ground water vary both spatially and temporally amplifies the complexity of redox assessments. Yet it is recognized that site-specific redox modeling is often a requirement for predicting future plume migration and for selecting the most successful and cost-effective remediation approaches.

The main objective of the workshop, therefore, was to provide a forum for the presentation, discussion, and synthesis of research on monitoring and interpreting ground-water redox conditions in the context of site evaluation, remedy selection, and performance monitoring. The workshop was attended by researchers, practitioners, and regulators from governmental agencies and non-governmental institutions. Workshop participants entered into a series of focused group discussions that explored redox processes within the organizational matrix of contaminant class (petroleum hydrocarbons, chlorinated solvents, and inorganics) and measurement type (geochemical parameters, dissolved gases, and solid-phase characterization). The principal findings of the workshop are reported in this document as extended abstracts of the invited platform presentations and summary chapters of the focused group discussions.

Richard T. Wilkin
Ralph D. Ludwig
Robert G. Ford

U.S. EPA
Office of Research and Development,
National Risk Management Research Laboratory,
Subsurface Protection and Remediation Division,
Ada, OK 74820

Steering Committee

Michael Barcelona
University of Michigan
Ann Arbor, MI 48109

Robert Puls
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Frank Chapelle
U.S. Geological Survey
Columbia, SC 29210

Stephen Schmelling
U.S. EPA, ORD/NRMRL
Ada, OK 74820

William Deutsch
RR-1 Box 1040
Sedgwick, ME 04676

John Westall
Oregon State University
Corvallis, OR 97331

Robert Ford
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Richard Wilkin
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Ralph Ludwig
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Richard Willey
U.S. EPA, Region 1
Boston, MA 02114

Carol Ptacek
Environment Canada
Burlington, ON L7R 4A6
Canada

John Wilson
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Workshop Participants

Jim Amonette
Pacific Northwest National Lab
Richland, WA 99353

Ann Azadpour-Keeley
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Jim Barker
University of Waterloo
Waterloo, Ontario N2L 3G1

Shawn Benner
University of Waterloo
Waterloo, Ontario N2L 3G1

Paul Bradley
U.S. Geological Survey
Columbia, SC 29210

Chris Braun
U.S. Geological Survey
Austin, TX 78754

Kyle Cook
SAIC
Cincinnati, OH 45206

Isabelle Cozzarelli
U.S. Geological Survey
Reston, VA 20192

Andy Davis
Geomega, Inc.
Boulder, CO 80303

John Fruchter
Pacific Northwest National Lab
Richland, WA 99352

Peggy Groeber
SAIC
Cincinnati, OH 45206

Douglas Grosse
U.S. EPA, ORD/NRMRL
Cincinnati, OH 45268

Allison Hacker
SAIC
Cincinnati, OH 45206

Evelyn Hartzell
SAIC
Cincinnati, OH 45206

Janet Herman
University of Virginia
Charlottesville, VA 22903

James Ingle
Oregon State University
Corvallis, OR 97331

Sonya Jones
U.S. Geological Survey
Austin, TX 78754

Donald Kampbell
U.S. EPA, ORD/NRMRL
Ada, OK 74829

Faruque Kahn
U.S. EPA, ORD/NRMRL
Ada, OK 74820

Roger Lee
U.S. Geological Survey
Dallas, TX 75202

Patrick Longmire
Los Alamos National Lab
Los Alamos, NM 87545

Michelle Lorah
U.S. Geological Survey
Baltimore, MD 21237

Daryl Luce
U.S. EPA, Region 1
Boston, MA 02114

Donald Macalady
Colorado School of Mines
Golden, CO 80401

Charlie Macon
Geomatrix Consultants, Inc.
Austin, TX 78703

Rick McGregor
302-285 Erb St. West
Waterloo, Ontario N21 1W5

Pat McLoughlin
Microseeps, Inc.
Pittsburgh, PA 15238

D. Kirk Nordstrom
U.S. Geological Survey
Boulder, CO 80303

Kirk O'Reilly
Chevron Research & Technology
Richmond, CA 94802

Keith Piontek
The Forrester Group
Chesterfield, MO 63017

Robert Pirkle
Microseeps, Inc.
Pittsburgh, PA 15238

Johnette Shockley
U.S. Army Corps of Engineers
Omaha, NE 68114

Tim Sivavec
GE Corp., R&D
Niskayuna, NY 12309

Chunming Su
ManTech Env.
Ada, OK 74820

Jim Szecsody
Pacific Northwest National Lab
Richland, WA 99352

Caroline Tebes Steven
U.S. EPA, ORD/NERL
Athens, GA 30605

Don Vroblesky
U.S. Geological Survey
Columbia, SC 29210

Scott Warner
Geomatrix Consultants, Inc.
Oakland, CA 94612

John Washington
U.S. EPA, ORD/NERL
Athens, GA 30605

Eric Weber
U.S. EPA, ORD/NERL
Athens, GA 30605

Todd Wiedemeier
Parsons Engineering Science
Denver, CO 80290

Barbara Wilson
Dynamac Corporation
Ada, OK 74820

Agenda

April 26: Breakout Sessions

Morning Sessions – *Redox and Remediation*

Session 1.   Redox Processes in Petroleum Hydrocarbon Remediation

Session 2.   Redox Processes in Chlorinated Hydrocarbon and MTBE Remediation

Session 3.   Redox Processes in Inorganic Remediation

Afternoon Sessions – *Redox Measurement*

Session 4.   Measurement Issues: Geochemical Parameters

Session 5.   Measurement Issues: Dissolved Gases

Session 6.   Measurement Issues: Solid Phase

April 27:   Summary Presentations

Session 1.   Michael Barcelona, Ralph Ludwig

Session 2.   Frank Chapelle

Session 3.   Robert Puls

Session 4.   Richard Wilkin

Session 5.   Frank Chapelle

Session 6.   Robert Ford

Acknowledgments

Extended Abstracts

Invited speakers who gave oral presentations on the first day of the Workshop prepared the following extended abstracts. The speakers and general topics of these presentations were selected by the steering committee. The plenary presentations covered a range of topics relating to redox chemistry in ground water as they relate to contaminant remediation. These presentations were intended to provide a foundation for discussion at the Workshop.

Role of Redox Processes and Spatial and Temporal Variability in Site Characterization

Michael J. Barcelona

The University of Michigan
Ann Arbor, MI 48109-2099

Site characterization represents the initial phase of active monitoring undertaken as part of active or passive organic contaminant remediation efforts. Initial characterization work sets the stage to evaluate the progress of transformations of contaminants. There have been frequent observations of: parent compound disappearance, active microbial populations with biotransformation capabilities, and the appearance/ disappearance of organic and inorganic constituents which provide indirect evidence of bioremediation at contaminated sites. However, quantitative evidence for sustained removal of toxic compounds from complex mixtures solely by biological processes is lacking. This is due largely to the reliance on monitoring well samples for evidence of biological activity rather than identification of the mass of contaminants (and total reactive organic carbon), redox capacities, and estimations of the net removal/transformation of reactive compounds over time.

A dynamic approach to quantitative site characterization is needed which recognizes intrinsic bioremediation as an active cleanup approach. Careful attention must be paid to the identification of the three-dimensional distribution of contaminant mass. Then, the correspondence between the contaminant distribution and favorable physical, geochemical and microbial conditions in the subsurface over time provide a basis for net contaminant removal estimates. Mere adaptations of detective ground-water monitoring networks are insufficient for the quantitative evaluation of intrinsic bioremediation technologies.

The practice of site characterization for remediation of subsurface organic contaminants has evolved slowly in the past decade. Early guidelines (Scalf et al., 1981; Barcelona et al., 1985; U.S. EPA, 1986), for minimal ground-water contamination detection monitoring (i.e., monitoring wells upgradient and downgradient) have been applied to many sites of potential concern from detection through remedial action selection phases.

This minimal approach has been used widely regardless of the physicochemical characteristics of contaminant mixtures or the complexity of hydrogeologic settings. For soluble inorganic constituents, this approach may be adequate for detection purposes, but assessment efforts require substantially more comprehensive approaches. For organic contaminant assessment efforts, (i.e., determinations of the nature and extent of contamination), wells alone have been found to be inadequate monitoring tools. Recognition of the value of subsurface soil vapor surveys for volatile organic components of fuel and solvent mixtures has led to modified, monitoring well-based site characterization approaches (Eklund, 1985). These approaches to site characterization and monitoring network design often suffer from the failure to identify the total mass of contaminant in the subsurface. There are three main reasons for this outcome.

First, although volatile organic compounds (VOC's) are mobile in ground water and frequently early indicators of plume movement (Plumb, 1987), their detection in vapor or well samples and apparent aqueous concentration distribution does not identify the total mass distribution of organic contaminant (Robbins, 1989). Secondly, efforts to correlate observed soil vapor or ground water VOC concentrations with those in subsurface solid cores have often been unsuccessful. This is because previous bulk jar collection/refrigeration at 4°C guidelines for core samples for VOC analyses lead to gross negative errors (U.S. EPA, 1992). Thirdly, "snapshots" (i.e., one-time surveys) of background and disturbed ground-water chemistry conditions have been interpreted as "constant" ignoring temporal variability in subsurface geochemistry, particularly redox conditions.

More recent guidelines and recommendations on network design and operations have led to more comprehensive, cost-effective site characterization advice (U.S. EPA, 1992; U.S. EPA, 1994). Also, excellent reviews of characterization and long term monitoring

needs and approaches in support of in-situ remediation efforts should guide us in this regard. Site characterization efforts provide a basis for long term monitoring design and actually continue throughout the life of a remediation project.

A dynamic, ongoing site characterization effort includes objectives to:

1) identify the spatial distribution of contaminants, particularly their relative fractionation in subsurface solids, water, and vapor, along potential exposure pathways recognizing that the mass of contaminants frequently resides in the solids;

2) determine the corresponding spatial distribution of total reactive organic matter (e.g., overall reduction capacity; degradable normal, aliphatic and aromatic hydrocarbon compounds, etc.). Overall microbial biomass and activity in the subsurface, (and other bioremediation indicators) are largely due to the total mass of reactive organic carbon;

3) estimate the temporal stability of hydrogeologic and geochemical conditions which favor microbial transformations in background, source and downgradient zones during the first year of characterization and monitoring;

4) derive initial estimates of net microbial transformations of contaminants, under known redox conditions, which may be refined in an efficient long-term monitoring network design. Over long time periods, redox conditions and rates of degradation can vary substantially near source areas.

The first three objectives establish the environment of major contamination and geochemical conditions under which bioremediation may occur. The latter two objectives are vitally important since the evaluation of the progress of intrinsic bioremediation processes depends on distinguishing compound "losses" due to dilution, sorption and chemical reactions from microbial transformations. This approach has been suggested emphatically by Wilson (Wilson, 1993) and was later developed into technical protocols by Wiedemeier, et al. (Wiedemeier et al., 1995; Wiedemeier et al., 1996) (See characterization detail, Table 1).

The initial site characterization phase should be designed to provide spatially dense coverage of critical data over volumes corresponding to ten to one-hundred year travel times along ground water flow paths. If the flowpath intersects a discharge zone in less than 100 years, then the volume should be scaled accordingly. For example, if the flowpath discharges after 10 years, the critical volume would be one year of travel time. The "volume-averaged" values of the contaminants, hydrogeologic and geochemical parameters within zones along the flow path(s) should be derived from large enough datasets to permit estimation of statistical properties (e.g., mean, median, correlation distance, variance, etc.). In general, this means that the datasets for derived mass loadings of contaminants, aquifer properties, and geochemical constituents (Table 1) derived from spatial averages of data points must include approximately 30 or more data points (Journel, 1986; Hoeksema and Kitanidis, 1985; Gilbert and Simpson, 1985). Indeed, this minimum dataset size strictly applies to points in a plane. Two major decisions which must be made with regard to how spatially averaged masses of contaminants, electron donors (e.g., organic carbon, Fe^{2+}, $S^=$, NH_3, etc.) and electron acceptors (e.g., O_2, NO_3^-, NO_2^-, Fe, and Mn oxides, $SO_4^=$, etc.) are to be estimated. Some attention should be given to field screening methods for free phase or high residual NAPL Phase. (Xie et al., 1999).

The dynamic approach to site characterization for chlorinated hydrocarbons is more demanding in review and data analysis than that for hydrocarbons. There are very few published examples of site characterization effects for these contaminants which have estimated mass loadings in specific media.

Table 1. *Site Specific Parameters to be Determined during Site Characterization (Modified from Wiedemeier et al., 1995)*

FRACTIONATION AND SPATIAL EXTENT OF CONTAMINATION

1. Extent and type of soil and ground water contamination.

2. Location and extent of contaminant source area(s).

   (i.e., areas containing free- or residual-phase product).

3. The potential for a continuing source due to leaking tanks or pipelines.

HYDROGEOLOGIC AND GEOCHEMICAL FRAMEWORK

4. Ground water geochemical parameter distributions.

5. Regional hydrogeology including:

   - Drinking water aquifers, and

- *Regional confining units.*

6. *Local and site-specific hydrogeology, including:*

- *Local drinking water aquifers,*

- *Location of industrial, agricultural, and domestic water wells,*

- *Patterns of aquifer use,*

- *Lithology,*

- *Site stratigraphy, including identification of transmissive and nontransmissive units,*

- *Grain-size distributions, (sand vs. silt vs. clay),*

- *Aquifer hydraulic conductivity determination and estimates from*

  grain-size distributions,

- *Ground water hydraulic information,*

- *Preferential flow paths,*

- *Location and type of surface water bodies,*

- *Areas of local ground water recharge and discharge,*

7. *Definition of potential exposure pathways and receptors.*

References

Barcelona, M. J., Gibb, J. P., Helfrich, J. A., and Garske, E. E. 1985. *Practical Guide for Ground-Water Sampling,* Illinois State Water Survey, SWS Contract Report 374, Ada, OK, U.S. Environmental Protection Agency.

Eklund, B. 1985. Detection of Hydrocarbons in Ground Water by Analysis of Shallow Soil Gas/Vapor, API Publication No. 4394, Washington, D.C.

Gilbert, R. O. and Simpson, J. C. 1985. Kriging for estimating spatial patterns of contaminants: Potential and problems. *Environmental Monitoring and Assessment*, v. 5, pp. 113-135.

Hoeksema, R. J. and Kitanidis, P. K. 1985. Analysis and spatial structure of properties of selected aquifers. *Water Resources Research*, v. 21, pp. 563-572.

Journel, A. G. 1986. Geostatistics: Models and tools for earth sciences. *Mathematical Geology*, v. 18, pp. 119-140.

Plumb, R. H. 1987. A comparison of ground-water monitoring data from CERCLA and RCRA sites. *Ground Water Monitoring Review*, v. 7, pp. 94-100.

Robbins, G. A. 1989. Influence of using purged and partially penetrating wells on contaminant detection, mapping and modeling. *Ground Water*, v. 27, pp. 155-162.

Scalf, M. R., McNabb, J. F., Dunlop, W. J., Cosby, R. L., and Fryberger, J. S. 1981. *Manual Of Groundwater Sampling Procedures*. National Water Well Association, 93 p.

U.S. Environmental Protection Agency. 1986. RCRA Technical Enforcement Guideline Document, OSWER-9950.1, U.S. Government Printing Office, Washington, D.C., 208 p.

U.S. Environmental Protection Agency. 1992. RCRA Ground Water Monitoring: Draft Technical Guidance Document, EPA/530-R-93-001, U.S. Government Printing Office, Washington, D.C.

U.S. Environmental Protection Agency. 1994. Proceedings of the Ground Water Sampling Workshop, Dallas, TX, December 8-10, 1993, U.S. Environmental Protection Agency, U.S. Government Printing Office, Washington, D.C.

Wiedemeier, T. H., Wilson, J. T., Kampbell, D. H., Miller, R. N., and Hansen, J. E. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural chemical attenuation for fuel contamination dissolved in groundwater. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.

Wiedemeier, T. H., Swanson, M. A., Moutoux, D. E., Gordon, E. K., Hansen, J. E., Hass, P., Wilson, J. T., Kampbell, D. H., and Chapelle, F. H. 1996. Draft protocol for evaluating natural attenuation of chlorinated solvents in groundwater. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.

Wilson, J. T. 1993. Testing bioremediation in the field. In *In Situ Bioremediation – When Does It Work?,* Committee on In-situ Bioremediation, Water Science and Technology Board National Research Council, National Academy Press, Washington, D.C., pp. 160-164.

Xie, G., Barcelona, M. J., and Fang, J. 1999. Quantification and interpretation of TPH in sediment samples by a GC-MS method and comparison with EPA 418.1 and a rapid field method. *Analytical Chemistry*, v. 71, pp. 1899-1904.

Identifying the Distribution of Terminal Electron-accepting Processes (TEAPS) in Ground-water Systems

Francis H. Chapelle, James E. Landmeyer, and Paul M. Bradley

U.S. Geological Survey
Columbia, SC 29210-7651

Introduction

The distribution of terminal electron-accepting processes (TEAPs) in ground-water systems can be assessed by documenting the availability of particular electron acceptors (oxygen, nitrate, Fe(III), sulfate), by showing the distribution of characteristic final products (Fe(II), sulfide, methane), and measuring concentrations of intermediate products (hydrogen) of microbial metabolism. When applied to a gasoline-contaminated site in South Carolina (Laurel Bay), this methodology shows that redox conditions changed continuously since the initial spill occurred in 1990. By 1994, oxygen had been depleted in the contaminated zone, and Fe(III) and sulfate-reduction were the predominant TEAPs. Methanogenesis was not measurable in 1994. By 1996, depletion of Fe(III) and sulfate resulted in the initiation of a discrete methanogenic zone in the source area. Between 1996 and 2000, this methanogenic zone progressively grew until most of the plume core was dominated by methanogenic metabolism. These dynamic spatial and temporal changes in TEAPs, which have been documented at several other sites as well, appear to be characteristic of redox processes in contaminated ground-water systems. The methodology for deducing TEAPs, which is illustrated in this paper by application to a gasoline-contaminated aquifer, is generally applicable to all ground-water systems.

Reduction-oxidation (redox) processes affect the chemical composition of ground water in all aquifer systems. In addition, ambient redox processes affect biodegradation or biotransformation rates of contaminants such as petroleum hydrocarbons, chlorinated solvents, and metals. Thus, reliable methods for characterizing redox processes are crucial to re-mediating contaminated ground-water systems. The purpose of this paper is to describe a non-equilibrium, kinetic framework for documenting the spatial and temporal distribution of microbially mediated terminal electron-accepting processes (TEAPs) in ground-water systems.

The Equilibrium Approach

The traditional approach for characterizing redox processes in ground water is based on conventions and methods developed in classical physical chemistry (Sillen, 1952). In particular, Back and Barnes (1965) used platinum electrode measurements to characterize the Eh of ground-water samples. This approach was systematized by Stumm and Morgan (1981), who suggested that the theoretical concentration of electrons in aqueous solution (pe), could be used in direct analogy to hydrogen ion concentration (pH) as a "master variable" to describe redox processes. In this treatment, the pe of a water sample is a linear function of Eh (pe = 16.9 • Eh at 25^oC).

The definition of Eh, and thus pe, is given by the Nernst equation (Equation 1), in which the Eh of a solution is related to concentrations of aqueous redox couples at chemical equilibrium and the voltage of a standard hydrogen electrode (E^o). For example, when concentrations of aqueous Fe^{3+} and Fe^{2+} are at equilibrium, Eh is defined as:

$$Eh = E^o + \frac{2.303\,RT}{nF} \log \frac{aFe^{3+}}{aFe^{2+}} \qquad (1)$$

Equation 1 illustrates an important point. Eh *is only uniquely defined when a system is at thermodynamic equilibrium* (Drever, 1982, p. 257). If the activity of Fe^{3+} and Fe^{2+} ions in Equation 1 are not at equilibrium, measured Eh (based on electrode potential) represents electrode response to all reactions active at the platinum surface, but will not be an "Eh" by the definition Equation 1.

In the 1960's and 1970's, when ground-water systems were thought to be largely sterile environments devoid of microbial life, assuming equilibrium or near-equilibrium conditions seemed to be a reasonable approach. However, in the early 1980's, it became clear that ground-water systems contained active, respiring, reproducing microorganisms (Wilson et al., 1983;

Chapelle et al., 1987). Furthermore, it gradually became clear that many of the important redox processes occurring in ground-water systems were catalyzed by microorganisms (Baedecker et al. 1988; Chapelle and Lovley, 1992; Baedecker et al., 1993). This realization coincided with growing evidence that Eh measurements of ground waters were problematic. In particular, it was shown that Eh measurements with platinum electrodes were usually not consistent with Eh's calculated from the Nernst equation using different redox couples (Lindberg and Runnels, 1984). There are several reasons for these problems. These include:

1. The actual concentrations of free electrons in water are so low ($\sim 10^{-55}$ M) that they are essentially zero (Thorstenson, 1984). Thus, while pe (and Eh) is a thermodynamically definable quantity, it is not practical to measure (as is pH).

2. The pH electrode responds to aqueous concentrations of hydrogen ions. However, the Eh electrode does not respond to aqueous concentrations of electrons, but rather to *electron transfers* between solutes (Thorstenson, 1984). A platinum Eh electrode, therefore, readily responds to concentrations of Fe^{2+} and Fe^{3+} because they react rapidly with platinum. However, because CO_2 and CH_4 react sluggishly on a platinum surface, the Eh electrode is relatively insensitive to the CO_2/CH_4 couple.

3. Microorganisms cannot actively respire and reproduce unless there is available free energy to drive their metabolism. That is, microorganisms *require that their immediate environment <u>not</u> be at thermodynamic equilibrium*. Thus, using Eh to describe redox processes driven by microbial processes violates the underlying equilibrium assumption of Eh.

In light of these difficulties, it is not surprising that Eh measurements in ground-water systems are so often problematic.

The Kinetic Approach

Equilibrium considerations are not the only way to describe redox processes. The metabolism of microorganisms is based on the cycling of electrons from electron donors (often organic carbon) to electron acceptors such as molecular oxygen, nitrate, ferric iron, sulfate, carbon dioxide, or other mineral electron acceptors. This flow of electrons is capable of doing work. Microorganisms capture this electrical energy, convert it to chemical energy, and use it to support their life

functions. If it is assumed that redox processes in ground-water systems are driven predominantly by microbial metabolism, it becomes possible to describe these processes by the cycling of electron donors, electron acceptors, and intermediate products of microbial metabolism. Because this is an inherently non-equilibrium, kinetic description, it is termed the "kinetic approach" (Lovley, Chapelle, and Woodward, 1994).

A kinetic description of redox processes in ground-water systems includes two components. These are (1) documenting the source of electrons (electron donor) that supports microbial metabolism, and (2) documenting the final sink for electrons (electron acceptors) that supports microbial metabolism. In many ground-water systems, identifying electron donors is not a difficult problem since particulate or dissolved organic carbon is the most common source of electrons for subsurface microorganisms. A more difficult problem is determining the terminal electron accepting processes (TEAPs) that occur in a system. This problem is made even more difficult by the inherent heterogeneity of ground-water systems. This heterogeneity causes both spatial (Chapelle and Lovley, 1992) and temporal (Vroblesky and Chapelle, 1994) variations in TEAPs.

This paper describes methodology for deducing the spatial and temporal distribution of TEAPs in ground-water systems. This methodology is illustrated using long-term monitoring data of a gasoline spill site in South Carolina.

Methodology for Deducing TEAPs

Microbial Competition

Studies in aquatic sediment microbiology have clearly demonstrated that microbially mediated redox processes tend to become segregated into discrete zones. When this happens, the observed sequence of redox zones follows a predicable pattern. At the sediment-water interface, oxic metabolism predominates. This oxic zone is underlain by zones dominated by nitrate reduction, manganese reduction, and ferric iron reduction (Froelich et al., 1979). In more organic rich marine sediments, it is commonly observed that a sulfate-reducing zone overlies a zone dominated by methanogenesis (Martens and Berner, 1977).

For many years, the mechanisms causing the observed segregation of redox zones were not clear. However, studies with pure cultures of methanogens and sulfate reducers (Lovley and Klug, 1983), followed by studies with aquatic sediments (Lovley and Klug, 1986;

Lovley and Goodwin, 1987), showed that redox zonation resulted from the ecology of aquatic sediments. In aquatic sediments, organic matter oxidation is carried out by food chains in which fermentative microorganisms initiate biodegradation with the production of fermentation products such as acetate and hydrogen (Figure 1). These fermentation products are then consumed by terminal electron-accepting microorganisms such as Fe(III)-reducers or sulfate reducers. Because Fe(III) reduction produces more energy per mole of acetate or hydrogen oxidation, Fe(III) reducers are able to lower environmental concentrations of these fermentation products below levels required by less efficient sulfate reducers. Thus, when Fe(III) is available, Fe(III)-reducers can outcompete sulfate reducers for available hydrogen (Figure 1), and sequester the majority (although not all) of the available electron flow. This, in turn, leads to the observed development of redox zones dominated by particular redox processes.

The principle mechanism of microbial competition is easily illustrated experimentally. If methanogenic aquatic sediments are placed in anoxic vials, with some vials amended with oxygen-free distilled water (methanogenic treatment), some amended with a 5 mM

nitrate solution (nitrate-reducing treatment), some amended with a suspension of amorphous ferric hydroxide suspension (Fe(III)-reducing treatment), and some amended with a 5 mM sulfate solution (sulfate-reducing treatment), hydrogen concentrations are observed to change over several days to different characteristic levels (Figure 2). Methanogenesis, the least efficient hydrogen-consuming TEAP, is characterized by the highest hydrogen concentrations (5-15 nM) by the end of the experiment. Sulfate reduction is characterized by hydrogen concentrations in the 1-4 nM range, Fe(III) reduction in the 0.2-0.8 nM range, and nitrate reduction having hydrogen concentrations < 0.1 nM at the end of the experiment. This leads to the tendency for discrete redox zones to develop in sediments. This overall principle, in turn, suggests a methodology for determining the distribution of redox zones in ground-water systems.

Interpreting Concentrations of Final Products and Intermediate Products

Ground-water systems are usually more complex hydrologic systems than aquatic sediments. Part of this complexity stems from the inherently heterogeneous lithologic and geochemical nature of ground-water systems (Cherry et al., 1995; Cozzarelli et al., 1999). Part
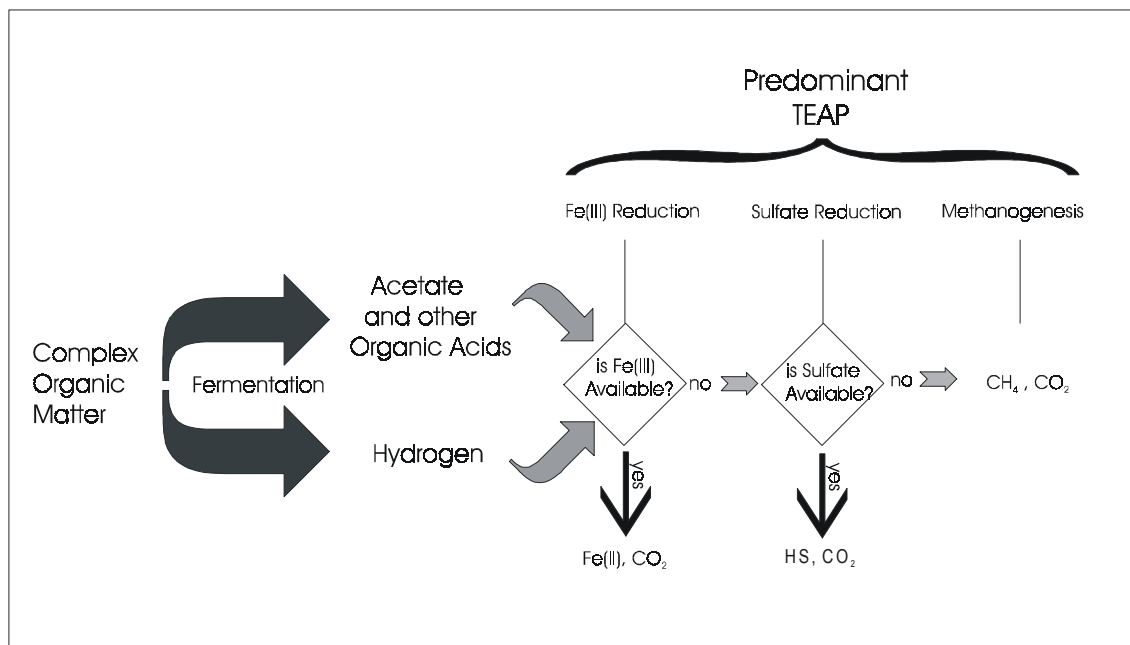
Figure 1. *Development of predominant terminal electron-accepting processes due to microbial competition for electron donors.*
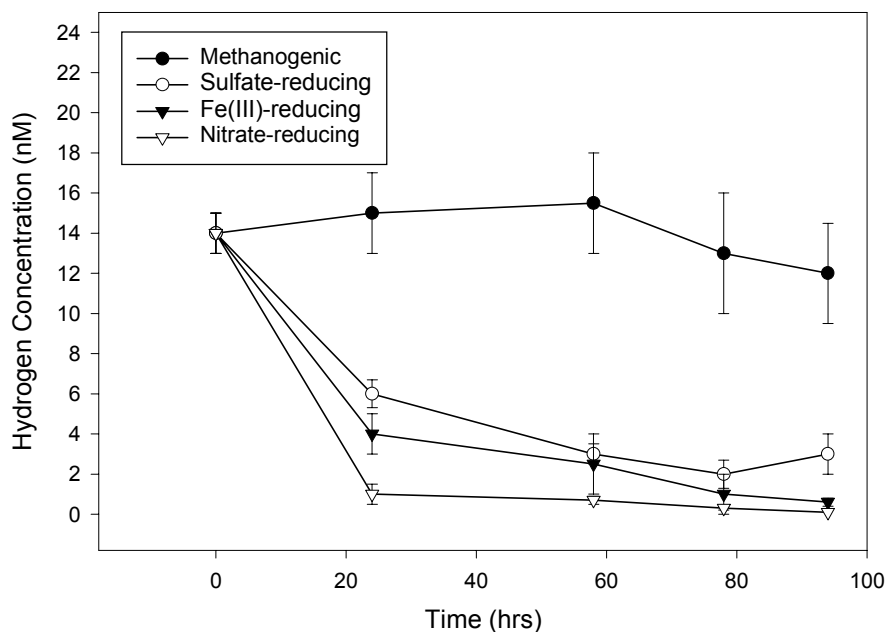
Figure 2. *Characteristic response of hydrogen concentrations to methanogenic, sulfate-reducing, Fe(III)-reducing, and nitrate-reducing conditions.*

of this complexity also stems from the predominance of advective ground-water flow as the principal solute transport mechanism, in contrast to molecular diffusion-dominated aquatic sediments. Nevertheless, because particular TEAPs require the presence of certain electron acceptors (nitrate or sulfate, for example), and because particular TEAPs produce characteristic final products (methane from methanogenesis, sulfide from sulfate reduction, Fe(II) from Fe(III) reduction), concentration trends of potential electron acceptors and final products through time and/or space can be used to deduce ongoing TEAPs. Similarly, concentrations of intermediate products such as hydrogen can provide insight into the spatial and temporal distribution of TEAPs. A schematic diagram showing the logic behind this methodology is shown in Figure 3.

If, for example, sulfate concentrations are observed to decrease with time or along a flowpath segment of a ground-water system, sulfide concentrations are observed to increase, and hydrogen concentrations are observed to be in the range characteristic of sulfate reduction, the occurrence of sulfate reduction can be identified in that portion of the aquifer with a high degree of confidence (Figure 3).

In practice, however, this methodology often encounters uncertainties. For example, if methane, sulfide, and Fe(II) concentrations are observed to increase along a flowpath segment or with time, it can be

concluded that methanogenesis, sulfate reduction, and Fe(III) reduction are ongoing (Baedecker et al., 1993). However, because methane, sulfide, and Fe(II) are actively transported by flowing ground water, it is often difficult to determine the spatial location of each redox zone. If methane is present in ground water at a particular well location, it cannot be concluded that methanogenesis is occurring in that well's screened interval. Rather, it can only be concluded that methanogenesis is occurring somewhere upgradient of that well. In these cases, concentrations of hydrogen, which is continuously cycled by microorganisms and thus not subject to significant advective transport, may more accurately identify redox zones. However, it is always possible that wells can be screened across different redox zones, leading to intermediate, non-diagnostic concentrations of hydrogen. Moreover, redox zones shift areally and temporally in response to recharge events (Vroblesky and Chapelle, 1994), the availability of organic matter, or other environmental factors. Because of this observed variability, the terminology "predominant" TEAPs, rather than "exclusive" TEAPs, is used. Under such dynamic conditions, discrete redox zones may not be well-developed. Such possible complexities must always be considered when using the methodology of Figure 3.

Redox Evolution, Laurel Bay, South Carolina

A gasoline-contaminated aquifer in Laurel Bay, South Carolina can be used to illustrate the methodology

8
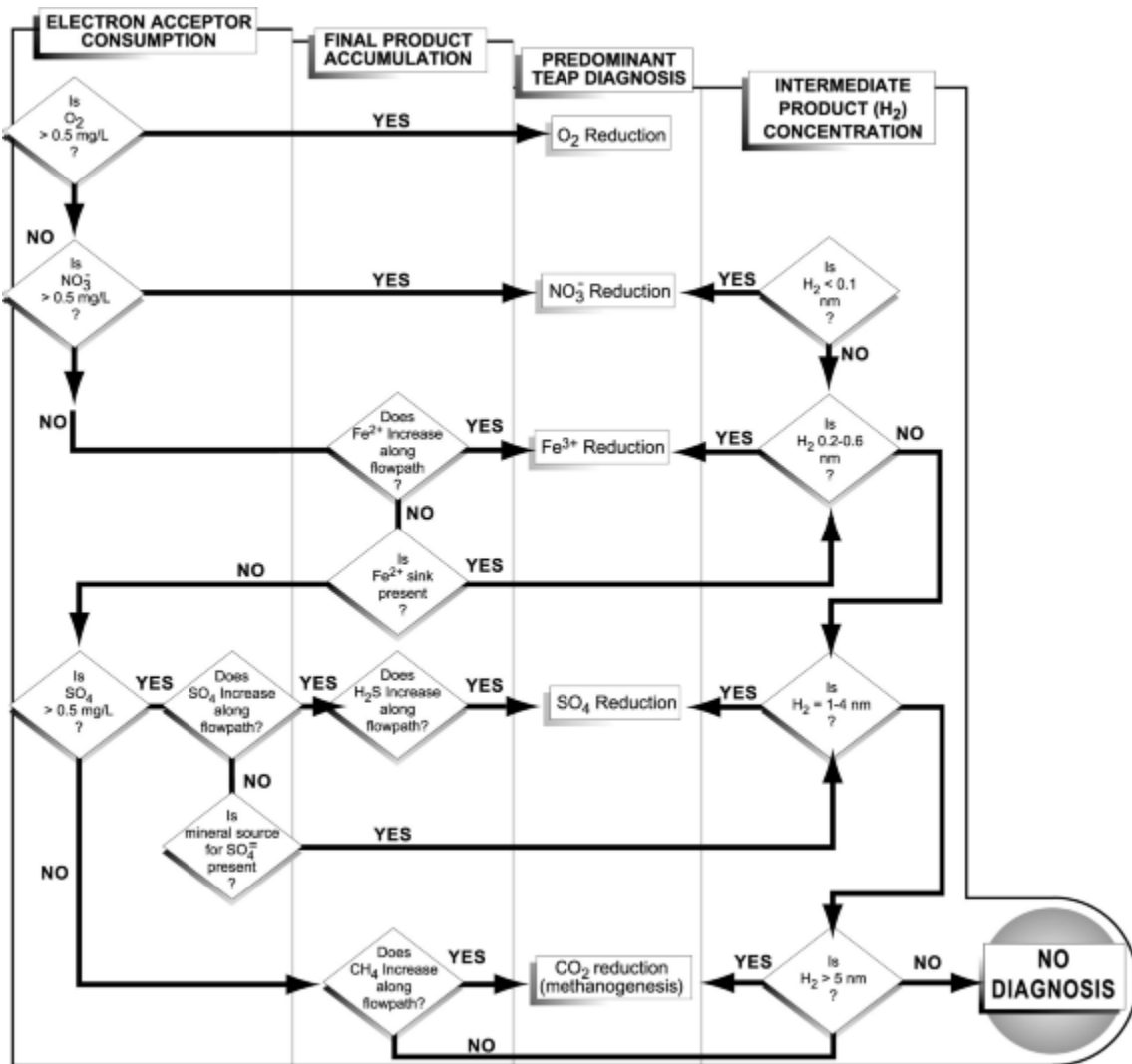
Figure 3. *Flowchart for deducing predominant terminal electron-accepting processes in ground-water systems.*

shown in Figure 3. This site has been previously described (Landmeyer et al., 1998). The aquifer consists of highly permeable and relatively homogeneous marine beach sands underlain by a clay confining bed. Gasoline leaked into the aquifer from an underground storage tank in about 1990 (Figure 4). The tank was removed in 1992, and an investigation of ground-water contamination initiated soon after. Figure 4 shows a cross section of this site along the direction of ground-water flow with the locations of monitoring wells used to delineate redox processes. Figures 5-9 show changes in redox conditions along the axis of this cross section during the time period 1994-2000.

In 1994, concentrations of benzene in the contaminant source area were in the 40 mg/L range, and

decreased downgradient (Figure 5a). Upgradient of the contaminant source area, ground water contained high concentrations of dissolved oxygen (Figure 5a) and sulfate (Figure 5c), which decreased rapidly as ground water moved into the contaminated zone. Fe(II) concentrations were low upgradient, and increased in the source area (Figure 5b). Concentrations of sulfide and methane were below detection levels (Figure 5c).

Based on the concentrations of electron acceptors (oxygen, sulfate) and metabolic products (methane, sulfide, Fe(II)), it can be deduced that Fe(III) reduction and sulfate reduction were ongoing in the source area in 1994, but that oxic metabolism predominated upgradient of the source area and downgradient of well LB-8. There was no evidence of methanogenesis in 1994.

9

Over the next several years, redox conditions changed markedly. By 1996, the anoxic zone was extending further downgradient (Figure 6a), and methanogenesis and sulfate reduction had become increasingly more prevalent processes. Concentrations of methane increased markedly (Figure 6b), and the zone of sulfate depletion which was confined to the source area in 1994 (Figure 5c), extended 200 feet downgradient in 1996 (Figure 6b). The initiation of methanogenesis in and near the source area is indicated both by the generation of methane (Figure 6b) and by the presence of hydrogen concentrations in the range characteristic of methanogenesis (Figure 6d).

This trend toward increasing importance of methanogenesis continued over time. By 1998, concentrations of dissolved oxygen were below 1 mg/L for the entire 600 foot plume (Figure 7a), concentrations of methane (Figure 7b) and sulfide (Figure 7c) continued to increase. Hydrogen concentrations were in the methanogenic range near the source area, decreased into the sulfate reducing range between 200 and 400 feet along the flowpath, and then decreased into the range characteristic of Fe(III) reduction (Figure 7d).

By January, 2000, low dissolved oxygen concentrations continued to dominate the core of the plume (Figure 8a), concentrations of methane remained relatively high (Figure 8b), sulfate concentrations remained relatively depleted (Figure 8c), and hydrogen concentrations in the range characteristic of methanogenesis extended from the source area to 400 feet downgradient.

The picture that emerges from this analysis at the Laurel Bay site using the logic of Figure 3, is that of an initially oxic aquifer (pre-1990), which became anoxic in the contaminant source area soon after the gasoline release (Figure 9). Once anoxic conditions were achieved (1994), the predominant TEAP was Fe(III) reduction with some evidence of sulfate reduction, but no evidence of methanogenesis. By 1996, the source area had become methanogenic, and this methanogenic zone gradually expanded until it reached 400 feet downgradient in 2000.

Similar evolution of redox zones in petroleum hydrocarbon-contaminated aquifers has been demonstrated previously (Baedecker et al., 1993; Cozzarelli et al., 1999), and so this overall behavior is expected. This analysis does illustrate, however, that a kinetic
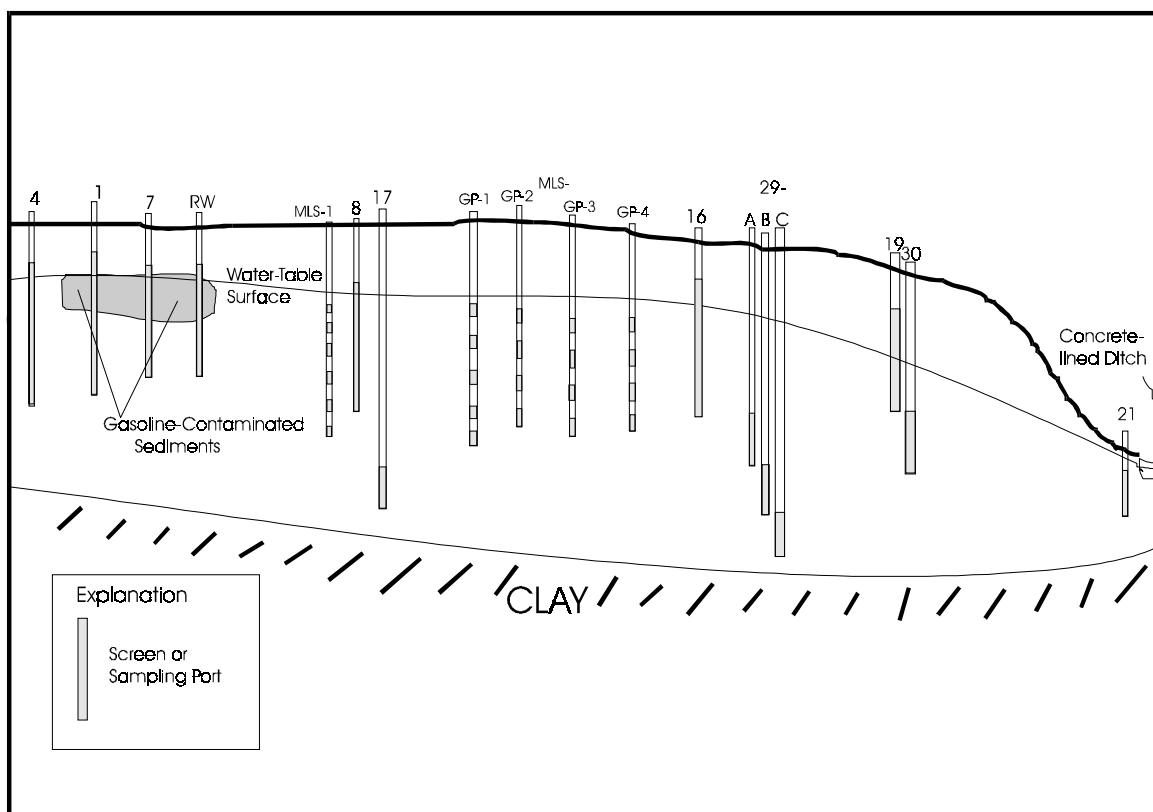
Figure 4. *Cross section showing location of contaminated zone, orientation of the contaminant plume, and locations of monitoring wells at the Laurel Bay site.*

10

March 1994
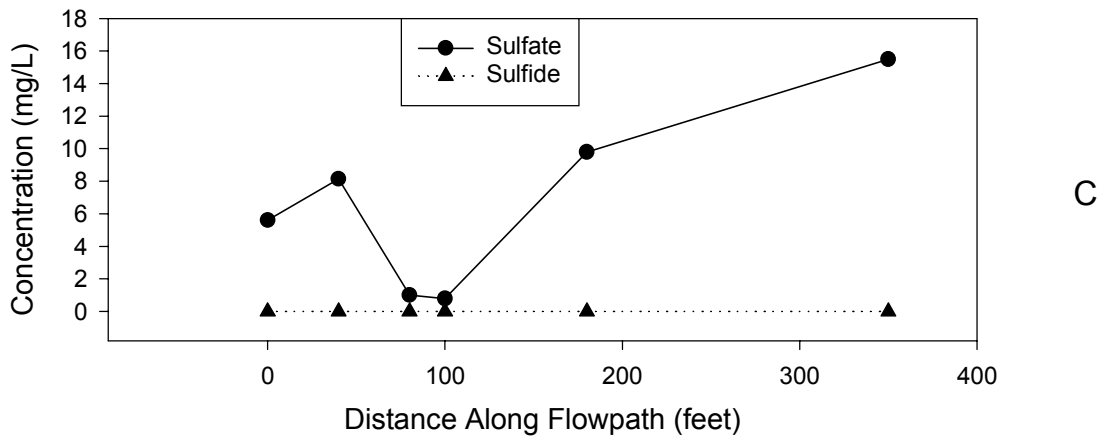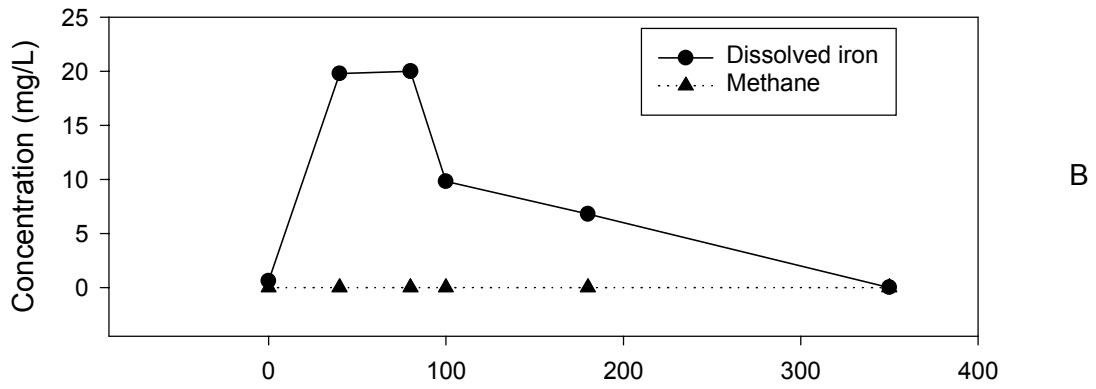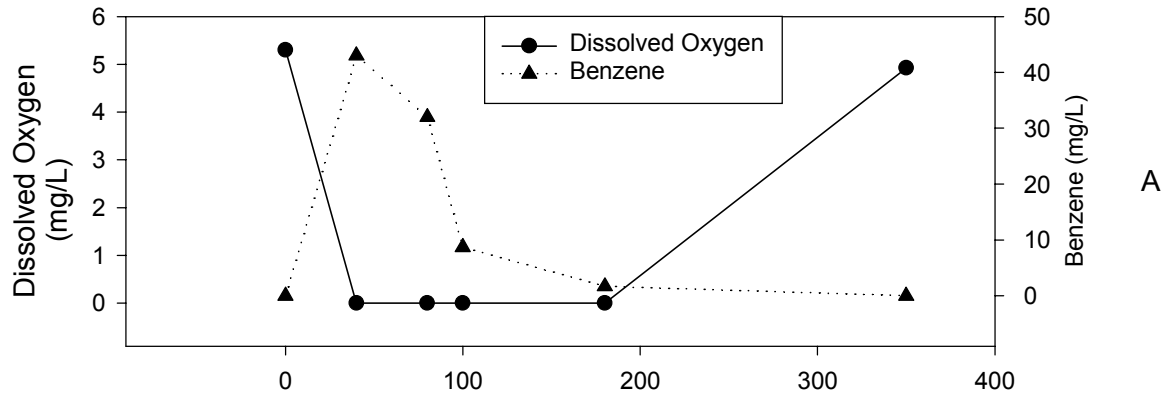
Figure 5. *Concentrations of redox-sensitive species at the Laurel Bay site, 1994.*

June 1996
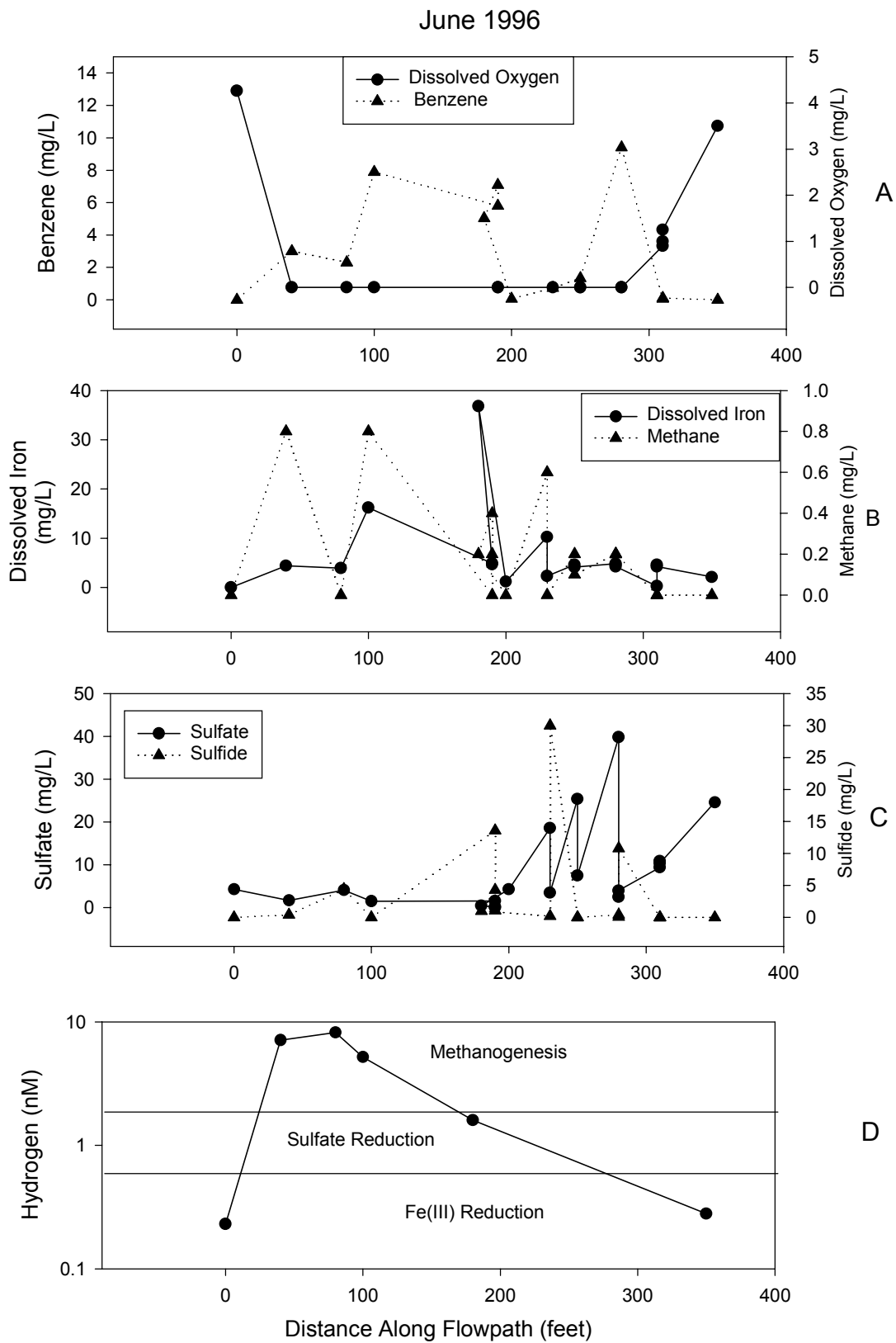
Figure 6. *Concentrations of redox-sensitive species at the Laurel Bay site, 1996.*

January, 1998
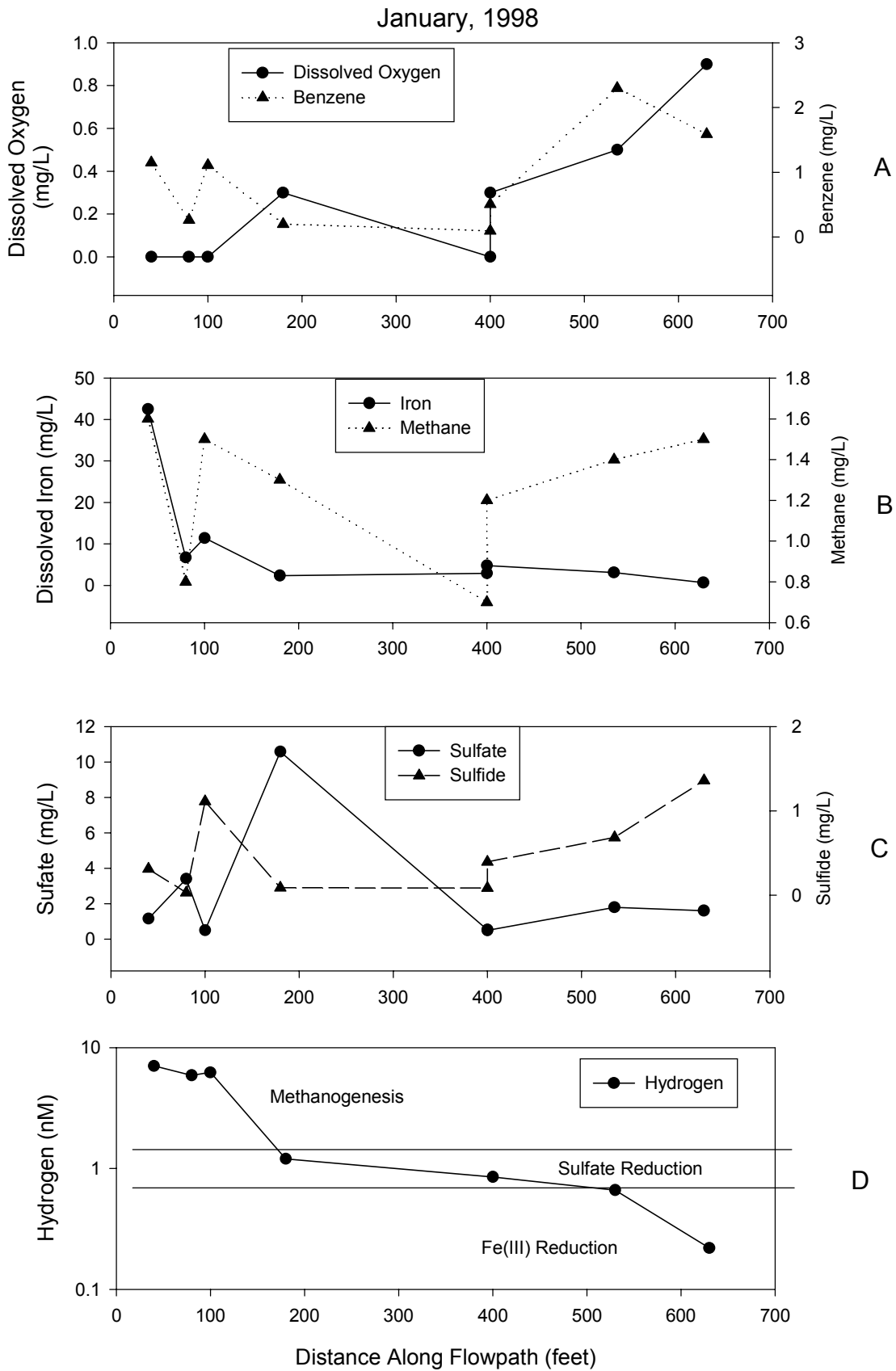
Figure 7. *Concentrations of redox-sensitive species at the Laurel Bay site, 1998.*

13

January 2000
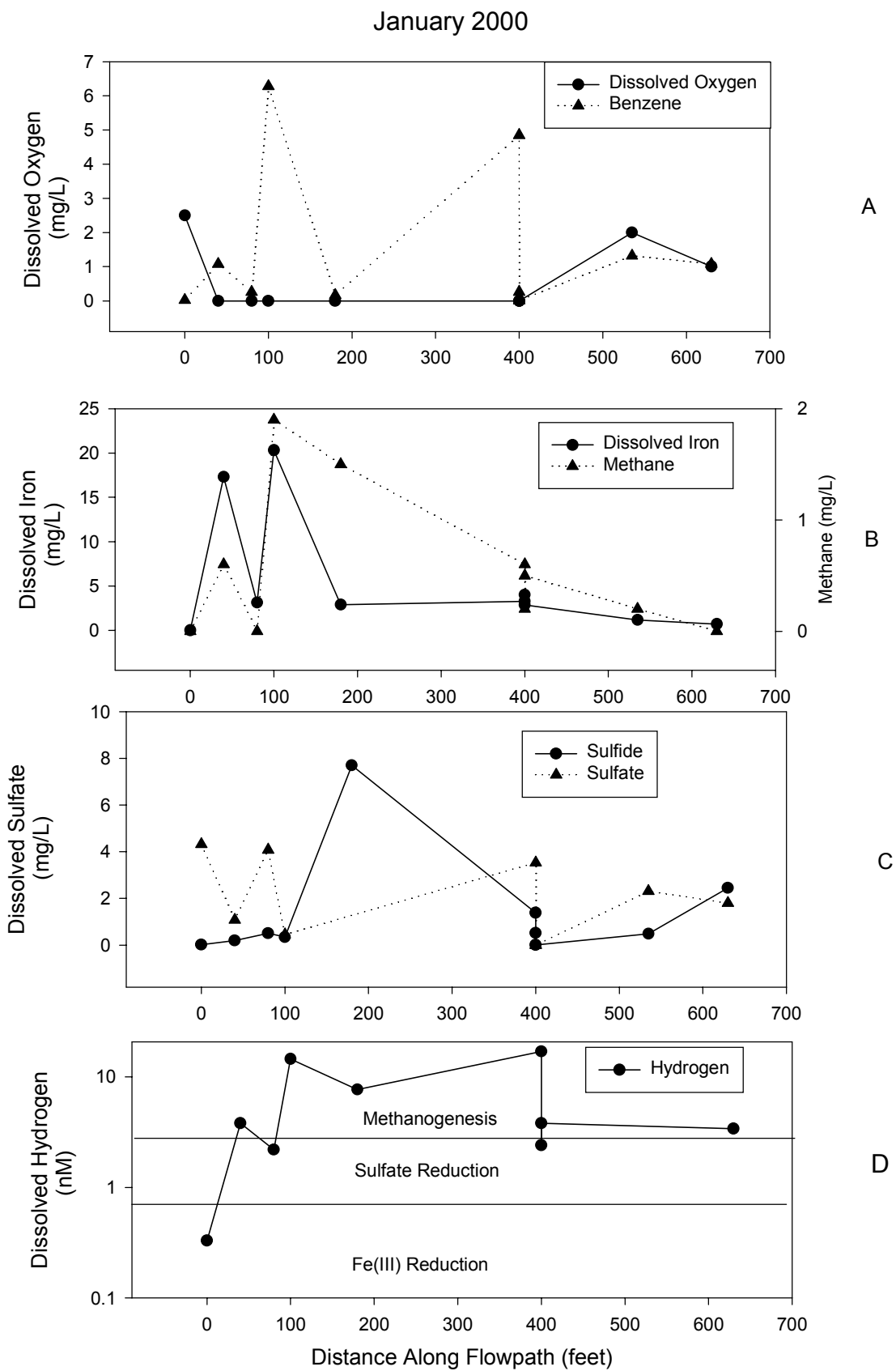
Figure 8. *Concentrations of redox-sensitive species at the Laurel Bay site, 1996.*

14

approach that considers sequential utilization of electron acceptors, production of final products, and concentrations of intermediate products can lead to an accurate evaluation of redox processes in ground-water systems.

Conclusions

The spatial and temporal distribution of redox conditions in ground-water systems are complex, even at relatively simple sites. For example, the Laurel Bay site is a relatively homogeneous aquifer, but the development of discrete redox zones occurred gradually over many years and involved considerable spatial variability. Nevertheless, the data show that the overall evolution of redox processes follows certain predictable patterns. Available electron acceptors at this site were consumed in the order $(O_2 > Fe(III) > SO_4 > CO_2)$ with methanogenesis (CO_2 reduction) occurring only after other available electron acceptors were exhausted. This is consistent with the model (Figure 2) of sequential electron-acceptor utilization, and the principle of microbial competition for available electron donors.
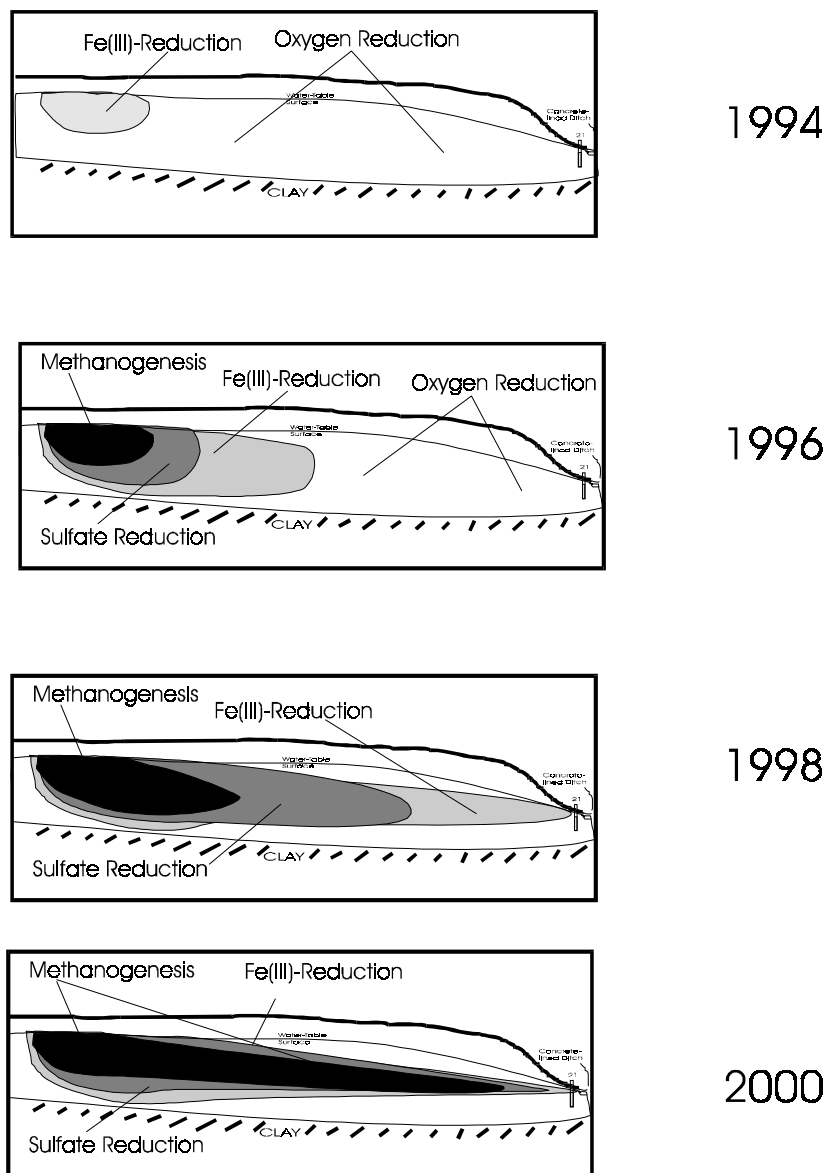
Figure 9. *Schematic diagram showing the evolution of redox zones at the Laurel Bay site, 1994-2000.*

15

The data clearly show, however, that the development of these redox zones is accompanied by considerable heterogeneity. For example, in 1996 concentrations of sulfate and sulfide were highly variable at the interface between low-sulfate ground water adjacent to the contaminant source area (Figure 6c), and high-sulfate ground water downgradient of this interface. Clearly, the shift between Fe(III) reduction to sulfate reduction involved interfingering, poorly defined redox zones. The development of these spatially complex zones probably depends on many factors including variations in contaminant concentrations, hydraulic conductivity, Fe(III) content of aquifer sediments, and sulfate concentrations.

In spite of this complexity, it is possible to document the distribution of redox processes in ground-water systems in both time and space using a kinetic approach based on well-known principles of microbial ecology (Figures 2 & 3). This kinetic approach provides a much better resolution of ongoing microbial processes than is afforded by traditional equilibrium approaches (Eh or pe) to redox processes. This, in turn, makes it possible to make more precise predictions concerning the fate and mobility of redox-sensitive contaminants in ground-water systems.

References

Back, W. and Barnes, I. 1965. Relation of electrochemical potentials and iron content to ground-water flow patterns. U.S. Geological Survey Professional Paper 498-C.

Baedecker, M. J., Siegel, D. L., Bennett, P. C., and Cozzarelli, I. M. 1988. The fate and effects of crude oil in a shallow aquifer:1. The distribution of chemical species and geochemical facies. In *U.S. Geological Survey Toxic Substances Hydrology Program Review*, eds. G. E. Mallard and S. E. Ragone, U.S. Geological Survey Water-Resources Investigations Report 88-4220, pp. 13-20.

Baedecker, M. J., Cozzarelli, I. M., Eganhouse, R. P., Siegel, D. I., and Bennett, P. C. 1993. Crude oil in a shallow sand and gravel aquifer, III. Biogeochemical reactions and mass balance modeling in anoxic ground water. *Applied Geochemistry*, v. 8, pp. 569-586.

Chapelle, F. H., Zelibor, J. L., Grimes, D. J., and Knobel, L. L. 1987. Bacteria in deep coastal plain sediments of Maryland: A possible source of CO_2 to ground water. *Water Resources Research*, v. 23, pp. 1625-1632.

Chapelle, F. H., and Lovley, D. R. 1992. Competitive exclusion of sulfate-reduction by Fe(Ill)-reducing bacteria: A mechanism for producing discrete zones of high-iron ground water. *Ground Water*, v. 30, pp. 29-36.

Chapelle, F. H., McMahon, P. B., Dubrovsky, N. M., Fujii, R. F., Oaksford, E. T., and Vroblesky, D. A. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse ground-water systems. *Water Resources Research*, v. 31, pp. 359-371.

Cherry, J. A., Barker, J. F., Feenstra, S., Gillham, R. W., Mackay, D. M., and Smyth, D. J. A. 1995. The Borden site for groundwater contamination experiments: 1978-1995. In *Groundwater and Subsurface Remediation: Research Strategies for In-situ Remediation*, eds. H. Kolbus, B. Barczewski, and H. P. Kosschitzky, Springer-Verlag, Berlin, pp.102-127.

Cozzarelli, I. M., Herman, J. S., Baedecker, M. J., and Fischer, J. M. 1999. Geochemical heterogeneity of a gasoline-contaminated aquifer. *Journal of Contaminant Hydrology*, v. 40, pp. 261-284.

Drever, J. I. 1982. *The Geochemistry of Natural Waters*. Prentice Hall, Englewood Cliffs, New Jersey, 388 p.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., and Dauphin, P. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta*, v. 43, pp. 1075-1090.

Landmeyer, J. E., Chapelle, F. H., Bradley, P. M., Pankow, J. F., Church, C. D., and Tratnyek, P. G. 1998. Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993-98). *Ground Water Monitoring and Remediation*, v. 18, pp. 93-102.

Lindberg, R. D. and Runnells, D. D. 1984. Ground-water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science*, v. 225, pp. 925-927.

Lovley, D. R. and Klug, M. J. 1983. Sulfate reducers can outcompete methanogens at fresh water sulfate concentrations. *Applied and Environmental Microbiology*, v. 45, pp. 187-192.

Lovley, D. R., and M. J. Klug. 1986. Model for the distribution of methane production and sulfate reduction in freshwater sediments. *Geochimica et Cosmochimica Acta*, v. 50, pp. 11-18.

Lovley, D. R. and Goodwin, S. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochimica et Cosmochimica Acta*, v. 52, pp. 2993-3003.

Hydrogen Measurements and Redox Dynamics in Ground-water Systems

Don A. Vroblesky and Francis H. Chapelle

U.S. Geological Survey
Columbia, South Carolina 29210-7651

The use of hydrogen, a transient intermediate product of anaerobic microbial metabolism, as an indicator of predominant terminal electron accepting processes (TEAPs) was introduced by Lovley and Goodwin (1988). The standard method used for measuring H_2 in ground water is a gas-stripping procedure that has previously been referred to as the "bubble strip" method (Vroblesky and Chapelle, 1994; Chapelle and McMahon, 1991; Chapelle et al., 1995). In this method, a standard 250 ml gas sampling bulb (Supelco) is continuously purged with ground water at a rate of about 500 mL/min. A 20-mL bubble of H_2-free N_2 gas is introduced into the sampling bulb through the septum. As the bubble is vigorously agitated by the stream of inflowing water, slightly soluble gases such as H_2 are stripped from the water to the gas phase over time, and asymptotically come into equilibrium with the water flowing through the bulb. After equilibrium is achieved (~20-30 min), a gas sample is withdrawn from the bulb by using glass syringes with stopcocks and analyzed for H_2. Analysis is done using gas chromatography with reduction gas detection (Trace Analytical, Menlo Park, California). Other methods that have been used to collect H_2 from ground water include a down-hole sampler, and a diffusion sampler (Chapelle et al., 1997).

Measurement of H_2 using the gas-stripping method can be affected by a variety of factors. A field investigation showed that one factor affecting the H_2 concentration is the type of pumping equipment. Four different methods for pumping ground water were evaluated. These were (1) a peristaltic pump (Geotech Environmental Equipment, Inc., Denver, Colorado), (2) a stainless steel piston pump (Bennet Sample Pumps, Inc., Amarillo, Texas), (3) a bladder pump (Well Wizard Bladder Pump, QED Environmental Systems, Ann Arbor, Michigan), and (4) a stainless steel submersible pump (MP-1, Grundfos Pumps, Corp., Clovis, California). The peristaltic pump draws water under negative pressure, the piston and bladder pumps push water under positive pressure, and the Grundfos pump pushes water under positive pressure by impellers driven by a Direct Current (DC) electrical motor.

The various pumps found that peristaltic, piston, and bladder pumps all gave similar results when applied to water produced from the same well (Chapelle et al., 1997). It was observed, however, that peristaltic-pumped water (which draws water under a negative pressure) enhanced the gas-stripping process and equilibrated slightly faster (~20 min) than either piston (~25 min) or bladder pumps (~30 min), which push water under a positive pressure (Figure 1A).

The direct current-driven submersible pump gave much higher H_2 concentrations than the other pumps. Because H_2 can be electrolytically produced by direct current, it is probable the high H_2 concentrations observed using this submersible pump reflect the interaction of direct current with water. Thus, direct current submersible pumps appear to not be suitable for measuring H_2 in ground water (Chapelle et al., 1997).

When the peristaltic pumping rate was increased from 500 to 1,000 mL/min, equilibration was achieved in proportionally less time (Figure 1B). These observations indicate that equilibration times, and thus the accuracy and reproducibility of the gas-stripping method, can vary depending on pumping methods and rates. These results indicate that specific combinations of pumping systems and rates should be individually tested to evaluate the length of time needed for gas-aqueous phase equilibration.

Measurements from two field sites indicate that iron or steel well casings produce H_2 ,which masks H_2 concentrations in ground water. PVC-cased wells, or wells cased with other materials that do not produce H_2, are necessary for measuring H_2 concentrations in ground water (Chapelle et al., 1997).

Measurements of the dissolved H_2 and other biologically active solutes in ground water from a shallow
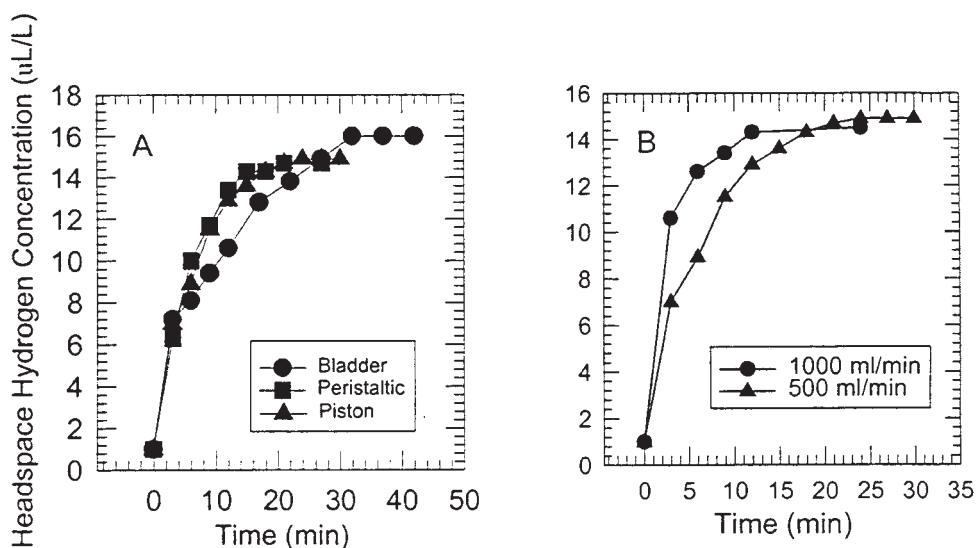
Figure 1. *(A) Comparison of equlibration time of the gas-stripping procedure using the bladder, piston, and peristaltic pumps, and (B) the influence of flow rate on equilibration times for the peristaltic pump (modified from Chapelle et al., 1997).*

petroleum hydrocarbon-contaminated aquifer indicate that the distribution of TEAPs is highly dynamic in time and space (Vroblesky and Chapelle, 1994). During times when little or no sulfate or oxygen is introduced to the ground water by recharge from rainfall or alternate sources, the available oxygen, Fe(III), and sulfate can be depleted by respiring bacteria, leaving methanogenesis as the predominant TEAP. Introduction of oxygen from rainfall infiltration into the methanogenic parts of the aquifer can cause precipitation of Fe(III) as grain coatings. Once the oxygen is depleted, Fe(III)-reducing bacteria can take advantage of the precipitated Fe(III) to sequester most of the electron flow from degradation of organic compounds. Introduction of sulfate into a methanogenic part of the aquifer can cause the predominant TEAP to shift to sulfate reduction. The shift from methanogenesis to sulfate reduction was observed to range from <10 days to about 3½ months, depending on the sulfate and organic carbon concentrations.

References

Chapelle, F. H., Vroblesky, D. A., Woodward, J. C., and Lovely, D. R. 1997. Practical considerations for measuring hydrogen concentrations in groundwater. *Environmental Science and Technology*, v. 31, pp. 2873-2877.

Chapelle, F. H., McMahon, P. B., Dubrovsky, N. M., Fujii, R. F., Oaksford, E. T., and Vroblesky, D. A. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse ground-water systems. *Water Resources Research*, v. 31, pp. 359-371.

Chapelle, F. H. and McMahon, P. B. 1991. Geochemistry of dissolved inorganic carbon in a coastal plain aquifer: Sulfate from confining beds as an oxidant in microbial CO_2 production. *Journal of Hydrology*, v. 127, pp. 85-108.

Lovley, D. R. and Goodwin, S. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochimica et Cosmochimica Acta*, v. 52, pp. 2993-3003.

Vroblesky, D. A. and Chapelle, F. H. 1994. Temporal and spatial changes of terminal-accepting processes in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation. *Water Resources Research*, v. 30, pp. 1561-1570.

Geochemical Equilibrium and the Interpretation of E_H

John C. Westall

Oregon State University
Corvallis OR 97331

Among the most important factors controlling the persistence, mobility, and biological effects of many organic and inorganic pollutants are oxidation-reduction (redox) transformations. For example, it is known that dehalogenation of aromatic compounds occurs most readily under anoxic conditions, while ring cleavage and conversion to CO_2 occurs most readily under oxic conditions. In design of in-situ remediation, control of microbial metabolism through the proper balance between carbon substrate and the terminal electron acceptor is critical in obtaining the desired transformation of an organic contaminant. In general, degradation rates and pathways of organic compounds are known to depend strongly on ambient redox conditions. Among inorganic chemicals, speciation, and hence transport and biological effects, depends strongly on redox reactions. For example, Cr(VI) is generally mobile and toxic, while Cr(III) is insoluble, immobile, and relatively nontoxic.

Thus, a clear understanding of the redox state and speciation of chemicals is required in virtually all aspects of hazardous materials management: evaluation of disposal options, risk assessments for contaminated sites, evaluation of clean-up options, and performance assessment. Thus, it is useful to recast the issue of "Geochemical Equilibrium and the Interpretation of E_H" in terms of the broader underlying questions, (i) what is the redox state of an environment?, and (ii) does a particular contaminant undergo a redox transformation under these conditions?

The Problem

All too often the problem of characterizing the redox state of an environment is approached in the following manner: (i) measure the apparent redox potential with a Pt electrode; (ii) calculate an equilibrium distribution of the pollutant from the measured redox potential and pH; (iii) remark in disgust that the calculated distribution does not match the observed distribution, that the Pt electrode does not really work for this application, and that the system is probably not at equilibrium anyway.

The pitfalls of redox potential measurements in the environment have been well documented (Morris and Stumm, 1967; Whitfield, 1974; Lindberg and Runnells, 1984): low redox buffer capacity of the aqueous phase, slow kinetics among the environmental redox reactions, and slow kinetics of the electrode itself. Still, Pt electrodes continue to be used, and in spite of these problems, appear to give useful data under some circumstances, as will be discussed.

Alternatives to the Pt-electrode include (i) direct determination of concentrations of all significant redox-active species in water samples; (ii) redox titrations of aquifer materials to determine an effective differential or integral "redox-capacity;" and (iii) active control of redox conditions in laboratory "redox-stats."

Stumm (1984) advances the concept of determining the concentrations of major redox active species as a means of characterizing the redox status of an environment. Frevert (1984) used commercially available metal and O_2 electrodes and a feedback system to attempt to control the redox status of a system. Although he considered slow kinetics of redox reactions in his study, he concluded that it is impractical to characterize the redox status of a sediment-water system in terms of a single parameter. Related work on redox capacities was carried out by Whitfield (1972), who investigated the voltammetric properties of sediment-water systems.

In summary, if one chooses to advance the argument that it is impossible to characterize the redox status of a natural system, there is certainly evidence to support the argument. On the other hand, if one recognizes that redox transformations are extremely important in transport of many elements and in degradation of many organic compounds, that some redox reactions are coupled, and that additional information on characterizing the redox status of the environment would be helpful, then there is evidence that much insight could be gained from further experimentation.

Approach to Characterizing the Redox Status

Our general conceptual approach to characterization of redox transformations of contaminants in the subsurface environment involves interactions along the three legs of a triangle, at the apices of which are: (i) the geochemical matrix, (ii) the redox sensor, and (iii) the redox-active contaminant. Coupling of redox processes must be understood at two different linkages: contaminant and matrix, and sensor and matrix. The contaminant-matrix linkage must be investigated on a species-by-species basis, without the a priori assumption of equilibrium.

The Geochemical Matrix

The "geochemical matrix" drives the redox trans-formations. One way to approach redox conditions in aquifers is to consider major oxidant and reductant species. In some regards, these species can be considered "redox poising" species.

O_2 - In the presence of significant concentrations of O_2, experimental E_H values (Pt electrode vs SHE) are relatively high (300 - 400 mV).

$MnO_2(s)/Mn(II)$ - Mn(III) and Mn(IV) oxide/hydroxide minerals are present in some aquifers; equilibrium potentials of this couple are relatively high, about 500-650 mV at pH 7, although appearance of Mn(II) is observed at lower potentials (200 to 300 mV).

$Fe(OH)_3(s)/Fe(II)$ - Fe(III) oxide/hydroxide minerals are found in many near surface aquifers. Iron is about ten times more abundant than manganese, and is therefore important in poising redox potential. Fe(III) is a considerably weaker oxidant than either O_2 or $MnO_2(s)$. The equilibrium redox potential is about 100-200 mV at pH 7.

$SO_4^{2-}/S^0/S^{2-}$ - The sulfur system is the most important inorganic system poising redox potentials in reducing conditions (E_H -100 to -300 mV).

Organic compounds are the ultimate reductants in natural systems and have a major role in defining redox conditions.

The Redox Sensor

To answer the underlying question, "will the contaminant undergo a redox transformation under the prevailing environmental conditions," the ideal sensor would obviously be based on the sensor itself. For example, if the contaminant could be either (i) immobilized on a suitable electrochemical or spectrochemical transducer, or (ii) injected, withdrawn, and chemically detected in a push-pull test, then one would have directly the information on the extent of conversion. As an alternative to the contaminant itself, redox indicators have been immobilized to form such redox sensors (Lemmon et al., 1996).

As surrogates for this direct information one can determine the concentration of chemical species that reflect the redox status of the environment. In environments with significant amounts of organic carbon and microbial activity, the redox status is probably best defined by the *terminal electron acceptor* for degradation of organic carbon (e.g., O_2, Mn(IV), NO_3^-, Fe(III), SO_4^{2-}, CO_2, H_2, etc.). Microbial degradation of organic compounds is generally most closely linked to this measure of redox status. Over the last several years Lovley, Chapelle and coworkers have advanced the idea that $H_2(g)$ is the best indicator of the metabolic state of a subsurface microbial system (Lovley et al., 1988, 1994; Chapelle et al., 1996); hence $H_2(g)$ could be the best indicator of the likelihood that a contaminant will undergo a redox transformation, particularly under reducing conditions. In environments in which transport processes are rapid compared to redox processes, the presence, absence, or concentration of a particular species may not alone be sufficient to indicate the primary terminal electron acceptor and the redox status of the environment. Therefore, rates of redox processes relative to rates of transport processes are important ancillary information.

From a practical point of view, the availability of facilities, personnel, and time for chemical analysis are important. If a method is impractical, it will not be used, even though it might give the best answer. If a simple method (e.g., Pt electrode) gives the same information as a more complex method (e.g. complete chemical analysis), is there any need for the complete chemical analysis? Associated with the use of the Pt electrode are an array of questions that ultimately determine its utility: What sorts of species poise the Pt electrode at each of the major terminal electron acceptor steps in a biologically active medium (e.g., O_2, Mn(IV), NO_3^-, Fe(III), SO_4^{2-}, CO_2, H_2 etc.)? What is the exchange current density, i.e., how well is the electrode poised (Bard and Faulkner, 1980)? Does it vary dramatically with redox level? What role is played by "mediators", i.e., soluble molecules that shuttle between particle surfaces and the electrode surface? Does the performance depend strongly on whether or not the electrode is in direct contact with the particles?

Contrary to what one may be led to believe by a superficial review of the literature, the Pt electrode can be of value in determining environmental redox

conditions. Data from experiments of Patrick and co-workers (e.g., Masscheleyn et al., 1990, 1992) show that redox transformations of inorganic species, and appearance and disappearance of terminal electron accepting species track very well Pt electrode potentials. This discussion is not to advance the argument that the Pt electrode even approaches an ideal indicator for environmental redox reactions, but just to say that its performance warrants serious consideration.

A complicating factor in almost all of the methods is that the majority of redox buffer capacity in the subsurface environment is associated with biotic, biogenic or mineral particles, not with the aqueous solution. Then one of the major issues in understanding redox transformations of environmental contaminants is the distinction between transformations that occur directly at particles (biotic or abiotic) vs. transformations that occur in solution, presumably via "mediator molecules" that conduct between the particle surfaces and the contaminant being transformed. This issue is important not only in characterizing transformations of contaminants, but also in how sensors work. Particle-free media are much more amenable to chemical analysis such as spectrophotometry, cyclic voltammetry, etc.

A further complication is the apparent redox "disequilibria" observed in many subsurface environments. These conditions arise when transport kinetics are rapid compared to reaction kinetics. Associated with this observation is the question, how do each of the various "redox sensor technologies" described above track these changes?

Summary

In assessing the redox status of the subsurface environment, it is important to pose the right question. Previous work has indicated that the question, "what is the E_H or $p\epsilon$ of a particular environment?" is not optimal; a better approach is to pose the question, "will a certain redox transformation take place under a certain set of conditions, and how can this set of conditions best be recognized?" Judging performance of redox sensors on this criterion may lead to the best decision.

References

Bard, A. J. and Faulkner, L. R. 1980. *Electrochemical Methods.* Wiley, New York, pp. 391 398.

Chapelle, F. H, Hack, S. K., Adriens, P., Henry, M. A., and Bradley, P. M. 1996. Comparison of E_H and H_2 Measurements for delineating redox processes in a contaminated aquifer. *Environmental Science and Technology*, v. 30, pp. 3565-3569.

Frevert, T. 1984. Can the redox conditions in natural waters be predicted by a single parameter? *Schweizerische Zeitschrift Fur Hydrologie*, v. 46, pp. 269 290.

Lemmon, T. L., Westall, J. C., and Ingle, J. D., Jr. 1996. Development of redox sensors for environmental applications based on immobilized redox indicators. *Analytical Chemistry*, v. 68, pp. 947-953.

Lindberg, R. D. and Runnells, D. D. 1984. Groundwater redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modelling. *Science*, v. 225, pp. 925-927.

Lovley, D. R. and Goodwin, S. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochimica et Cosmochimica Acta*, v. 52, pp. 2993-3003.

Lovley, D. R., Chapelle, F. H., and Woodward, J. C. 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environmental Science and Technology*, v. 28, pp.1205-1210.

Masscheleyn, P. H., DeLaune, R. D., and Patrick, W. H., Jr. 1990. Transformations of selenium as affected by sediment oxidation-reduction potential and pH. *Environmental Science and Technology*, v. 24, pp. 91-96.

Masscheleyn, P. H., Pardue, J. H., DeLaune, R. D., and Patrick, W. H., Jr. 1992. Chromium redox chemistry in a lower Mississippi bottomland hardwood wetland. *Environmental Science and Technology*, v. 26, pp. 1217-1226.

Morris, J. C. and W. Stumm. 1967. Redox equilibria and measurements of potentials in the aquatic environment. In *Equilibrium Concepts in Natural Water Systems*, ed. W. Stumm, Advances in Chemistry Series No. 67, American Chemical Society, Washington, D.C., pp. 270-285.

Stumm, W. 1984. Interpretation and measurement of redox intensity in natural waters. *Schweizerische Zeitschrift Fur Hydrologie*, v. 46, pp. 291-296.

Whitfield, M. 1972. The electrochemical characteristics of natural redox cells. *Limnology and Oceanography*, v. 17, pp. 383-393.

Whitfield, M. 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnology and Oceanography*, v. 19, pp. 857-865.

Abiotic Aquatic Redox Chemistry near the Oxic/Anoxic Boundary

Donald L. Macalady

Colorado School of Mines
Golden, CO 80401

Considerations of ground water oxidation/reduction chemistry are often predicated on chemical measurements designed to determine the "redox state" of the system under investigation. There has been a long-standing tendency to seek one or more universal parameters that will serve as uniformly applicable indicators of the redox-state of any ground-water system. The desired outcome is a set of measured characteristics that enable prediction of redox *processes*. There is abundant literature to document that such a universal mechanism for prediction of redox processes is not forthcoming (see for example Lyman et al., 1987 and references therein).

For any measured set of activities of the constituent chemicals of a redox couple, there is a corresponding Nernstian electrochemical potential. The disturbing fact relative to the chemistry of natural waters is that parallel determinations of electrochemical potentials calculated from different redox couples in the same water sample often imply distinctly different redox conditions (White et al., 1990; Walton-Day et al., 1990). These and other studies imply that the lack of a definable "redox state" of an aquatic system, is a consequence of the lack of thermodynamic equilibrium among the components of the system.

This condition is particularly prevalent in a class of systems that is especially important in considerations of contaminant transformations in ground water. By this is meant those ground-water systems that are substantially depleted in dissolved oxygen (DO). The most commonly used methods of analyses for DO have detection limits greater than 2 μmolar, a concentration much greater than the detection limits for most other redox-active species in natural and contaminated ground waters.

Several examples from the literature will confirm that many ground waters in the regime between truly anoxic and 2 μmolar DO are characterized by pronounced spatial and/or temporal disequilibria (Peiffer et al., 1999; Walton-Day et al., 1990; Walton-Day, 1991; Eary and Schramke, 1990). In these systems, both electrode measurements of Eh and determinations of specific redox-active species such as ferrous iron are likely to erroneously imply extremely low oxygen partial pressures.

A seldom-used colorimetric method is described that uses a proprietary redox-sensitive dye and allows accurate detection of DO levels as low as 0.2 μmolar. Use of this technique illustrates the importance of this low oxygen tension regime as far as comprehensive understandings of ground-water redox conditions are concerned. Detectable DO in waters containing measurable ferrous iron and sulfide, for example, is not uncommon. Eh measurements in such systems typically imply oxygen partial pressures 10-20 orders of magnitude lower than measured values (White et al., 1990).

In other words, redox disequilibrium is perhaps most commonplace in the types of ground-water systems most relevant to considerations of contaminant transformation. Furthermore, the causes of such disequilibria can commonly be the presence or absence of precisely those chemical or biological processes that are most important in considerations of the rates and mechanisms of contaminant transformations.

Many of these disequilibria are "intentionally" maintained by the selective mediation of electron transfer processes by microbial systems. Thus, sulfate/sulfide ratios in systems containing active sulfate reducing bacterial populations may represent Nernstian potentials vastly different from those calculated from "abiotic" couples present in the same system. There is little evidence for any universal electron transfer mediator that rapidly reacts to assure redox equilibria among the many redox active species in a natural or contaminated ground-water system.

Perhaps the closest approach to this notion of a "universal" electron transfer mediator is the complex mixture of substances commonly called natural organic matter (NOM). NOM in both the dissolved and particulate phases of ground-water systems is capable of mediating

a wide range of electron transfer processes. NOM in this context refers to the suite of extracellular organic chemicals present in any natural water system. The components of NOM can vary from molecules recently excreted by active microorganisms to facilitate electron transfer process of utility to the microbial community to "abiotic" degradation products from the debris of long inactive living systems. The ability to mediate electron transfer processes seems to be ubiquitous among NOM samples (Macalady and Ranville, 1998; Tratnyek and Macalady, 2000).

NOM has been shown to be an effective mediator of electron transfer in a wide variety of redox processes. Included are the reduction of nitroaromatic compounds, azo compounds, halogenated organic chemicals, metals and metal/organic complexes (see for example, Macalady and Ranville, 1998; Larson and Weber, 1994; Curtis and Reinhard, 1994; Wolfe et al., 1986; Wittbrodt and Palmer, 1996; Skogerbee, 1981; Matthiessen, 1996). NOM can also serve as an electron transfer mediator in microbial processes, e.g. the microbial reduction of solid iron (III) oxyhydroxides (Lovley et al., 1996). The role of NOM in mediating the transfer of electrons in the opposite direction has received less attention, but the oxidation of sulfide and ferrous iron is clearly enhanced in the presence of oxidized NOM. In fact, one of the few redox processes that is apparently not mediated by NOM is the reduction of molecular oxygen (Peiffer, unpublished data).

The mechanism(s) by which NOM facilitates electron transfer processes is only partially understood. Clearly quinone-like functional groups within NOM structures are an important part of this reactivity. However, in certain pH ranges, other functional groups may be important (Dunnivant et al., 1992; Perlinger et al., 1996; Schwarzenbach et al., 1990; Gantzer and Wackett 1991; Schindler et al., 1976).

Attempts to determine the role of NOM in specific ground-water redox processes are related to both the solution phase and particulate NOM fractions in the aquifer matrix. The potential roles of NOM include direct participation as an electron transfer mediator and an indirect role as a transport inhibitor (particulate NOM) or facilitator (dissolved and/or colloidal NOM). Specific examples of such processes serve to illustrate the importance of NOM in such considerations.

References

Curtis, G. P. and Reinhard, M., 1994. Reductive dehalogenation of hexachlorethane, carbon tetrachloride, and bromoform by anthrahydroquinone disulfonate and humic acid. *Environmental Science and Technology*, v. 28, pp. 2393-2401.

Dunnivant, F. M., Schwarzenbach, R. P. and Macalady, D. L. 1992. Reduction of substituted nitrobenzenes in aqueous solutions containing natural organic matter. *Environmental Science and Technology*, v. 26, pp. 2133-2141.

Eary, L. E. and Schramke, J. A. 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. In *Chemical Modeling of Aqueous Systems, II, Chapter 30*, eds. D. C. Melchior and R. L. Bassett, American Chemical Society, Washington, D.C., pp. 379-396.

Gantzer, C.J. and Wackett, L.P., 1991. Reductive dechlorination catalyzed by bacterial transition-metal coenzymes. *Environmental Science and Technology*, v. 25, pp. 715-722.

Larson, R. A. and Weber, E. J. 1994. *Reaction Mechanisms in Environmental Organic Chemistry*. Lewis Publishers, Chelsea, Michigan, pp. 169-273.

Lovley, D. R., Coates, J. D., Blunt Harris, E. L., Phillips, E. J. P. and Woodward, J. C. 1996. Humic substances as electron acceptors for microbial respiration. *Nature*, v. 382, pp. 445-448.

Lyman, W. J., Bodek, I., Reehl, W. F., Rosenblatt, D. H. 1987. Electron transfer reactions. In *Methods for Estimating Physicochemical Properties of Inorganic Chemicals of Environmental Concern, Final Report, Chapter 2*, U.S. Army Medical Research and Development Command, Contract DAMD 17-83-C-3274.

Macalady, D. L. and Ranville, J. F. 1998. The chemistry and geochemistry of natural organic matter. In *Perspectives in Environmental Chemistry, Chapter 5*, ed. D. L. Macalady, Oxford University Press, New York, pp. 94-137.

Matthiessen, A. 1996. Kinetic aspects of the reduction of mercury ions by humic substances. *Fresenius Journal of Analytical Chemistry*, v. 354, pp. 747-749.

Perlinger, J. A., Angst, W., and Schwarzenbach, R. P. 1996. Kinetics of the reduction of hexachloroethane by juglone in solutions containing hydrogen sulfide. *Environmental Science and Technology*, v. 30, pp. 3408-3417.

Peiffer, S., Walton-Day, K., Macalady, D. L., 1999. The interaction of natural organic matter with iron in a wetland receiving acid mine drainage. *Aquatic Geochemistry*, v. 5, pp. 207-223.

Schindler, J. E., Williams, D. J., Zimmerman, A. P. 1976. Investigation of extracellular electron transport by humic acids. In *Environmental Biogeochemistry, Vol. 1.*, ed. J. O. Nriagu, Ann Arbor Science, Ann Arbor, Michigan, pp. 109-115.

Schwarzenbach, R. P., Stierli, R., Lanz, K. and Zeyer, J. 1990. Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution. *Environmental Science and Technology*, v. 24, pp. 1566-1574.

Skogerboe, R. K. 1981. Reduction of ionic species by fulvic acid. *Analytical Chemistry*, v. 53, pp. 228-232.

Tratnyek, P. G. and Macalady, D. L. 2001. Oxidation-reduction reactions in aquatic systems. In *Estimation of Chemical Properties for the Environmental and Health Sciences: A Handbook of Methods,* eds. B. Boethling and D. Mackay, Ann Arbor Press, Ann Arbor, Michigan.

Walton-Day, K., Macalady, D. L., Brooks, M. H., Tate, V. T. 1990. Field methods for measurement of ground water redox chemical parameters. *Ground Water Monitoring Review*, v. 10, pp. 81-89.

Walton-Day, K. 1991. *Hydrology and Geochemistry of a Natural Wetland Affected by Acid Mine Drainage, St. Kevin Gulch, Lake County, Colorado.* Ph. D. Thesis, Colorado School of Mines, Golden, CO, 300 p.

White, A. F., Peterson, M. L., Solbau, R. D. 1990. Measurement and interpretation of low levels of dissolved oxygen in ground water. *Ground Water,* v. 28, pp. 584-589.

Wittbrodt, P. R. and Palmer, C. D. 1996. Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. *Environmental Science and Technology*, v. 30, pp. 2470-2477.

Wolfe, N. L., Kitchens, B. E., Macalady, D. L., and Grundl, T. J. 1986. Physical and chemical factors that influence the anaerobic degradation of methyl parathion in sediment systems. *Environmental Toxicology and Chemistry*, v. 5, pp. 1019-1026.

Current State of Practice for Evaluation of Oxidation Reduction Processes Important to the Biological and Chemical Destruction of Chlorinated Organic Compounds in Ground Water

John T. Wilson

U.S. Environmental Protection Agency
Ada, OK 74820

The most important oxidation reduction process involved in the destruction of chlorinated organic compounds in ground water is biological sequential reductive dechlorination (Vogel and McCarty, 1985). In some cases this process does not provide benefit to the organisms that carry it out, the process is entirely accidental, and may be considered a form of co-metabolism. In other cases the biological process yields energy to the microorganisms and can support their growth and proliferation (Maymo-Gatell et al., 1995). In this circumstance the process functions as a respiration, and has been termed halorespiration (See discussion in Chaper 6, Wiedemeier et al., 1999). Chlorinated organic compounds may also be destroyed by chemical reaction in aquifers, usually involving direct chemical reaction with sulfide or ferrous iron. Examine Butler and Hayes (1999), and Devlin and Muller (1999) for illustrations of recent research.

In "The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water", the U.S. Environmental Protection Agency used a scoring system to identify sites where geochemical conditions were appropriate or not appropriate for biological reductive dechlorination of chlorinated solvents. Weights were given to the concentrations of important electron acceptors, including oxygen, nitrate, and sulfate, to the concentrations of important electron donors including molecular hydrogen, volatile fatty acids, dissolved native organic carbon (TOC), and petroleum derived monoaromatic hydrocarbons (BTEX), and the concentrations of metabolic end products including methane, ferrous iron, sulfide, chloride and carbon dioxide represented as increases in carbon dioxide or alkalinity. Weights were also given to general descriptions of the oxidation/reduction environment such as electrode potential, pH, and temperature. Finally, weight was given to the accumulation of metabolic daughter products including dichloroethylene, dichloroethane, vinyl chloride, ethene, or ethane. Weight was only given when the daughter products were not originally present in the material that was released to the environment. The weighted scores were totaled, and compared to a table that interpreted the scores as providing either inadequate evidence, limited evidence, adequate evidence, or strong evidence of anaerobic biodegradation of chlorinated organic compounds.

The National Research Council (2000) in the report *Natural Attenuation for Groundwater Remediation* noted on pages 210 and 211 that

Unfortunately, this scoring system is being widely adopted for uses that the authors never intended. For example, many states are using it to evaluate natural attenuation for all types of chlorinated solvents. Tables of natural attenuation scores are showing up in remedial investigation reports at Superfund sites. Maps and cross sections showing natural attenuation scores are being included in final reports as a key line of evidence. Some regulators are accepting this inappropriate use of scoring.

* *The method applies only to chlorinated ethenes.*

* *The scores emphasize reducing environments more than dehalogenation reactions.*

* *A reduced geochemical environment does not guarantee that natural attenuation will occur, because geochemical environments can be very reduced without reductive dehalogenation of chlorocarbons occurring (for example, if dehalogenating bacteria are not present).*

* *The scoring system included items that are of current research interest (for example, hydrogen concentration), but that may have limited practical impact on making remediation decisions.*

Table 1. *Analytical Parameters and Weighting for Preliminary Screening for Anaerobic Biodegradation processes used in the Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, U.S. EPA, 1998*

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen*	>5 mg/L	Not tolerated: however, VC may be oxidized aerobically	-3
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	2
Ferrous iron	>1 mg/L	Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions	3
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	>1 mg/L	Reductive pathway possible	3
Methane*	<0.5 mg/L >0.5 mg/L	VC oxidizes Ultimate reductive daughter product, VC Accumulates	0 3
Oxidation Reduction Potential* (ORP) against Ag/AgCl electrode	<50 millivolts (mV) <-100mV	Reductive pathway possible Reductive pathway likely	1 2
pH*	5 < pH < 9 5 > pH >9	Optimal range for reductive pathway Outside optimal range for reductive pathway	0 -2
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	> 20°C	At T >20°C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1
Alkalinity	>2x background	Results from interaction between CO_2 and aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Tetrachloroethene		Material Released	0
Trichloroethene*		Material released Daughter product of PCE	0 2[a/]
DCE*		Material released Daughter product of TCE. If cis is > 80% of total DCE it is likely a daughter product 1,1-DCE can be chemical reaction product of TCA	0 2[a/]
VC*		Material released Daughter product of DCE	0 2[a/]
1,1,1-Trichloroethane*		Material released	0
DCA		Daughter product of TCA under reducing conditions	2
Carbon Tetrachloride		Material Released	0
Chloroethane*		Daughter product of DCA or VC under reducing conditions	2
Ethene/Ethane	>0.01mg/L >0.1 mg/L	Daughter product of VC/ethene	2 3
Chloroform		Material Released Daughter Product of Carbon Tetrachloride	0 2
Dichloromethane		Material Released Daughter Product of Chloroform	0 2

* Required analysis. a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

* *The system identifies interactions between contaminants only for electron donors.*

The National Research Council (2000) recommended on page 15 of their report that national consensus guidelines be created for evaluation of natural attenuation, and that

* *The national consensus guidelines and future protocols should eliminate the use of "scoring systems" for making decisions on natural attenuation. The evaluation methods outlined in Chapter 4 [of their report], using conceptual and footprints of natural attenuation, should replace scoring systems.*

Nyer et al. (1998) cautioned against the use of the scoring system as a primary method to substantiate natural attenuation, because the system failed to recognize natural attenuation at a site where subsequent sampling and evaluation revealed that natural attenuation was believed to be occurring. In other words, the scoring system produced false negatives.

To improve the site-screening methodology for evaluating sites where natural reductive dechlorination may be selected as a remedial option, Stiber et al. (1999) constructed a causative model for the reductive dechlorination process, then solicited expert knowledge from twenty-two experts on reductive dechlorination in ground water. He solicited expert opinion on fourteen types of evidence in "The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (EPA, 1998). The experts were asked to provide their estimates of the probability that reductive dechlorination was occurring at a site based on site conditions for each type of evidence. The expert opinions were scaled by comparing the difference in the logarithm of the odds ratios where

ΔLOR = log [prior probability (true | evidence)/ posterior probability (false | evidence)] - log [posterior probability (true | evidence)/ prior probability (false | evidence)]

The experts put the greatest weight and greatest trust on data showing the accumulation of metabolic

Table 2. *Values for the change in the log of the odds ratio (DLOR) for the probability that anareobic degradation is occurring by reductive dechlorination associated with findings from screening data with respect to different types of evidence. The more positive the change with positive findings, the greater the weight the experts put in that type of evidence. The more negative the change with negative findings, the greater the weight the experts put in that type of evidence. These data are extrapolated from the Average Model in Figure 4 of Stiber et al., 1999.*

Type of Evidence	Positive Findings	Negative Findings
Terminal Electron Accepting Process	0.07	-0.15
Hydrogen	0.10	-0.15
Oxidation Reduction Potential	0.07	-0.15
Dissolved Organic Carbon	0.04	-0.10
BTEX	0.02	-0.10
TPH	0.02	-0.05
Oxygen	0.03	-0.15
Temperature	0.01	-0.01
pH	0.01	-0.10
Dichloroethene	0.63	0.80
Vinyl Chloride	0.95	0.40
Ethene and Ethane	0.78	0.25
Methane	0.43	0.38
Chloride	0.50	0.30

transformation products, and methane and chloride (Table 2). They put much less weight on data concerning electron acceptors, hydrogen, oxidation reduction potential, dissolved oxygen, TPH, and BTEX. They put little weight on data concerning pH and essentially no weight on data concerning temperature. Stiber et al. (1999) noted that "Simply identifying that prerequisite conditions are adequate is not sufficient; experts want to see products to have confidence that reductive dechlorination is occurring." They also noted that measuring the concentration of molecular hydrogen was a particularly divisive issue. "Some experts believe that, if performed correctly, hydrogen measurements provide the best means to assess the reducing conditions. Others feel that there are too many variables in microbial communities for hydrogen to be a reliable measurement."

Measurement of hydrogen in ground water is a particularly powerful technique to understand electron flow in microbial communities (Lovley et al., 1994). However, measurement of hydrogen requires careful sampling as well as state-of-art laboratory analytical measurements (Chapelle et al., 1997). At this point the use of hydrogen to understand reductive dechlorination has had mixed results. It is not clear if this mixed performance is a result of inadequate field protocols for collection and analysis of hydrogen, or is a result of real variations in the concentrations of hydrogen from one time to another in the same plume, or from one plume to another.

Recent work has shown that reductive dechlorination may proceed in ground water at relatively low concentrations. Smatlak et al. (1996) observed that the physiological threshold for the concentration of hydrogen that allowed growth of dechlorinating microorganisms in their laboratory cultures was less than 2 nM. Yang and MacCarty (1998) compared the presence or absence of cis-dichloroethylene on the equilibrium concentration of hydrogen in batch microcosms fed with benzoate as a fermentable source of hydrogen. In the presence of cis-dichloroethylene, reductive dechlorination to ethene dominated electron flow, and the concentration of hydrogen was poised at 2.2 +/- 0.9 nM. In the cultures that did not have cis-dichloroethylene, the cultures were methanogenic and the equilibrium concentration of hydrogen was 10.9 +/- 3.3 nM. The dechlorinating microorganisms out-competed methanogenic micro-organisms, and poised the concentration of hydrogen gas in the ground water.

Jakobsen et al. (1998) showed from theoretical calculations and field data from Denmark, that the equilibrium concentration of hydrogen in cold ground waters (near 10° C) should be approximately half of the equilibrium concentration of hydrogen expected in warmer ground waters and laboratory studies (near 20° C to 25° C). A concentration hydrogen of at least 1.0 nM would be required to sustain dechlorinating microorganisms in colder ground waters.

One of the most problematic issues in evaluation of natural attenuation is the tendency of reductive dechlorination to "stall" in many plumes at the level of dichloroethylene, presumably because they have depleted their sources of reducing power. In these plumes the dichloroethylene persists without further metabolism to vinyl chloride, ethene, or ethane. Concentrations of hydrogen significantly below 1.0 nM may indicate that further reductive dechlorination should not be expected.

In other plumes dichloroethylene and vinyl chloride do not accumulate because these compounds are directly oxidized by aerobic microorganisms (Davis and Carpenter, 1990; Bradley and Chapelle, 2000; Hartmans and de Bont, 1992; Klier et al., 1998), or iron reducing bacteria (Bradley and Chapelle, 1996, 1997; Bradley et al., 1997) or manganese reducing bacteria (Bradley et al., 1998), or by bacteria using native humic material as the electron acceptor (Bradley et al., 1998). A concentration of hydrogen above 1.0 nM may indicate that reductive dechlorination is on-going in these plumes, and the reduction transformation products are not accumulating because they are destroyed by the oxidative processes described above. Analysis for hydrogen could be used to distinguish between active plumes and inactive plumes that have low concentrations of vinyl chloride, ethene, and ethane because reductive dechlorination is limited and these compounds were not produced in the first place.

Suggestions for Consideration by the Work Groups

The use of geochemical parameters to determine the "footprint" of a plume can be useful in determining whether an apparent attenuation in the field is real, or whether it is an artifact of an inadequate network of monitoring wells. The primary use of information on the distribution of oxidation/reduction parameters should shift. Instead of using the oxidation/reduction parameters to identify plumes or regions of plumes where conditions

for natural attenuation are favorable, the parameters should be used for establishing "footprints" of plumes.

The most direct limitation on microbial activity is the supply of the requisite substrates for metabolism. However, the parameters that address the requisites for reductive dechlorination (such as hydrogen, BTEX, volatile fatty acids, and dissolved native organic matter) have little weight in the evaluation of natural attenuation by subject matter experts. Data use and data quality objectives should be developed for the geochemical parameters that measure the requisites for metabolism of contaminants in aquifers. Field protocols should be developed for sampling, preservation, and analysis of these parameters.

The most convincing evidence of natural attenuation is direct evidence of transformation of the contaminants. The "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (U.S. EPA, 1998) relied on the accumulation of transformation products as evidence of transformation. Biodegradation of organic compounds may also result in isotopic fractionation of the contaminants remaining. Natural attenuation due to biodegradation could be distinguished from simple dilution or dispersion because the isotopic ratio of the contaminant remaining in the plume would become progressively heavier as biodegradation proceeded. Data on stable isotope ratios could be used as a second line of evidence to support an evaluation of natural attenuation (see Hunkeler et al., 1999 for a recent application of this approach to a PCE spill in Canada). Data use and data quality objectives should be developed for the use of stable isotope ratios to document contaminant biodegradation in ground water.

References

Bradley, P. M. and Chapelle, F. H. 1996. Anaerobic mineralization of vinyl chloride in Fe(III)-reducing aquifer sediments. *Environmental Science and Technology*, v. 30, pp. 2084-2092.

Bradley, P. M. and Chapelle, F. H. 1997. Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions. *Environmental Science and Technology*, v. 31, pp. 2692-2696.

Bradley, P. M. and Chapelle, F. H. 2000. Aerobic microbial mineralization of dichloroethene as sole carbon substrate. *Environmental Science and Technology*, v. 34, pp. 221-223.

Bradley, P. M., Chapelle, F. H, and Lovley, D. R. 1998. Humic acids as electron acceptors for anaerobic microbial oxidation of vinyl chloride and dichlorethene. *Applied and Environmental Microbiology*, v. 64, pp. 3102-3105.

Bradley, P. M., Chapelle, F. H., and Wilson, J. T. 1997. Field and laboratory evidence of intrinsic biodegradation of vinyl chloride contamination in a Fe(III)-reducing aquifer. *Journal of Contaminant Hydrology*, v. 31, pp. 111-127.

Bradley, P. M., Landmeyer, J.E., and Dinicola, R. S. 1998. Anaerobic oxidation of [1,2-^{14}C]dichloroethene under Mn(IV)-reducing conditions. *Applied and Environmental Microbiology*, v. 64, pp. 1560-1562.

Butler, E.C. and Hayes, K. F. 1999. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide. *Environmental Science and Technology*, v. 33, pp. 2021-2027.

Butler, E.C. and Hayes, K. F. 2000. Kinetics of the transformation of halogenated aliphatic compounds by iron sulfide. *Environmental Science and Technology*, v. 33, pp. 422-425.

Chapelle, F. H., Vroblesky, D. A., Woodward, J. C., and Lovely, D. R. 1997. Practical considerations for measuring hydrogen concentrations in groundwater. *Environmental Science and Technology*, v. 31, pp. 2873-2877.

Davis, J. W. and Carpenter, C. L. 1990. Aerobic biodegradation of vinyl chloride in ground water samples. *Applied and Environmental Microbiology*, v. 56, pp. 3878-3880.

Devlin, J. F., and Muller, D. 1999. Field and laboratory studies of carbon tetrachloride transformation in a sandy aquifer under sulfate reducing conditions. *Environmental Science and Technology*, v. 33, pp. 1021-1027.

Hartmans, S., and de Bont, J. A. M. 1992. Aerobic vinyl chloride metabolism in mycobacterium aurum Li. *Applied and Environmental Microbiology*, v. 58, pp. 1220-1226.

Jakobsen, R., Albrechtsen, H-J., Rasmussen, M., Bay, H., Berg, P. L., and Christensen, T. H. 1998. H_2 concentrations in a landfill leachate plume (Grindsted, Denmark): In situ energetics of terminal electron acceptor processes. *Environmental Science and Technology*, v. 32, pp. 2142-2148.

Klier, N. J., West, R. J., and Donberg, P. A. 1998. Aerobic biodegradation of dichloroethylenes in surface and subsurface soils. *Chemosphere*, v. 38, pp. 1175-1188.

Lovley, D. R., Chapelle, F. H., and Woodward, J. C. 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environmental Science and Technology*, v. 28, pp.1205-1210.

Maymo-Gatell, X., Tandoi, V., Gossett, J. M., and Zinder, S. H. 1995. Characterization of an H_2-utilizing enrichment culture that reductively dechlorinates tetrachloroethylene to vinyl chloride and ethene in the absence of methanogenesis and acetogenesis. *Applied and Environmental Microbiology*, v. 61, pp. 3928-3933.

National Research Council. 2000. *Natural Attenuation for Groundwater Remediation,* 219 p.

Nyer, E., Mayfield, P., and Hughes, J. 1998. Beyond the AFCEE protocol for natural attenuation. *Ground Water Monitoring Review*, Summer, pp. 70-77.

Smatlak, C. R., Gossett, J. M., and Zinder, S. H. 1996. Comparative kinetics of hydrogen utilization for reductive dechlorination of tetrachloroethene and methanogenesis in an anaerobic enrichment culture. *Environmental Science and Technology,* v. 30, pp. 2850-2858.

Stiber, N. A., Pantazidou, M., and Small, M. J. 1999. Expert system methodology for evaluating reductive dechlorination at TCE sites. *Environmental Science and Technology*, v. 33, pp. 3012-3020.

U.S. Environmental Protection Agency. 1998. The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, EPA/600/R-98/128, U.S. Government Printing Office, Washington, D.C.

Vogel, T. M., and McCarty, P. L. 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Applied and Environmental Microbiology*, v. 49, pp. 1080-1083.

Wiedemeier, T. H., Rafai, H. S., Newell, C. J., and Wilson, J. T. 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*, John Wiley & Sons, New York, 617 p.

Yang, Y. and McCarty, P. L. 1998. Competition for hydrogen within a chlorinated solvent dehalogenating anaerobic mixed culture. *Environmental Science and Technology*, v. 32, pp. 3591-3587.

Redox Processes in Petroleum Hydrocarbon Remediation or Why I Never Want to Measure Eh Again

J. F. Barker

University of Waterloo
Waterloo, ON, Canada N2L3G1

The Context for Redox Processes in Monitored Natural Attenuation of Petroleum Hydrocarbons

The study of transport and fate of petroleum hydrocarbons in ground water is "mature" and has evolved into a remedial technology – monitored natural attenuation (MNA). For example, the US EPA OSWER Directive 9200.4-17P (April, 1999) states: "Natural attenuation processes, particularly degradation, are currently best documented at petroleum fuel spill sites. Under appropriate field conditions, the regulated compounds benzene, toluene, ethylbenzene, and xylene (BTEX) may naturally degrade through microbial activity and ultimately produce non-toxic end products (e.g., carbon dioxide and water)." The natural BTEX degradation is "through microbial activity", so microbial activity is the key process. Microbial activity must be considered in the context of the field conditions.

Classification of subsurface microbial activity is commonly via the dominant terminal electron accepting process (TEAP). Thus we can identify sulfate reduction as being the dominant TEAP and can discuss BTEX biodegradation by a community in which sulfate is the dominant electron acceptor (EA). This is the link between petroleum hydrocarbon MNA and redox processes. Geochemically, a TEAP is considered a redox process.

The OSWER Directive requires monitoring programs that, among other things, demonstrate that natural attenuation is occurring and that deleterious "changes in environmental conditions" are not. Collection of site-specific data is required "to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives." The current distribution of contaminants must be adequately defined and it must be sufficiently clear, from field monitoring data, that potential receptors are protected. A three-tiered approach is recommended, each providing successively more detailed information. These "three lines of evidence" are:

1. historical data that demonstrate loss of contaminant mass and/or concentrations over time,
2. hydrogeologic and geochemical data to demonstrate indirectly the type(s) of NA processes active at the site and their rate(s),
3. data from field or microcosm studies which directly demonstrate the occurrence of a particular NA process at the site.

For selecting MNA for petroleum hydrocarbons, demonstrating an understanding of how the current contamination was produced and how it will likely evolve is useful, if not essential. While contaminant distribution is the primary evidence, the need for a credible story should not be dismissed. It both relies upon and demonstrates the scientific underpinning for MNA.

Not being microbial ecologists, hydrogeologists and geochemists have had to simplify the evaluation of microbial activity. Since microbial ecologists seemed to be willing to discuss biodegradation in terms of TEAPs, that compromise has been accepted and subsurface environments and geochemical processes have been grouped in terms of TEAPs. Under current guidance (e.g., Wiedemeier et al., 1999), we are directed to examine the apparent utilization of EAs and to define the distribution of dominant TEAPs in plumes. That has led us to redox processes.

Thus, redox processes and measurements are not of primary importance in MNA for petroleum hydrocarbons. They are only important as they affect the supporting "story".

Challenges for MNA for Petroleum Hydrocarbons

Site assessment

The critical need at research and "real" sites is insight into what has occurred and what is occurring in the subsurface. A noted contaminant hydrogeologist characterised MNA, especially for chlorinated solvents as "1990's microbiology; 1970's hydrogeology".

Chapelle (1999) states: "The most important lesson that can be gleaned from the history of petroleum hydrocarbon bioremediation is the critical importance of accurately assessing the hydrogeology of each site." It is clear to hydrogeologists that the critical weakness in the application of MNA lies within their discipline.

Quantitative EA-Organic Mass Balances Don't Add Up

If MNA is really mature, shouldn't we expect quantitative balances between EAs consumed and petroleum hydrocarbons biodegraded, at least at "research sites"? A controlled, in place source experiment at CFB Borden has been recently reported (King and Barker, 1999). About 70 kg of coal tar creosote (CTC) was emplaced below the water table and the plumes of dissolved chemicals that developed were monitored with six "snapshot" samplings over four years, each using 450 to 2800 samples from multilevel monitoring wells. The analysis of background/plume redox-sensitive species indicated that the major TEAPs were aerobic respiration and sulfate reduction. Mass balance calculations suggested the apparent consumption of EAs would support biodegradation of about 300 g of CTC organics in the plumes. However, more than 1200 g of CTC organics was apparently biodegraded in the plume.

Usually, it is expected that more EAs will appear to be utilized than can be balanced by organic contaminant loss. This is because of the presence of other, non-target organics that exert a demand for EAs. In the CTC case, the likely problem is the incomplete transformation of organics. The above mass balance assumed complete mineralization. Significant concentrations (up to 18 mg/L) of aromatic acids, the probable metabolites, were found in a very superficial sampling of nine points. In this, the biodegradation reactions would need to be re-written based on actual transformations; not a quantitative process at present.

While depletion of electron acceptors and donors and the appearance of reaction products can be qualitatively supported at most sites, acceptable balance between EAs and organics consumed is unlikely to be demonstrated, especially when "real world" monitoring (5 – 40 points, typically) is the basis. That is not a very secure scientific underpinning for MNA. Some credible quantitative mass balances need to be produced.

Transport of EA Utilization Indicators

Delineation of redox environments or TEAPs appears useful/essential in developing the story supporting MNA of petroleum hydrocarbons. Albrechtsen et al. (1999) captured the problem very well: "Delineations of redox environments have been based mainly on the concentrations of redox sensitive components in ground water. However, since most of the reactive components may be transported by ground water, for example, methane and Fe(II), their presence in a sample does not necessarily reflect redox conditions at the sampling location but perhaps conditions at an upgradient location."

The promise of H_2

Hydrogen appears to this desperate researcher as potentially the "ideal" indicator of the TEAP active at the monitored location. While H_2 can be transported, it is sensitive to local microbial activity and so its concentration is adjusted to reflect local conditions (Lovley et al., 1994). As such, it overcomes the transport problem of the other geochemical indicators. I sense a healthy reluctance to accept this hypothesis and look forward to further demonstration such as reported by Albrechtsen et al. (1999). The key is to compare H_2 concentrations directly to microbially-significant aspects of TEAP and hydrocarbon degradation, not to flawed (transported, reactive) aqueous geochemical data.

Research Needs

MNA for petroleum hydrocarbons is underpinned by a demonstrated understanding of the controlling processes. The key is the transport and fate of contaminants, but EAs and TEAPs (perhaps defined as redox processes) are involved.

One aspect is to determine the distribution, in space and perhaps in time, of TEAPs. The researchers from the Groundwater Research Centre at the Technical University of Denmark (TUD) have provided the most comprehensive characterization of ground-water redox environments, not in BTEX plumes, but in landfill leachate plumes. They have used essentially all the techniques, many of which are referenced by Albrechtsen et al. (1999).

To demonstrate understanding of interactions of inorganics/organics/minerals/microbial communities insightful geochemical interpretation must be employed. Since transport is significant, I think we are admitting that the processes might be more complex than can be handled by "typical" site monitoring, supported by simple spreadsheet models. We need at least a few detailed field studies in which all important parameters are measured and interpretation is quantitative. If the problem is as

complex as I have suggested, then qualitative demonstration of process understanding will require sophisticated flow-transport-reaction models.

Using reactive transport modeling, certain key redox features can be reproduced, but it is clear that matching all features, especially pH in poorly buffered systems, strains our conceptual understanding. At actual field sites major hydrogeological uncertainties, unknown source functions, and temporal variability will be added. If we are to demonstrate a comprehensive understanding of the redox processes involved in biodegradation of petroleum hydrocarbons, we must do so through matching results from such models with detailed field observations from at least a few sites.

Do we need this for MNA of petroleum hydrocarbons? We needed it five years ago to provide the underpinning for current guidance. Do we still need it? MNA is being selected, errors will be made, and the blame shouldn't reside with bad scientific underpinning. So, I think this research is still essential.

Is it being done? The modeling tools appear to be sufficiently developed (e.g., BIORXNTRN, Hunter et al., 1998; Mayer, 1999) and some models are being employed in this area (e.g., Curtis et al., http://wwwmn.cr.usgs.gov/bemidji/). Certainly, TUD researchers have the field studies and experience for landfill leachate plumes. The USGS is apparently well along at the Bemidji site (http://wwwmn.cr.usgs.gov/bemidji) and other hydrocarbon-contaminated sites (e.g., Wurtsmith) have major components of this in place. All of these sites (perhaps less so at Bemidji) suffer from uncertainties about the source and/or complex hydrogeology. Too bad the controlled field experiments in simple hydrogeological settings (e.g., Barker et al., 1987; King and Barker, 1999) were not more comprehensive. With simple hydrogeology, simple and known sources, mass balances, etc. would have been a reasonable expectation and the concept would have been quantitatively evaluated.

The Role of Redox Processes in Practical MNA for Petroleum Hydrocarbons

Is proper redox characterization <u>required</u> to implement MNA for petroleum hydrocarbons?

No. The primary information is the distribution of contaminants. Redox characterization only contributes to the credibility of the story of how the plume got to the current status.

Is proper redox characterization <u>required</u> for remedy selection? Also, no. I might reject MNA for BTEX plumes in naturally anaerobic aquifers, since I don't feel benzene degrades reliably under such conditions. However, I would acknowledge others would not share this pessimism and so my redox-based view would not be compelling. We would, I am sure, need to rely on the primary line of evidence - the distribution of BTEX and interpretation of apparent attenuation.

Is proper redox characterization <u>required</u> for performance assessment? Again, no. While, for example, assessment of deleterious "changes in environmental conditions" might be tracked through redox measurements, direct contaminant measurements will likely be the assessment criteria. Perhaps redox contributes to the credibility of the assessment. For example, if benzene is found beyond the predicted point, perhaps noting the unexpected extent of reduced conditions would be useful.

Redox processes are part of the supporting story for MNA of petroleum hydrocarbons. As such, it is probably more important that research-level studies demonstrate understanding of redox-related processes. Our goal should be to demonstrate this. We should then assure hydrogeologists that they must rely primarily on hydrogeological studies, not assessments of redox processes, in applying MNA to BTEX-contaminated groundwater.

References

Albrechtsen, H. J., Bjerg, P. L., Ludvigsen, L., Rugge, K. and Christensen, T. H.. 1999. An anaerobic field injection experiment in a landfill leachate plume, Grindsted, Denmark 2. Deduction of anaerobic (methanogenic, sulfate-, and Fe(III)-reducing) redox conditions. *Water Resources Research*, v. 35, pp.1247-1256.

Barker, J. F., Patrick, G. C., and Major, D. 1987. Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monitoring Review*, v. 7, pp. 64-71.

Chapelle, F. H. 1999. Bioremediation of petroleum hydrocarbon-contaminated ground water: The perspectives of history and hydrology. *Ground Water*, v. 37, pp. 122-132.

Curtis, G. P., Cozzarelli, I. M., Baedecker, M. J., and Bekins, B. A. Coupled biogeochemical modeling of ground water contamination at the Bemidji Minnesota crude oil spill site, from http://wwwmn.cr.usgs.gov/bemidji/.

Hunter, K. S., Wang, Y., and Van Cappellen, P. 1998. Kinetic modeling of microbially-driven chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry. *Journal of Hydrology*, v. 209, pp. 53-80.

King, M. W. G., Barker, J. F., Devlin, J. F., and B. J. Butler. 1999. Migration and natural fate of a coal tar creosote plume; 2. Mass balance and biodegradation indicators. *Journal of Contaminant Hydrology*, v. 39, pp. 281-307.

Lovley, D. R., Chapelle, F. H., and Woodward, J. C. 1994. Use of dissolved H_2 concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environmental Science and Technology*, v. 28, pp. 1205-1210.

Mayer, K. U. 1999. A numerical model for multicomponent reactive transport in variably saturated porous media, Ph.D. thesis, University of Waterloo, Waterloo, Ontario, Canada.

Wiedemeier, T. H., Rafai, H. S., Newell, C. J., and Wilson, J. T. 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*, John Wiley & Sons, New York, 617 p.

Alteration of Reactive Mineral Surfaces by Ground Water

Janet S. Herman[1]
Aaron L. Mills[1]
Isabelle M. Cozzarelli[2]

[1]University of Virginia
Charlottesville, VA 22904
[2]U. S. Geological Survey
Reston, VA 20192

Two different investigations of shallow sandy aquifers inform our thinking about the role of reactive iron minerals in hydrogeological systems. Ground water in a number of settings has been described as having elevated concentrations of dissolved iron in anoxic portions of contaminant plumes (e.g. Baedecker et al., 1993; Lyngkilde and Christensen, 1992), and the coupling of microbial reduction of Fe(III) to the degradation of organic compounds links the study of the biogeochemistry of iron to our desire to understand processes influencing contaminated aquifers. Questions about the transport and fate of reactive constituents in ground water are linked to the study of iron through recognition of the importance of sorption processes on sesquioxide mineral surfaces common in sedimentary aquifers limiting the migration of metals, anions, and bacteria. We have been grappling with questions related to the stability of iron mineral phases in contaminated aquifers and the role of Fe(III)-bearing minerals and grain coatings as sorption substrates.

In our ongoing study of the transport of bacteria through an unconsolidated sandy aquifer in the Coastal Plain of Virginia, we address a number of questions related to the potential for bacterial attachment to mineral solids. In laboratory and field-scale experiments, the presence of these positively charged metal-oxide coatings on quartz sand has been shown to greatly affect the sorption and transport of reactive constituents. The mineralogy of the metal oxide affects the affinity its surface has for ion sorption. The presence of more than one oxide in a system may affect the sorption characteristics as well. In addition to metal-oxide abundance, surface area is commonly employed as an estimator of total sediment reactivity, and the result can be inconsistent with an assessment of that portion of the surface that actually participates in reactions.

Our investigation was undertaken on the Eastern Shore near the village of Oyster where depositionally similar sediments have been exposed to chemically distinct ground-water conditions. In a narrow, organic-rich leachate plume derived from vegetable waste pits, dissolved oxygen was only 0 to 0.9 mg L^{-1}, whereas it was 5.0 to 11 mg L^{-1} in the regionally extensive aerobic, uncontaminated ground water. In addition, the amount of dissolved iron in the aerobic ground water was 0.001 to 0.01 mg/L^{-1}, but it was 12 to 42 mg/L^{-1} in the anaerobic zone. Samples of sediments from cores were subjected to metal-oxide extractions and determination of operationally defined fractions of iron (ferrous and ferric) and aluminum. The amount of extractable iron was an order of magnitude higher for the aerobic sediments than for the anaerobic sediments indicating that reductive dissolution removed the oxide coatings. The total iron in the HCl extracts of the aerobic sediments ranged from 3.2 - 52 µmol/g whereas it was only 0.9 - 2.4 µmol/g in the anaerobic sediments (Table 1). There was very little ferrous iron (Fe(II)) extracted from either of the two zones, and the values from each zone only ranged from 0.01 - 0.5 µmol/g of Fe(II) extracted. It is likely that microbial oxidation of organic contaminants is linked to the reduction of iron from the surfaces of sediments in the polluted portion of the aquifer. Although the majority of the iron had been removed from the surfaces of the anaerobic sediments, there was still an appreciable amount of surface area measured.

We sought a means to characterize the aquifer solids for their potential for bacterial attachment, and we developed a single-point sorption determination for a reactive anion. In attempting to evaluate the reactivity of mineral surfaces in an aquifer setting, sorption of solutes directly probes that portion of the solid surface that participates in reactions involving other negatively charged reactive constituents, including bacteria. The reactivity of the sediment surfaces, as indicated by the sorption of $^{35}SO_4^{2-}$, was an order of magnitude higher in the aerobic *vs.* anaerobic sediments. The sulfate sorbed to the aerobic sediments (2.2 to 50 µmol/g) was an order of magnitude greater than for the anaerobic sediments (0.007 to 0.25 µmol/g). The presence of anaerobic

Table 1. *Concentration of total extractable iron with depth (below the water table) for samples from aerobic and anaerobic cores.*

Aerobic Core		Anaerobic Core	
Depth (m)	Total Fe (μmol/g)	Depth (m)	Total Fe (μmol/g)
		-0.31	3.35
		-0.81	18.4
		-1.31	5.49
-1.36	2.10		
-1.44	1.54		
-1.53	1.88		
-1.61	2.16		
-1.69	2.12		
-1.77	2.32		
		-1.81	10.5
-1.88	2.45		
-2.32	2.40		
-2.80	1.27		
		-2.31	52.4
		-2.81	10.5
		-3.31	4.26
		-3.81	3.16
-3.88	1.97		
-4.26	1.34		
		-4.31	10.9

conditions did not significantly alter the amount of extractable aluminum oxides on the surface of the sediments, and those coatings helped to maintain a high surface area for the anaerobic sediments. It appears that the removal of the iron oxides from the surfaces under anaerobic conditions was solely responsible for the significant reduction of sediment reactivity observed.

The iron-oxide content was the only one of the surface properties to be significantly altered by the anaerobic conditions with a concomitant alteration in the ability of the sediments to retain the anion sulfate (Knapp et al., in review). It appeared, therefore, the presence or absence of iron oxides was the dominant factor controlling sulfate sorption. These results would indicate an alteration in the reactive surfaces of minerals when exposed to anaerobic ground water and the potential for greater movement of reactive constituents, including bacteria, through these aquifer sediments.

As redox conditions in a contaminant plume change with the depletion of oxygen and nitrate as electron acceptors, ferric iron is consumed as an electron acceptor coupled to the oxidation of organic matter (e.g. Lovley et al., 1989). The glacial-outwash, sandy aquifer at the USGS Toxic Substances Hydrology site near Bemidji, MN, became contaminated by crude oil in 1979. Observations since nearly the time of the pipeline burst show accumulations of Fe(II) in the site ground water over time, whereas no ferrous iron was found in the uncontaminated background water (e.g. Baedecker et al., 1993). Previous field and microcosm results (Baedecker et al., 1993, Lovley et al., 1989) indicate the degradation of toluene may proceed according to

$$C_7H_8 + 36Fe(OH)_{3(s)} + 65H^+ \rightarrow 7HCO_3^- + 36Fe^{2+} + 87H_2O$$
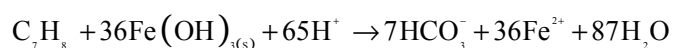
In this study, we examined the distribution of Fe in the sediments of the aquifer in order to assess the magnitude of impact of Fe(III) reduction in the contaminant plume on the geochemistry of the sediments. Sampling and extraction of sediments revealed that the average HCl-extractable Fe(III) concentration in the most contaminated portion of the aquifer was 16.2 μmol/g, a 30% reduction from the value in background sediments of 23.8 μmol/g (Tuccillo et al., 1999). Comparison between HCl extractions that should capture poorly crystalline Fe(III) solids and Ti-citrate-EDTA-bicarbonate extractions that should reductively dissolve amorphous and crystalline Fe(III) oxides indicates that the bulk of the microbially mediated iron reduction is dissolving amorphous or poorly crystalline oxides.

In contrast to the study in Virginia in which virtually no Fe(II) was extracted from aquifer solids, at Bemidji we found 19.2 μmol/g Fe(II), as much as 4 times the background sediments with 4.6 μmol/g Fe(II) (Figure 1). Scanning electron microscopy detected authigenic ferroan calcite in the anoxic sediments (Baedecker et al., 1992; Tuccillo et al., 1999). Likely the contrast can be attributed to the availability of minerals that buffer pH, giving the contaminated ground water at Bemidji at pH near 6.9 whereas at the Oyster, VA, site it is closer to 6.3 in the anaerobic ground water.

One of the most striking features of the distribution of iron content of the aquifer sediments was the extreme concentration at the anoxic/oxic transition zone. HCl-extractable Fe(III) reached values as great as 49.8 μmol/g at this boundary (Figure 1). This 70% increase in total extractable Fe at the interface indicates the reoxidation and precipitation of Fe mobilized from aquifer sediments
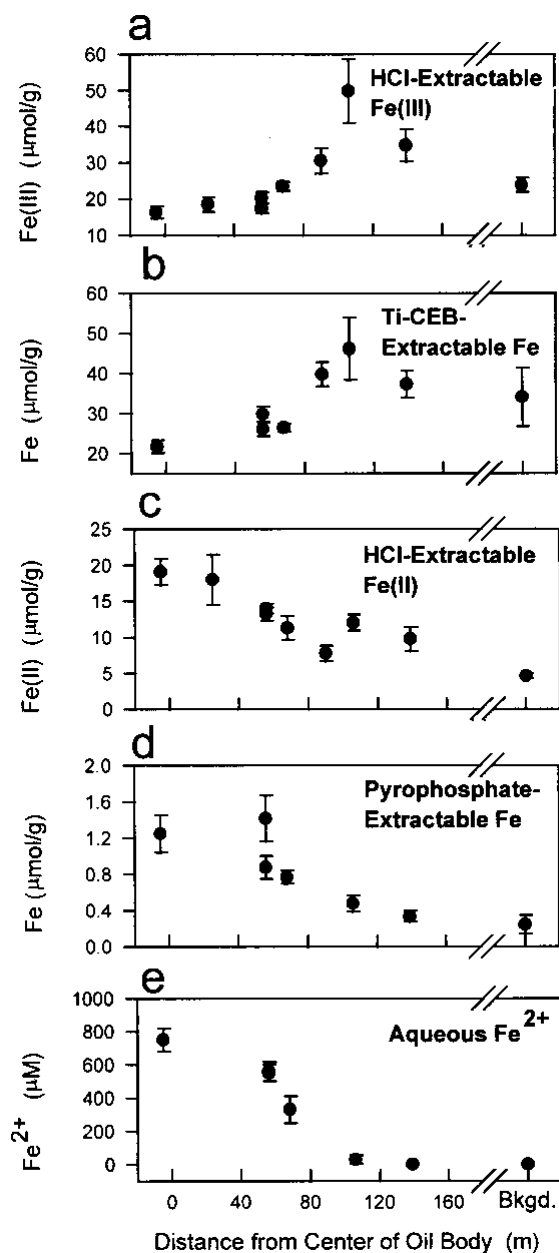
Figure 1. *Graphs of various fractions of iron extracted from the sediments and of aqueous Fe^{2+} in pore waters vs. distance from the center of the oil body. Circles represent the mean of samples from all depths for each core. Error bars represent standard errors $(s.d./n^{0.5})$ which gives an indication of within-core variability.*

located upgradient in the anoxic, contaminated groundwater plume as that water flows downgradient into an oxic background ground water. Scanning electron microscopy confirmed the abundant Fe(III) oxyhydroxides at the anoxic/oxic boundary (Tuccillo et al., 1999).

The alteration of sediment chemistry has implications for the availability of electron acceptors and the biodegradation of contaminant organics. As availability of Fe(III) decreases, alternate hydrocarbon degradation processes linked to methanogenesis will be less efficient and intermediate metabolic products of biodegradation will persist and be transported in the ground water. The Fe(II) that is mobilized out of the sediments in the most contaminated portion of the aquifer will be reoxidized at some location downgradient and precipitate as an "iron curtain" that can alter not only the reactivity of the solid phase but can also change the permeability as mineral grains are cemented together and the interstitial spaces filled with Fe(III) precipitates. The high Fe(III) content of that anoxic/oxic boundary gives rise to a sorptive capacity of the transition-zone sediments that is enhanced above both background and anoxic sediments. The presence of the Fe(III) oxyhydroxides has implications for the reactivity of aquifer sediments, altering the nature and extent of reaction between sorbing species and mineral surfaces. The contaminants that may be retarded in their transport are not just those of the original crude oil spill but potentially include bacteria, anions, and metals. Improved understanding of the biogeochemistry of iron in contaminated sedimentary aquifers likely will lead to a better ability to anticipate the rate of transport of a variety of solutes and colloids.

References

Baedecker, M. J., Cozzarelli, I. M., Evans, J. R. and Hearn, P. P. 1992. Authigenic mineral formation in aquifers rich in organic material. In *Water-Rock Interaction: Proceedings of the 7th International Symposium on Water-Rock Interaction*, eds. Y. K., Kharaka, and A. S. Maest, Balkema, pp. 257-261.

Baedecker, M. J., Cozzarelli, I. M., Eganhouse, R. P., Siegel, D. I., and Bennett, P. C. 1993. Crude oil in a shallow sand and gravel aquifer - III. Biogeochemical reactions and mass balance modeling in anoxic groundwater. *Applied. Geochemistry*, v. 8, pp. 569-586.

Knapp, E. P., Herman, J. S., Mills, A. L., and Hornberger, G. M. 2001. Redox alternation of reactive mineral surfaces in biologically active groundwater. *Applied Geochemistry*, in review.

Lovley, D. R., Baedecker, M. J., Lonergan, D. J., Cozzarelli, I. M., Phillips, E. J. P., and Siegel, D. I. 1989. Oxidation of aromatic contaminants coupled to microbial iron reduction. *Nature*, v. 339, pp. 297-299.

Lyngkilde, J. and Christensen, T. H. 1992. Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, v. 10, pp. 273-289.

Tuccillo, M. E., Cozzarelli, I. M., and Herman, J. S. 1999. Iron reduction in the sediments of a hydrocarbon-contaminated aquifer. *Applied. Geochemistry*, v. 14, pp. 71-83.

Aqueous Redox Chemistry and the Behavior of Iron in Acid Mine Waters

D. Kirk Nordstrom

U.S. Geological Survey
Boulder, CO 80303

Introduction

The earth's surface is in a steady struggle between oxidation, driven by oxygen in the atmosphere, and reduction, driven by organisms and organic matter. The redox cycle established about 600 million years ago by photosynthesizing and respiring organisms, organic burial, and weathering processes maintains the biogeochemical conditions we enjoy today. Without this constant redox disequilibria in the air and in waters and in rocks, life would not exist. Plants and petroleum would spontaneously combust and the atmosphere would become a sea of nitrogen oxides.

Confusion regarding redox (reduction-oxidation) potentials and redox chemistry of aquatic systems stems from misunderstandings of how aqueous redox reactions occur and from misunderstandings of the assumptions that enter into any calculations. Specific conceptual difficulties arise in the following three areas: (1) the existence and representation of the aqueous electron, (2) the kinetics of electron transfer reactions, and (3) the measurement and interpretation of redox in water bodies. This paper discusses these various issues, shows examples of equilibria and disequilibria of redox chemistry in natural waters with particular attention to the ferrous-ferric redox couple, and explains the challenges of modeling redox geochemistry.

The Aqueous Electron

Free aqueous electrons have been synthesized in solution at micromolar concentrations by intense radiation, either by flash photolysis or pulse radiolysis (Hart and Anbar, 1970). These hydrated electrons are extremely ephemeral, having half-lifes of 230 μs at pH of 7. They quickly form hydrogen atoms and hydrogen gas. Their concentrations in natural waters would be negligible to nonexistent (Hostetler, 1984; Thorstenson, 1984). Hence, discussions of the activity of aqueous electrons, designated as a_{e^-}, do not relate to a physically meaningful quantity. This fact distinguishes aqueous electrons from aqueous protons because a_H+ *is* a physically meaningful quantity. The mathematical entity "pH" is physically measurable and has chemical significance whereas the entity "p$\in$," or - log a_{e^-}, does not have physicochemical significance when applied to aqueous electrons. There is no analogy between pH and p$\in$ in a chemical sense. To draw the analogy in a mathematical sense can be very misleading.

Kinetics of Electron Transfer Reactions

Reactions involving aqueous solutions are divided into homogeneous (occurring only within the solution phase) and heterogeneous (occurring between a solid or gas surface and the solution phase). Homogeneous redox reactions can go quickly if only one electron is being transferred at a time and if the activation barrier is not too large. However, numerous examples show that large activation barriers do exist – otherwise nitrogen, oxygen, methane, and carbon dioxide would not all coexist in the atmosphere as they do. Eary and Schramke (1990) showed clearly the wide range of oxidation rates for several inorganic reactions as a function of pH and dissolved oxygen. Redox reactions involving two electrons (more than two per reaction step is generally forbidden) or involving heterogeneous reactions are usually slower unless catalysts or high temperatures are provided.

Empirical homogeneous redox reactions are described by the usual kinetic equations (zero-order, first-order, second-order, Michaelis-Menten for enzyme catalysis, etc.) but electrode kinetics are described by the current-overpotential equation:

$$i = i_0 \left[\frac{C_o(0,t)}{C_o^*} e^{-\alpha n F \eta / RT} - \frac{C_r(0,t)}{C_r^*} e^{-(1-\alpha)nF\eta/RT} \right] \quad (1)$$

where the exchange current, i, is dependent on the equilibrium exchange current, i_0, the concentration gradient for the oxidized species between the surface, $C_o(0,t)$, and the bulk solution, C_o^*, the concentration gradient for the reduced species, $C_r(0,t)$, and the bulk solution, C_r^*, the symmetry factor, a, the overpotential, h, the Faraday constant, F, the ideal gas constant, R, and

the Kelvin temperature, T (Bard and Faulkner, 1980). If the surface concentrations do not differ significantly from the bulk solution concentrations then equation (1) reduces to the Butler-Volmer equation developed in the 1920's:

$$i = i_o \left[e^{-\alpha n F \eta / RT} - e^{-(1-\alpha) n F \eta / RT} \right] \qquad (2)$$

Equation (2) shows how the current across a metal-solution interface depends on the difference in potential between the actual non-equilibrium and equilibrium potential differences, $\eta = E - E_{eq}$. When this difference (the overpotential) goes to zero, the equation reduces to the well-known Nernst equation of equilibrium thermodynamics written here for a half-cell with one reduced and one oxidized species:

$$E = E^o + \frac{RT}{nF} \ln \frac{a^{\nu}_{oxidized}}{a^{\nu}_{reduced}} \qquad (3)$$

where E^o is the standard electrode potential based on the standard hydrogen electrode, the natural logarithm contains the ratio of the activity of the oxidized species to the activity of the reduced species, each taken to the exponent represented by the stoichiometric coefficient, ν. The equation is also commonly written with a negative sign before the log term with reduced species activity on the top and the oxidized underneath. These equations remind us that the Nernst equation is a special case of the more general equation of electrode kinetics. The challenge is knowing when a system is in equilibrium and when it is not.

There are two systems being considered with respect to equilibrium conditions. One system is the electrode-solution interface and the other is the environmental system composed of gases, waters, rocks, and biological activity. This section addresses the electrode-solution system and the next section addresses the environmental system.

The ease with which electrons are transferred across the metal-solution interface depends on the nature of the metal, the nature of the aqueous redox-sensitive species, and the solvent properties. Metal electrodes need to be non-reactive and electrically conductive. Thus, gold, platinum, and graphite have worked well and among these platinum is most frequently used. The metal is not usually a limiting factor in reaching equilibrium as long as the surface is free of electroactive coatings and other adsorbed impurities. For aqueous redox species, there are some serious limitations: (1) the net exchange current across the interface must be effectively zero, i.e. electrochemical reversibility must be maintained, (2) to maintain

reversibility, redox ions must have individual exchange currents greater than 10^{-7} amp cm^{-2} (Morris and Stumm, 1967), which translates into concentrations of about 10^{-5} m or greater for two redox constituents in natural waters: Fe(II/III), S(II-), and possibly U(IV/VI). Several examples in the literature have shown the equilibrium maintained between the Pt electrode and the Fe(II/III) redox couple in laboratory studies (Morris and Stumm, 1967; Macalady et al., 1990; Stipp, 1990). Peschanski and Valensi (1949) showed that the Pt electrode responded quantitatively and reversibly to changes in sulfide ion activity in the S(II-/0) system in the laboratory. Experiments designed to examine the electrochemical reversibility of the As(III/V) and Se(IV/VI) redox couples showed that they do not reach equilibrium (Kempton et al., 1990; Runnells et al., 1987; Runnells and Skoda, 1990). Hence, only iron and reduced sulfur species demonstrate electrochemical reversibility for aqueous conditions likely to be found in the environment.

Measurement and Interpretation of Redox in Waters

Two facets of redox chemistry need to be considered when examining redox in aquatic systems: the attainment of equilibrium for a redox couple at a Pt electrode surface and the attainment of equilibrium between different redox couples in ground water or surface water. Field measurements and their interpretation are not simple and proper precautions should be exercised (Langmuir, 1971; Nordstrom and Wilde, 1998). Laboratory and theoretical considerations would lead to the view that only rarely would redox potential measurements in waters reflect equilibrium and even then it should only be observed for iron and reduced sulfur. Field work confirms this view. For the iron system, an update of the original diagram by Nordstrom et al. (1979) that compares measured *vs.* calculated Eh for more than 60 acid mine waters is shown below in Figure 1. The calculated Eh values were based on ferrous and ferric iron determinations (To et al., 1999), complete water analyses, and speciation based on output from the WATEQ4F program (Ball and Nordstrom, 1990).

The agreement is generally excellent with most Eh values agreeing to within 25 mV except at low Eh where a strong positive deviation occurs. Figure 2 plots the difference between calculated and measured Eh as a function of total dissolved iron concentrations. Marked deviations occur below 10^{-5} m as predicted from lab studies. These results reflect the mixed potential effect as the iron concentrations become too low to be electroactive and oxygen begins to be sensed by the
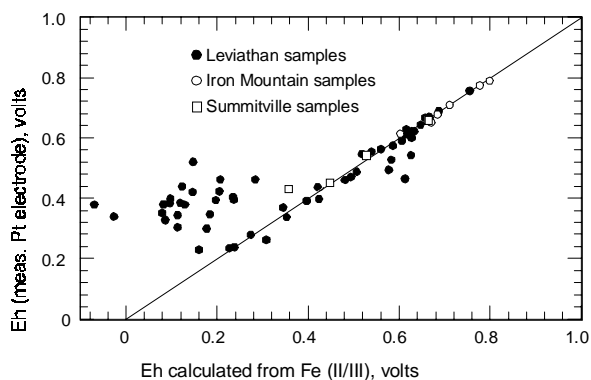
Figure 1. *Comparison of calculated with measured Eh.*
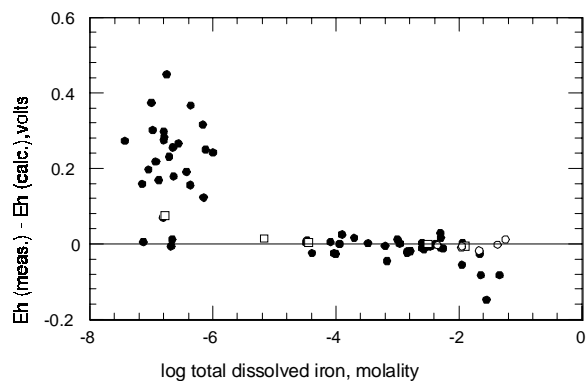
Figure 2. *Difference in Eh as a function of Fe molarity.*

electrode. However, the O_2/H_2O redox equilibrium potential is never reached because oxygen is not sufficiently electroactive. Hence, field studies have been able to demonstrate the same equilibrium response of a platinum electrode to the Fe(II/III) redox couple as in the lab. This study also shows the reliability of the speciation code. Similar success has been shown with over 50 measurements of $a_{sulfide}$ compared to Eh electrode measurements by Berner (1963) for anoxic marine sediments. Boulegue and Michard (1979) made similar measurements in sulfide-rich springs using acid-base titrations. The difficulty with these field measurements is that the slightest trace of oxygen can produce polysulfides, thiosulfate, and elemental sulfur which will cause deviations in the Eh measurement. Likewise, for anoxic ground waters high in iron, the introduction of a well, pumps, and sampling lines causes oxygen to enter the sampling system and instantaneously oxidizes any reduced ferrous iron if the pH is circumneutral. The result is the precipitation of hydrated ferric oxides which will tend to cause a $Fe(II)/Fe(OH)_3$ redox couple to occur regardless of whether or not it actually occurs in the unaltered ground water. The only other example that

might be approaching equilibrium is the U(IV/VI) redox equilibrium for 6 Finnish ground-water samples from the work of Ahonen et al. (1994). No other redox couples in natural aquatic systems are known to produce an equilibrium potential at an electrode surface. Furthermore, when two or more redox couples have been measured on the same water sample, they do not give the same Eh value (Nordstrom et al., 1979; Lindberg and Runnells, 1984), and they should not be expected to give the same value because they tend to react at different rates with different mechanisms. If redox species all came to equilibrium it would destroy life. Life depends on redox gradients and redox disequilibria. Geochemical codes that force redox equilibrium for all elements are grossly oversimplified and cannot be expected to reflect realistic redox conditions (unless temperatures $> 100°C$). There are only three approaches that will permit successful application of geochemical models to redox reactions: (1) determine individual redox species analytically, (2) apply independent speciation to reduced and oxidized forms of the species, and (3) apply mass balances (Parkhurst and Plummer, 1993). Changes in pH that reflect pyrite oxidation and aqueous iron oxidation can be simulated effectively by speciation and mass balances if a judicious choice of equilibrium constants is made (Nordstrom, 2000). The only way to determine the redox conditions of a water is to analyze the sample for those redox species of specific concern. There are several examples of the same water containing two or more of the following constituents O_2, Fe(II), Fe(III), N_2, NO_3, NH_3, H_2S, SO_4, CH_4, CO_2, and H_2. There can be no such thing as redox equilibrium or a single redox potential in these waters. The way to understand redox chemistry is to learn the rates and mechanisms of reactions, the main catalysts in the environment, and the main sources and sinks of redox active species.

Conclusions

Redox studies on aquatic systems in the lab and in natural waters lead to the following conclusions:

1. The absence of aqueous electrons in natural waters means they cannot be measured nor defined by analogy with aqueous protons.

2. Ground waters and surface waters do not have a "redox potential," $p\in$, or Eh but they do have a pH. To speak of a redox potential of an aqueous solution or natural water does not have any meaning.

3. Redox species in waters do not reach an equilibrium state readily, if at all. Redox disequilibria is the rule.

4. Redox potential measurements with platinum (or similar) electrodes are generally useless except to estimate ferrous-ferric activity ratios or sulfide activities when the concentrations are greater than about 10^{-5} m. Otherwise the potential may drift according to electrokinetic phenomena, mixed potentials, or impurities at the metal electrode surface. It is more reliable to measure such concentrations directly, where possible, and calculate the activities with a speciation model.

5. To determine the redox chemistry of a water it is necessary to determine all the relevant redox species directly. These species can be expected to react in different ways and at different rates. Homogeneous redox reactions can be rather slow and heterogeneous redox reactions can be even slower.

6. Redox species can be very sensitive to atmospheric contamination. Contamination and interferences begin with drilling a well, continue with the manner and rate of pumping, and end with a set of data that is often inconsistent or discrepant.

7. A judicious choice of redox parameters depends on site characteristics, budget, and objectives.

8. A monitoring schedule depends on site-specific factors such as flow rates, types of redox species present, rates of redox reactions, redox capacity of the system, and rates and mechanisms of processes in the vadose zone.

9. Research knowledge is in the process of finding out how redox works and how fast. The knowledge is not at a point where we can say definitively what the protocol for redox is nor can we model any specific site to predict just what will happen over time except in a general, but not necessarily helpful, sense.

References

Ahonen, L., Ervanne, H., Jaakola, T., and Blomqvist, R. 1994. Redox chemistry in uranium-rich groundwater of Palmottu uranium deposit, Finland. *Radiochimica Acta*, v. 20, pp. 1-7.

Ball, J. W. and Nordstrom, D. K. 1990. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters U.S. Geological Survey Open-File Report, 91-183, 189 p.

Bard, A. J. and Faulkner, L. R. 1980. *Electrochemical Methods.* John Wiley and Sons, New York, 718 p.

Berner, R. A. 1963. Electrode studies of hydrogen sulfide in marine sediments. *Geochimica et Cosmochimica Acta*, v. 27, pp. 563-575.

Boulegue, J. and Michard, G. 1979. Sulfur speciation and redox processes in reducing environments. In *Chemical Modeling in Aqueous Systems, Chapter 2*, ed. E. A. Jenne, American Chemical Society Symposium Series 93, American Chemical Society, Washington, D.C., pp. 25-50.

Eary, L. E. and Schramke, J. A. 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. In *Chemical Modeling of Aqueous Systems, II, Chapter 30*, eds. D. C. Melchior and R. L. Bassett, American Chemical Society, Washington, D.C., pp. 379-396.

Hart, E. J. and Anbar, M. 1970. *The Hydrated Electron.* Wiley Interscience, New York, 267 p.

Hostetler, J. D. 1984. Electrode electrons, aqueous electrons, and redox potentials in natural waters. *American Journal of Science*, v. 284, pp. 734-759.

Kempton, J. H., Lindberg, R. D., and Runnells, D. D. 1990. Numerical modeling of platinum Eh measurements by using heterogeneous electron-transfer kinetics. In *Chemical Modeling in Aqueous Systems II, Chapter 27*, eds. D. C. Melchior and R. L. Bassett, American Chemical Society Symposium Series 416, American Chemical Society, Washington, D.C., pp. 339-349.

Langmuir, D. 1971. Eh-pH determination. In *Procedures in Sedimentary Petrology, Chapter 26*, ed. R. E. Carver, Wiley-Interscience, New York, pp 597-635.

Lindberg, R. D. and Runnells, D. D. 1984. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science*, v. 225, pp. 925- 927.

Macalady, D. L., Langmuir, D., Grundl, T., and Elzerman, A. 1990. Use of model-generated Fe^{3+} ion activities to compute Eh and ferric oxyhydroxide solubilities in anaerobic systems. In *Chemical Modeling in Aqueous Systems, Chapter 28*, ed. E. A. Jenne, American Chemical Society Symposium Series 93, American Chemical Society, Washington, D.C., pp. 350-367.

Morris, J. C. and Stumm, W. 1967. Redox equilibria and measurements of potentials in the aquatic environment. In *Equilibrium Concepts in Natural Water Systems, Chapter 13*, ed. W. Stumm, American

Chemical Society Advances in Chemistry Series 67, American Chemical Society, Washington, D.C., pp. 270-285.

Nordstrom, D. K. 2000. Advances in the hydrogeochemistry and microbiology of acid mine waters. *International Geology Review*, v. 42, pp. 499-515.

Nordstrom, D. K. and Wilde, F. D. 1998. Reduction-oxidation potential (electrode method). In *National Field Manual for the Collection of Water-Quality Data*, eds. F. D. Wilde, D. B. Radtke, J. Gibs, and R. T. Iwatsubo, U.S. Geological Survey Techniques in Water-Resources Investigations Book 9, Handbooks for Water-Resources Investigations, A6.5.

Nordstrom, D. K., Jenne, E. A., and Ball, J. W. 1979. Redox equilibria of iron in acid mine waters. In *Chemical Modeling in Aqueous Systems, Chapter 3*, ed. E. A. Jenne, American Chemical Society Symposium Series 93, American Chemical Society, Washington, D.C., pp. 51-79.

Parkhurst, D. L. and Plummer, L. N. 1993. Geochemical models. In *Regional Ground-Water Quality, Chapter 9*, ed. W. M. Alley, Van Nostrand Reinhold, New York, pp. 199-226.

Peschanski, D. and Valensi, G. 1949. Contribution a l'electrochemie des solutions aqueuses de polysulfures. *Journal de Chimie Physique*, v. 46, pp. 602-619.

Runnells, D. D. and Skoda, R. E. 1990. Redox modeling of arsenic in the presence of iron: Applications to equilibrium computer modeling. In *Proceedings: Environmental Research Conference on Groundwater Quality and Waste Disposal*, EPRI Report EN-6749, Palo Alto, California.

Runnells, D. D., Lindberg, R. D., and Kempton, J. H. 1987. Irreversibility of Se(VI)/Se(IV) redox couple in synthetic basaltic ground water at 25°C and 75°C. *Materials Research Society Symposium Proceedings*, v. 84, pp. 723-733.

Stipp, S. L. 1990. Speciation in the Fe(II)-Fe(III)-SO_4-H_2O system at 25°C and low pH: Sensitivity of an equilibrium model to uncertainties. *Environmental Science and Technology*, v. 24, pp. 699-706.

Thorstenson, D. C. 1984. The concept of electron activity and its relation to redox potentials in aqueous geochemical systems. U.S. Geological Survey Open-File Report 84-072, 45 p.

To, T. B., Nordstrom, D. K., Cunningham, K. M., Ball, J. W., and McCleskey, R. B. 1999. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. *Environmental Science and Technology*, v. 33, pp. 807-813.

Redox Processes in Inorganic Remediation

Bill Deutsch

Sedgwick, ME 04676

Redox processes can play a role in subsurface remediation by either removing inorganic contaminants from ground water and immobilizing them in the solid phase or enhancing mobility in the aquifer so that the contaminants can be removed from the system. The redox process may directly or indirectly lead to remediation. An example of direct remediation is the reduction of Cr(VI) to Cr(III) and precipitation of a less soluble Cr(III) hydroxide solid. Indirect redox remediation would occur when dissolved ferrous iron is added to ground water followed by iron oxidation, precipitation of hydrous ferric oxide (HFO) and adsorption and removal of arsenic or other inorganic contaminants from ground water. Conversely, arsenic might be mobilized and removed from an aquifer by injecting a reductant to dissolve arsenic-adsorbing solids and release arsenic to the ground water, which would then be pumped from the aquifer. The purpose of this paper is to:

♦ Identify redox-sensitive contaminants

♦ Discuss natural redox conditions that attenuate movement

♦ Describe applied redox methods that immobilize contaminants

♦ Describe applied redox methods that mobilize contaminants

Additional activities at the Redox Workshop related to inorganic contaminants will generate site characterization requirements and methods of measuring important parameters. Data interpretation and use will also be discussed separately.

Redox-Sensitive Elements

Elements that occur in more than one valence state in natural environments and may be present as contaminants are listed in Table 1. These elements may be amenable to direct redox manipulation methods to produce remediation or at least contaminant concentration reduction. These elements may also be affected by

indirect redox remediation. Elements that are not redox-sensitive (such as Pb, Zn and Al) may also be affected by indirect redox methods.

Table 1. *Redox-Sensitive Elements Potentially Present as Contaminants in the Environment*

Elements	Redox State
Antimony (Sb)	III, V
Mercury (Hg)	0, I, II
Arsenic (As)	III, V
Nitrogen (N)	-III, 0, III, V
Carbon (C)	-IV to IV
Molybdenum (Mo)	III, IV, V, VI
Chromium (Cr)	III, VI
Selenium (Se)	-II, 0, IV, VI
Copper (Cu)	I, II
Sulfur (S)	-II to VI
Iron (Fe)	II, III
Vanadium (V)	III, IV, V
Manganese (Mn)	II, III, IV
Uranium (U)	IV, VI

Many applied remediation methods for inorganic compounds are based on natural processes that attenuate or immobilize these compounds in the subsurface. This discussion of remediation methods will start by looking at these natural environments that concentrate inorganic compounds by redox processes.

Redox Barriers to Inorganic Compounds

The concept of a geochemical barrier in the natural system was first suggested by Perel'man in 1961 (Perel'man, 1986, Geochemical barriers: theory and practical applications. *Applied Geochemistry*, 1:669-680). A geochemical barrier is a zone in the subsurface characterized by a sharp change in physical or chemical environment along the flowpath and is often associated

with the precipitation of elements from solution. Redox barriers are classified as a type of physico-chemical barrier, which also includes alkaline, acidic, adsorption, evaporation and thermodynamic barriers. Three types of redox barriers have been described: oxidizing, reducing with sulfide, and reducing without sulfide. Because barriers represent a change in environmental condition, each type of barrier must be considered in the context of the three redox types of water that might enter the barrier. For example, weakly oxidizing water may encounter a strongly oxidizing barrier or a reducing barrier with or without sulfide. Finally, the pH of the aquifer will affect the type of element immobilized by the geochemical barrier. Table 2 provides the potential encounters developed by Perel'man and the elements that might be concentrated at the three redox barriers.

Examples of the geochemical barriers listed in Table 2 include oxidation and precipitation of iron from mildly oxidizing or reducing waters without sulfide downgradient of a landfill; presence of U, As, and Mo in roll front deposits formed by reduction of oxidizing water; and precipitation of metal sulfides when oxidizing water becomes reduced by organic matter in the presence of sulfide. Table 2 shows the types of direct redox remediation that might occur in geochemical barriers. The barrier will lower concentrations of inorganic contaminants, however the table does not provide information on whether the resulting concentration will be below a remediation cleanup level. The equilibrium

solution concentration will be the solubility of the mineral in the barrier environment. This can be estimated by proper characterization of the environment and calculating the solubility of minerals in that environment.

An indirect natural redox attenuation process is the precipitation of iron and manganese hydroxides followed by adsorption of other contaminants. These solids have a predominantly positive surface charge at neutral to acidic pH, and in this pH range will preferentially adsorb elements that are anionic in groundwater such as arsenic (AsO_4^{3-}, $AsO_3^{3-)}$), chromium (CrO_4^{2-}), selenium (SeO_4^{2-}, SeO_3^{2-}), and molybdenum (MoO_4^{2-}). At pH higher than 7 to 8, the mineral surfaces are predominantly negatively charged and they will be better adsorbents for cations such as Cu^{2+}, Cd^{2+}, Zn^{2+} and Ba^{2+}.

Nitrate is an inorganic contaminant that does not form minerals and thus would not be removed from solution and concentrated in a geochemical barrier. The fate of nitrate is usually tied to biological redox processes that reduce nitrogen to N_2 or NH_4^+.

Methods of Immobilizing Inorganic Contaminants

Applied techniques for immobilizing inorganic contaminants are generally based on the well-documented natural processes that impact element mobility, particularly at geochemical barriers. If manganese concentrations in mildly oxidizing water downgradient from a landfill must be lowered, Table 2 suggests either

Table 2.   *Elements Concentrated at Geochemical Redox Barriers (after Perel'man 1986)*

Barrier Type	pH < 3	pH 3 – 6.5	pH 6.5 – 8.5	pH > 8.5
	Oxidizing	**Water Entering**	**Barrier**	
Oxidizing	Fe	Fe, Mn, Co	Mn	-
Reducing w/ H₂S	Tl, Cu, Hg, Pb. Cd, Sn, As, Sb, Mo, U	Tl, Mn, Co, Ni, Cu, Zn, Pb, Cd, Hg, Sn, Cr, Mo, U	Tl, Cr, Mo, U, Se, V	Cu, Ag, Zn, Cr, Mo, U, V, As
Reducing w/o H₂S	Cu, U, Mo	Cu, U, Mo	Cu, Cr, U, Mo, Se, V	Cu, Ag, Cr, Mo, U, Se, V, As
	Reducing	**H₂S Water Into**	**Barrier**	
Oxidizing	S, Se, (Fe)	S, Se	S, Se	S, Se
Reducing w/ H₂S	-	-	-	-
Reducing w/o H₂S	-	-	-	-
	Reducing	**Water w/o H₂S**	**Into Barrier**	
Oxidizing	Fe	Fe, Mn, Co	(Fe), Mn, Co	(Mn)
Reducing w/ H₂S	Tl, Pb, Cd, Sn	Tl, Fe, Co, Ni, Pb, Cu, Zn, Cd, Hg, U	Tl, Fe, Co, Ni, Cu, Zn, Cd, Hg, (Mo, U)	Tl, Cu, Zn, Cd, Hg, Mn, (Fe, Co, Ni, U)
Reducing w/o H₂S	Cu, U, Mo	Cu, U, Mo	Mo, U	Mo, U

Elements in parentheses are less commonly found in the association

Table 3. *Potential Oxidants and Reductants for Inorganic Remediation*

Oxidants	Elements Tested
Dissolved Oxygen	Fe
Air	U
Ozone	
Oxygen Release Compound (ORC®)	
$KMnO_4$	
Fenton's Reagent	
Reductants	**Elements Tested**
Fe^o	Cr, U, Tc, NO_3^-, Mo
Dithionite ($S_2O_4^{2-}$)	Cr, U, Tc, Pu
Na_2S	U, Cr (Ag, As, Cd, Hg, Ni, Pb, Zn)
H_2S	Cr
$FeSO_4 \cdot xH_2O$	Cr
Hydrogen Release Compound (HRC™)	Cr
Organic Material	SO_4^{2-}, NO_3^-, Se, Fe(S), Ni(S)

increasing the redox potential to precipitate a less soluble Mn(IV) oxide or reducing the redox potential and adding sulfide to form a less soluble sulfide mineral. Some of the issues to consider in the applied redox approach are the type and amount of reactant, means of emplacement, reaction kinetics, unwanted byproducts, solubility of contaminant-containing mineral, and geochemical stability of the imposed barrier environment.

The types of oxidizing and reducing compounds that have been tested or suggested to lower inorganic contaminant concentrations in an aquifer are listed in Table 3. Most of these compounds can be dissolved in water and injected into the aquifer. Air and ozone are added to the subsurface in a vapor phase. Elemental iron (Fe^o) is a solid that is emplaced in a trench that intercepts the contaminated water. It has been shown to be effective not only at reducing the concentrations of inorganic contaminants (particularly chromate and uranium) but also chlorinated volatile organic compounds such as PCE and TCE. As shown in Table 3, the current list of reagents is fairly limited and the elements tested are not extensive. This type of remediation is expected to expand as its effectiveness becomes more widely known and the injection of reagents to achieve remediation becomes more commonly accepted by regulatory agencies.

In general, the amount of oxidant or reductant that must be added to achieve remediation will not exceed 100 mg/L. For example to reduce 50 mg/L Cr(VI) in CrO_4^{2-} to Cr(III) would require only 12 mg/L sulfide, assuming all the sulfide is oxidized to sulfate. An important consideration for some reactions is the rate of oxidation or reduction, which may be slow in relation to

a remediation timeframe. For example, the half-life for chromium reduction may be several years at pHs greater than 7 unless a strong reductant is applied. The solubility of the reaction product containing the contaminant can be estimated by ion speciation calculation using the projected environmental conditions during reagent injection. The long-term solubility of the mineral must also be estimated using the aquifer geochemical conditions that are expected to prevail after active remediation has ceased.

Methods of Mobilizing Inorganic Contaminants

It is preferable to leave a contaminant in place if its mobile concentration can be reduced to below a cleanup level, however in some instances immobilization may not be possible and removal is necessary. Removal of an inorganic contaminant requires not just extraction of contaminated ground water but also dissolution of contaminant-containing minerals and perhaps desorption of the contaminant from the surface of solids. Table 2 can be used to develop redox methods of removing contaminants from the solid phase. For example, if Table 2 shows that an element is concentrated under reducing conditions (e.g., Cr, U, Mo, Se), then creating oxidizing conditions in the aquifer should mobilize the contaminant. This is exactly the process used to mine uranium by in-situ leach methods. Oxygen is added to the subsurface where uranium has been concentrated by natural processes in the reduced U(IV) mineral uraninite (UO_2). Uraninite is soluble under the imposed oxidizing conditions leading to its dissolution and the removal of dissolved uranium in extraction wells.

Table 4.   *Redox Manipulation to Mobilize Inorganic Contaminants*

Mobilizing Environments	pH < 3	pH 3 – 6.5	pH 6.5 – 8.5	pH > 8.5
Reducing w/o Sulfide	Fe, Se, S	**Initial Oxidizing** Fe, Mn, Co, Se, S	**Environment** Fe, Mn, Co, Se, S	Mn, Se, S
Oxidizing	**Initial** Tl, Cu, Hg, Pb. Cd, Sn, As, Sb, Mo, U	**Reducing w/ S^{2-}** Tl, Mn, Co, Ni, Cu, Zn, Pb, Cd, Hg, Sn, Cr, Mo, U	**Environment** Tl, Cr, Mo, U, Se, V	Cu, Ag, Zn, Cr, Mo, U, V, As
Oxidizing	**Initial** Cu, U, Mo	**Reducing w/o S^{2-}** Cu, U, Mo	**Environment** Cu, Cr, U, Mo, Se, V	Cu, Ag, Cr, Mo, U, Se, V, As

Table 4 shows imposed redox conditions that are expected to mobilize contaminants concentrated in three types of subsurface environments. The methods of inducing redox conditions are the same as those given in Table 3. Mobilization of contaminants can be complicated by the strong adsorption and high capacity of iron and manganese oxyhydroxides for other metals. If oxidizing conditions are generated in a reducing environment to mobilize metals, iron and manganese solids may precipitate and remove from solution some of the metals that are the target of remediation. This occurrence may require a stepwise mobilization process to first oxidize the elements in the minerals and then reduce and dissolve iron and manganese oxyhydroxides to release adsorbed contaminants.

Natural and applied redox processes can be used to achieve remediation goals at sites contaminated with inorganic compounds. This has been documented for many elements by the existence of natural geochemical barriers, and recent applied techniques have shown that the natural redox processes can be enhanced by chemical addition. A goal of the Redox Workshop has been to expand the use of redox processes for inorganic remediation by providing examples of natural attenuation analogues and the application of these natural processes to enhance applied restoration techniques.

The Relevance of Redox to Remediation

Andy Davis

Geomega
Boulder, CO 80303

Introduction

Redox conditions represent an important control on the speciation of metals including As (III/V), Cr (III/VI), Sb (III/V), and Se (IV/VI). Although the measurement and environmental geochemistry of these constituents is well understood, application of this knowledge in setting regulatory standards for soils, ground water, surface water and sediments is rare. Hence, bulk chemistry is usually considered in setting standards rather than evaluating the ameliorating effect of metal valence on toxicity and mobility. Given the escalating costs of environmental restitution, it is critical that reasonable options, including the influence of valence, be considered in setting realistic, risk-based cleanup goals.

This paper provides examples of the value of understanding redox conditions and species in the environment. Arsenic is less bioavailable in the As(III) form in mine wastes due to sparing dissolution of these less soluble forms in the short GI tract residence times, while selenium form in sediment is important because Se(IV) is less toxic than Se(VI). AVS/SEM analysis on both metalloids has demonstrated that they are incorporated in framboidal pyrite, rendering them non-bioavailable.

In addition, novel approaches to constrain metal solubility by modifying the valence state are realistic goals. For example, the mitigating influence of precipitation reactions in sediments is demonstrated through sulfate/sulfide reduction/precipitation and coincident encapsulation of metals in a biologically active system in Richmond, California. For example, the solubility of Cr(III) in acid ground waters can be reduced by careful pH control while remediation of acid pit lakes can be effected by modification of the pH with concomitant precipitation of amorphous ferric hydroxide as the Fe(II)/Fe(III) ratios change, and sequestration of previously soluble ions.

The practical application of redox conditions to remedial actions is of interest, first from the perspective of "does it matter," and secondly in defining how to implement closure in the event that redox conditions are relevant. From the closure/remediation perspective, the importance of redox is closely related to the implied risk associated with different valence states. For example, As(III) is more toxic in groundwater whereas As(V) may be more toxic in an estuarine setting, depending on the exposure pathway; Cr(VI) is generally more toxic than Cr(III), while Se(VI) is more toxic than Se(IV).

From a pragmatic perspective, although the relative risk associated with different valence states may be known, translating theory into practical closure that meets regulatory standards is rare. For example, contaminated environmental systems are complex and heterogeneous, frequently consisting of multiple compartments and contaminants, while translating theory into practical reality is fraught with uncertainty. In addition, the significance of the issue and a reasonable benchmark representing success is generally not understood by the decision maker, while with few exceptions, the remedial actions do not finesse the benefit to be accrued by altering valence states in the environment.

Despite such recidivism, where viable, manipulation of redox conditions may portend significant financial benefit and should be included as a weapon in the remedial arsenal. The application of redox can be divided into the following areas:

1) Active manipulation (e.g., redox control/response)

2) Constraints on risk (e.g., definition of valence in land application, metal bioavailability), and

3) Passive long-term (e.g., intrinsic remediation by dechlorination)

This paper reviews the genesis of the redox-based standards, describes a few examples where redox states have been incorporated into closure/remedial measures, forecasts what may work and whether success or failure can be predicted, and discusses issues that are likely to become important in the future.

The Evolution of Valence-Based Risk

Promulgation of the Aquatic Water Quality Control (AWQC) Standards may represent the initial foray that led to a description of the relative toxicities of metal valences in the "Gold Book" (EPA, 1986). The later document identified a range of conditions that affect different trophic levels. For example, the alga, selenastrum capricornutum was reported 45 times more sensitive to As(V) than As(III), although other data present conflicting information. In general, the resiliency to arsenic is species and salinity specific.

Chromium toxicity appears more straightforward, in that there is general concurrence that Cr(III) is less toxic than Cr(VI). For example the AWQC standard for Cr(VI) is 100 µg/l, while for Cr(III) it is 3,433 µg/l. In freshwater, the acute toxicity for Se(IV) is reported as 260 µg/l, while for Se(VI) it is 760 µg/l. However, there has been no directives that clearly identify the relationship between valence species and the total dissolved concentration in aqueous or sediment systems, and the ramifications to risk assessments and, ultimately, to selection of cleanup standards.

Precipitation of Chromium from Ground Water

At a former chemical facility in Wilmington, a historical release of chromium sulfate has generated an acidic plume (pH~3) of Dense Aqueous Phase Liquid (DAPL) with complex chemical characteristics. A Release Abatement Measure (RAM) is being instituted to assess the effectiveness of *in-situ* precipitation of ground water solutes using various chemical agents applied in solution or slurry through existing wells with the objective of raising the pH, while avoiding oxidation of the Cr(III) to soluble Cr(VI). The effectiveness will be determined by monitoring the areal extent of DAPL precipitation. The goal of this treatment is to mitigate the flux of solutes from the DAPL to the overlying ground water that discharges into the on-site ditch system, hence reducing precipitates forming in the ditch as ferrous iron in solution discharges and precipitates in surface water.

In the target area, the local ground water/diffuse layer/DAPL profile consists of approximately 6 feet of DAPL overlain by a 3 foot thick diffuse layer. Comparison of ground water surface elevations from co-located wells in the region of the ditches demonstrates that ground water discharges to the ditch system resulting in the formation of floc. It is anticipated that the DAPL RAM will inter DAPL, reducing the solute flux to the South Ditch, and eventually floc formation.

Bench-scale studies observed decreases in metal concentrations attributed both to precipitation reactions and to changes in solubility due to the more neutral pH achieved through treatment. For example, chromium decreased from 2,000 mg/l to < 0.1mg/l, while similar decreases were observed for Al and Fe. Additionally, sulfate concentrations decreased by up to 30%. Hence, neutralization of acidic DAPL to circumneutral (~6) conditions should result in a decrease in DAPL solubility by a precipitation reaction of the form:

$$9 \ Fe^{+2} + \ Cr_2[SO_4]_3 + \ 24 \ OH^- \Rightarrow 8 \ Fe_{0.75}Cr_{0.25}(OH)_3 + 3FeSO_4^0 + 6 \ e^-$$
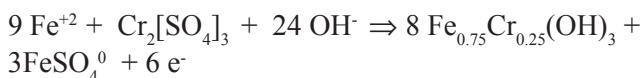
with the relevant redox reaction controlled by oxidation of ferrous to ferric iron and coprecipitation of Cr(III) in the amorphous ferric hydroxide matrix. The optimal liquor concentration determined from the bench scale testing will be applied to the target area. The neutralizing liquor and the sodium bromide tracer (at 100 mg/L effective bromide concentration) will be initially delivered into the injection well by passive head differential. As delivery slows, the liquor may be pumped under pressure if feasible.

Minimizing risk by recognizing inert sedimentary phases

Castro Creek, an industrial drainage ditch that historically received disposed process fluids, contains residual arsenic in the sediments. This project initially identified solubility-constraining reactions and then sought to enhance the natural conditions to further influence pore water arsenic.

The molar SEM/AVS ratios for arsenic are well below 1, ranging from 0.0003 at B2 to 0.62 at F. Although SEM/AVS data for arsenic has not been directly coupled with arsenic toxicity, other studies (Davis et al., 1996) have demonstrated that when the SEM/AVS ratio is <1, bioaccumulation of arsenic does not occur in higher trophic level receptors (fish). Therefore, based on these studies (Davis et al., 1996), the ambient geochemical conditions of the creek sediments facilitates sequestration of arsenic in insoluble mineral phases such as Fe(As)S, Fe(As)SO$_4$, and AsS$_2$ that are likely to reduce As bioavailability in a manner akin to the metal-sulfide complexes described by DiToro (1990 and 1992).

Encouraging Arsenic Reduction in Sediments

Recognizing the benefits to be realized from a reducing sediment environment resulted in research (currently ongoing) to facilitate additional removal of

arsenic from pore water at the site. Currently a remedial design scheme intended to remove arsenic (As) and control remnant As mobility in marsh sediment using a Peat-Iron-Gypsum (PIG) blanket to minimize As solubility by reducing As(V) to As(III) and facilitating co-precipitation of As in an inert FeS_2 (e.g., $Fe_xAs_{1-x}S_2$ and $Fe_xAs_{1-x}SO_4$) phase is being investigated.

Iron oxide and sulfates containing up to 3,000 mg/kg As have been found precipitating in creek sediments suggesting that natural conditions in these areas are conducive to immobilization of incorporated As. Theoretically, addition of appropriate amendments would attenuate most of the remaining soluble pore-water As over the ambient range of redox conditions, also reducing the flux of As into the creek.

A bench scale study was run for 24 hours (thought to be an adequate period for pyrite precipitation; Rickard 1995) under zero-head space conditions in a nitrogen atmosphere and each bottle sacrificed after 7 days. The aqueous and solid phases were separated by centrifugation and samples of each collected and analyzed. Measured geochemical parameters include SO_4^{2-}, S^{2-}, Fe(II), Fe(III), pH, Eh, and specific conductivity. A sample was also analyzed for inorganic arsenic species [As (III)/(V)]. The results were surprising in that the reaction kinetics were much slower than has been reported in the literature using pure materials.

Demonstrating pesticide dechlorination as part of intrinsic remediation

An investigation was undertaken to ascertain the potential and actual degradation of chlorinated pesticides (α-, β-, and γ-BHC, DDT, and DDD), and the purgeable aromatic compounds (ethylbenzene and xylene) at the Marzone Superfund Site, Tifton, Georgia. The objective was to test the hypothesis that Monitored Natural Attenuation (MNA) would provide an effective ground-water polishing strategy to augment the remedial collector trench recently installed downgradient of the site. The trench effectively intercepted over 90% of the mass of all Compounds of Concern (COCs) while concentrations downgradient of the trench are at, or close to, the relevant numerical standards.

The geochemical conditions were characterized by analyzing redox chemistry (Eh, iron and sulfur valence states), gas concentrations (hydrogen, methane, ethane, ethene), and other indicators (chloride, alkalinity, etc). These data demonstrated that upgradient ground water that was unaffected by the historical Marzone Site

operations is moderately aerobic and oxidizing, becoming moderately reducing proximal to the operating facility. In the core of the plume, conditions become strongly reducing based on the increase in the relative ratio of hydrogen, the presence of dissolved iron exclusively in the ferrous form, and on the concomitant sag in the oxygen ratio. Downgradient of the plume core, redox conditions are moderately reducing and methanogenic, and again become more oxidizing at the furthest downgradient location, where site ground-water oxygen concentrations are highest.

The historical COC data demonstrated that in most wells, COC concentrations have decreased over the 8 years since monitoring began, while a suite of degradation products provided conclusive evidence for dechlorination. The results provide evidence that the geochemical environment is conducive for mineralization, while the analytical chemical data demonstrate that MNA represents a viable alternative to reach the final remedial goals.

Closure of Bald Mountain Heap #1

Placer Dome is in the process of obtaining approval from the Nevada Division of Environmental Protection (NDEP) to close heap leach Pad #1 at the Bald Mountain Mine (BMM), located in White Pine County, Nevada. Specifically, the closure includes:

♦ Applying heap effluent to site soils and possibly increasing the application rate by enhancing evaporation,

♦ Re-grading the pad to stabilize the pad slopes for erosion control and to control runoff, and

♦ Covering the heap with site soils and revegetating to minimize runoff and infiltration of meteoric waters, while meeting risk objectives for plants, livestock, and wildlife.

Groundwater in the vicinity of the site is approximately 500 feet below the surface (Hydro-Search, 1981), and is therefore unlikely to be impacted at reasonable application rates.

Water quality in the barren and pregnant ponds associated with Pad #1 are shown for constituents that have on occasion exceeded standards since 1998. Concentrations of a few constituents have decreased since 1998 to below or near NDEP standards (CN, Hg, Ni), while others have consistently remained above the standards (Sb, As, NO_3-NO_2, Se, SO_4, pH).

A batch attenuation test indicated Langmuirean solute behavior, from which n and K_d were obtained. For some compounds (e.g., SO_4) sorption is minimal, while for others (e.g., As) sorption will effectively attenuate solutes in the soil horizon.

Results from the speciation analyses for As, Se, and Sb show that the predominant species are As(V), Se(VI), and Sb(V). For As and Sb, the predominant valence state is the less toxic of the forms, while Se (VI) is of similar toxicity to Se (IV). The predominant species detected for As, Se, and Sb are consistent with the generally oxidizing and alkaline geochemical conditions measured for the heap effluent. For example, As(V) constituted >80% of the total As, Se(VI) was >90% of the total Se, and Sb(V) was >90% of the total Sb analyzed. The total solute concentration based on the sum of the two valence states is also in good agreement with the total solute concentration reported by SVL Analytical. The effect of attenuation on solute concentration where solute lost from solution by sorption to soils is illustrated by the difference between the sorption data and the theoretical 1:1 equivalence curve.

Conclusions

Redox can play a significant role in modifying metal solubility. The applications are far-reaching, ranging from incorporation in human health and ecological risk assessments, the development of novel methods to remediate sites, to demonstration of natural attenuation. However, while understanding and applying redox strategies is important, the evolving technology must be applied within a regulatory framework that will allow their incorporation into the panoply of environmental data interpretation and restitution. At the same time, it is incumbent on industry to demonstrate that redox strategies really do provide meaningful and realistic solutions to environmental problems.

References

Davis, A. and Olsen, R. L. 1995. The geochemistry of chromium migration and remediation in the subsurface. *Ground Water*, v. 33, pp. 759-768.

DiToro, D., Mahoney, J., Hansen, D., Scott, K., Hicks, M., Mayr, S., and Redmond, M. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environmental Toxicology and Chemistry*, v. 9, pp. 1487-1502.

DiToro, D., Mahoney, J., Hansen, D., Scott, K., Carlson, A., and Ankley, G. 1992. Acid volatile sulfide predicts acute toxicity of cadmium and nickel in sediments. *Environmental Science and Technology*, v. 26, pp. 96-101.

PTI. 1997. *Evaluation of Reactive Barrier Effectiveness Batch and Column Tests at the Wilmington, Massachusetts Site*. December, 1997.

Rickard, D. T. 1995. Kinetics of FeS precipitation: Part 1. Competing reaction mechanisms. *Geochimica et Cosmochimica Acta*, v. 59, pp. 4367-4379.

Group Discussion Summaries

Six breakout sessions were organized to summarize and evaluate key considerations during assessment and implementation of remedial strategies for redox sensitive contaminants. Three concurrent sessions took place in the morning and afternoon of the second day of the Workshop. The focus of the three morning sessions centered on identification of approaches and parameters necessary to evaluate remediation of petroleum hydrocarbons, chlorinated hydrocarbons, MTBE, and inorganics. The focus of the three afternoon sessions centered on aqueous, gas phase, and solid phase measurement issues. Items emphasized during the afternoon sessions, in part, depended on the outcome of the morning sessions.

Before arriving at the workshop participants were delivered a set of questions that along with the Plenary Presentations, served as a launch point for the small group discussions. These questions are provided below.

Session 1. Redox processes in petroleum hydrocarbon remediation

(R. Ludwig, M. Barcelona, A. Azadpour-Keeley, J. Barker, P. Bradley, I. Cozzarelli, R. Ford, S. Warner, E. Hartzell, D. Macalady, K. O'Reilly, K. Piontek, D. Vroblesky, D. Kampbell)

What remediation processes specific to petroleum hydrocarbons require the need for redox measurements during site characterization and/or remediation (e.g., MNA, electron acceptor addition, thermal treatment, surfactant flushing, etc)? Do we need to distinguish between categories of petroleum hydrocarbons (e.g., aromatics, PAHs, alkenes, alkanes, etc.)? What specific redox measurements are required (e.g., Eh, pH, DO, Fe^{2+}, etc) and how are the measurements used (e.g., determining feasibility *vs.* non-feasibility of specific remedial processes, predicting rates of clean-up, determination of enhancements that could potentially be used to accelerate clean-up, etc.)?

Session 2. Redox processes in chlorinated hydrocarbon and MTBE remediation

(J. Wilson, F. Chapelle, J. Amonette, C. Braun, J. Ingle, S. Jones, R. Lee, M. Lorah, C. Macon, P. Groeber, R. Pirkle, T. Sivavec, J. Szecsody, C. Tebes Steven, J. Washington, E. Weber, T. Wiedemeier, B. Wilson)

What remediation processes specific to chlorinated hydrocarbons and MTBE require the need for redox measurements during site characterization and/or remediation (e.g., MNA, enhanced bioremediation, zero valent metal treatment, *in-situ* oxidation, in-situ redox manipulation, etc.)? Do we need to distinguish between categories of chlorinated hydrocarbons (e.g., chlorinated methanes, chlorinated ethenes, chlorinated ethanes, etc.)? What specific redox measurements are required (e.g., Eh, pH, DO, Fe^{2+}, etc.) and how are the measurements used (e.g., determining feasibility *vs.* non-feasibility of specific remedial processes, predicting rates of clean-up, determination of enhancements that could potentially be used to accelerate clean-up, etc.)?

Session 3. Redox processes in inorganic remediation

(R. Puls, B. Deutsch, J. Westall, S. Benner, A. Davis, J. Fruchter, J. Herman, P. Longmire, D. Luce, R. McGregor, D.K. Nordstrom, C. Ptacek, S. Schmelling, J. Shockley, C. Su, R. Wilkin, D. Willey, K. Cook)

What remediation processes specific to inorganic contaminants require the need for redox measurements during site characterization and/or remediation (e.g., MNA, zero valent metal treatment, *in-situ* redox manipulation, etc.)? What parameters must be measured during site assessment and remediation? Are the required parameter measurements universal or contaminant-specific? Is there a universal set of parameters that is sufficient for all remedial strategies? What specific redox measurements are required (e.g., Eh, pH, DO, Fe^{2+}, etc) and how are the measurements used? Is there a need to evaluate redox characteristics of the solid matrix in addition to the mobile phase?

Session 4. Measurement Issues: Geochemical Parameters

(R. Wilkin, C. Ptacek, A. Azadpour-Keeley, B. Deutsch, J. Fruchter, J. Ingle, P. Longmire, M. Lorah, D. Luce, K. Cook, D. Macalady, D.K. Nordstrom, T. Sivavec, C. Su, J. Westall, B. Wilson, J. Wilson, T. Wiedemeier, K. Piontek)

Participants in this breakout group will identify and discuss the techniques used to determine the concentrations of key redox indicator species, such as Dissolved Oxygen, Ferrous Iron, and Hydrogen Sulfide, as well as the Oxidation-Reduction Potential (ORP/Eh). Group discussion will focus on identifying the best practices for sample collection, sample handling, documentation, and measurement techniques for these key parameters. We will attempt to identify rigorous QA/QC procedures that can be adopted in the field, and determine how these parameters may be practically applied to understand the migration and evolution of contaminant plumes.

Session 5. Measurement Issues: Dissolved Gases

(D. Kampbell, F. Chapelle, J. Barker, P. Bradley, C. Braun, S. Jones, R. Lee, R. Ludwig, P. McLoughlin, K. O'Reilly, P. Groeber, R. Pirkle, J. Shockley, D. Vroblesky, S. Warner)

Participants in this breakout group will identify the acceptable methods for determining the concentrations of dissolved gases in ground water. Discussion will be primarily focused on hydrogen, ethene/ethane, and methane. Group discussion will center on the best practices for sample collection, sample handling, documentation, and measurement techniques for these gas species. A specific question to be discussed is how is gas phase characterization used to recognize the footprint and dynamics of a contaminant plume?

Session 6. Measurement Issues: Solid Phase

(R. Ford, J. Herman, J. Amonette, M. Barcelona, S. Benner, I. Cozzarelli, A. Davis, C. Macon, R. McGregor, R. Puls, S. Schmelling, J. Szecsody, C. Tebes Steven, J. Washington, E. Weber, E. Hartzell)

Participants in this breakout group will identify the key solid phase parameters relevant to redox-controlled processes active during *in-situ* remediation of ground water. In addition, we will identify acceptable methods for sample collection and characterization. Emphasis will be placed on solid-phase iron. An example question to be addressed is what is the most appropriate method(s) for quantifying the fraction of Fe-bearing minerals that function as electron acceptors during microbially mediated redox transformation of a contaminant? Discussion will also address analytical characterization and the role of solid phase sulfur and carbon during remedial assessment and implementation.

Session 1 Summary:
Redox Processes in Petroleum Hydrocarbon Site Characterization and Remediation

Ralph Ludwig, Michael Barcelona, and Keith Piontek

1.1 Introduction

The objective of this session was to evaluate the value and potential role of redox parameter measurements in petroleum hydrocarbon site characterization and remediation. (Redox parameter measurements are herein defined as any parameter measurement that provides insight into the electron transfer status of an aquifer system or the propensity of an aquifer system to donate or accept electrons.) General conclusions of the session included:

1. The need to measure redox parameters at petroleum hydrocarbon impacted sites will depend on site-specific questions that need to be answered and the remedial strategies that are under consideration. Knowledge of the electron transfer (redox) status within an aquifer will not always be required.

2. Collection of at least some redox parameters such as dissolved oxygen, dissolved (ferrous) iron, and dissolved manganese can be very beneficial in the initial stages of site characterization to help develop a conceptual model for the site and to aid in screening potential remedial strategies. The success or failure of some remedial strategies can be impacted by the electron transfer status of the aquifer.

3. Additional redox parameter measurements including dissolved nitrate/nitrite, dissolved sulfate, methane, dissolved carbon dioxide (as measured by acidimetric titration), and oxidation-reduction potential (e.g., electrode-based ORP measurements) may be useful particularly in cases where a natural or enhanced bioremediation strategy is under consideration.

4. In cases where an electrode-based redox potential (ORP) measurement is made, the measurements should be used for qualitative purposes only to support other redox parameter measurements in the development of the site conceptual model. No direct effort should be made to link electrode-based redox potential (ORP) measurements to specific electron acceptor pathways or to the speciation of redox sensitive species in the aquifer.

5. Redox parameter measurements should not be used as surrogate measurements to reduce the number of hydrocarbon monitoring locations or reduce the frequency of hydrocarbon sample collection. Redox parameter measurements should be used strictly in support of direct hydrocarbon measurements to better understand (conceptualize) subsurface processes and plume behavior at the site.

1.2 Role of Redox Parameter Measurements

Extensive research addressing petroleum hydrocarbon behavior and fate in ground water has been conducted over the past twenty years. Various in situ and ex situ technologies for remediating petroleum hydrocarbon impacted sites have been developed and utilized with varying degrees of success. Evaluation of the feasibility of using one or more remedial technologies at a particular site may in some cases benefit significantly from knowledge of the redox conditions in the subsurface. Knowledge of specific redox parameters and conditions at a site can aid in establishing baseline conditions from which the existing behavior or anticipated future behavior of a hydrocarbon plume can be evaluated. In some cases, redox parameters may also be used as a cost-effective means of evaluating the performance of specific remedial technologies.

Three key questions will generally need to be answered in assessing the role of redox parameter measurements at petroleum hydrocarbon impacted sites.

1. Will knowledge of the redox status in the aquifer be of any value in evaluating the feasibility of potential remedial strategies at the site?
2. If so, which redox parameter measurements might be useful?
3. Will the redox parameter measurements be used for qualitative or quantitative purposes?

Knowledge of the redox status of a hydrocarbon impacted aquifer system could certainly be important should in-situ bioremediation technologies be under consideration. Specifically, the presence/absence and distribution of electron acceptors can have important implications with regard to biodegradation pathways and plume behavior. Petroleum hydrocarbons (aromatics, PAHs) as well as coal-derived hydrocarbons (e.g., cresols, phenols) generally undergo much more rapid and efficient biodegradation under aerobic (oxidizing) conditions. Thus, knowledge of the presence/absence of oxygen (and other potential electron acceptors) provides insight into existing electron and biological activity and the means by which bioactivity can potentially be enhanced. Knowledge of redox conditions can also be important in evaluating the biodegradation potential of gasoline additives such as methyl-tert butyl ether (see Session 2 Summary).

The potential use of redox parameter measurements in the evaluation of technologies other than bioremediation for hydrocarbon impacted aquifer systems will not be so obvious and will generally need to be considered on a case by case basis. For example, in the case where a thermal based remediation technology might be the preferred remedy, redox parameter measurements are not likely to be of any value. Alternatively, if a remedy involving delivery of oxygen to the subsurface is to be considered, then knowledge of specific redox parameters (e.g., dissolved iron and manganese concentrations) in the ground water and their potential impact on system performance can be important.

The use of redox data for qualitative or quantitative purposes will depend on how the redox data are to be utilized. If the objective is simply to determine which redox processes might be dominant at a particular location, then establishment of the relative presence/absence of selected electron acceptors within and outside a hydrocarbon plume will generally suffice. However, if an effort is being made to answer questions regarding electron acceptor capacity and longevity (e.g., for a monitored natural attenuation remedy), then a quantitative approach may be needed. This would require a more rigorous and defensible (and generally more sophisticated) data collection and analyses process than would be required for a qualitative analysis. The significant spatial and temporal variability of many redox parameters can make quantitative analyses at sites extremely challenging.

1.3 Site Characterization Applications

The need to collect redox parameter measurements at petroleum hydrocarbon impacted sites will depend on the site-specific questions that need to be answered. The most important information regarding petroleum hydrocarbon plume migration and behavior will generally be gained from direct knowledge of both the temporal and spatial distribution of specific contaminants of concern (e.g., BTEX compounds). Redox parameter measurements are best used as secondary lines of evidence for locating residual source areas and for better understanding, predicting, and/or confirming dissolved hydrocarbon plume migration and behavior. It is known that a strong correlation generally exists between petroleum hydrocarbon concentrations and the relative distribution of various electron acceptors and reduction products including dissolved oxygen, ferrous iron, manganese, nitrate, sulfate, and methane. This correlation results from the utilization of electron acceptors in a favored sequential order by microorganisms during oxidation (metabolism) of hydrocarbon compounds. The use of oxygen as an electron acceptor allows for the greatest energy gain (and thus the most efficient and rapid degradation) during oxidation of hydrocarbons by microorganisms. Thus, as long as oxygen is available, oxygen will be the predominant and preferred electron acceptor utilized by microorganisms. However, once oxygen is depleted, microorganisms must turn to less favorable electron acceptors, which results in the oxidation process becoming increasingly less efficient. The relative relationships between petroleum hydrocarbon concentrations, electron acceptors, and redox potential are illustrated in Figure 1.1. It should be noted that the relative relationships are equilibrium tendencies and may or may not be correlated directly.

Collection of selected redox parameter measurements in the initial stages of site characterization may aid in establishing the feasibility of one or more technologies at a given site as well as evaluating the stability of the

TPH-BTEX	Oxygen $O_2\rightarrow H_2O$	Nitrate $NO_3^-\rightarrow N_2$	Manganese $Mn^{4+}\rightarrow Mn^{2+}$	Iron $Fe^{3+}\rightarrow Fe^{2+}$	Sulfate $SO_4^{2-}\rightarrow H_2S$	CO_2 $CO_2\rightarrow CH_4$	Redox Potential

Order of electron acceptor use during biodegradation

Relative aqueous-phase concentrations

Low	High	High	Low	Low	High	Low	High
	O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	CH_4	
High	Low	Low	High	High	Low	High	Low
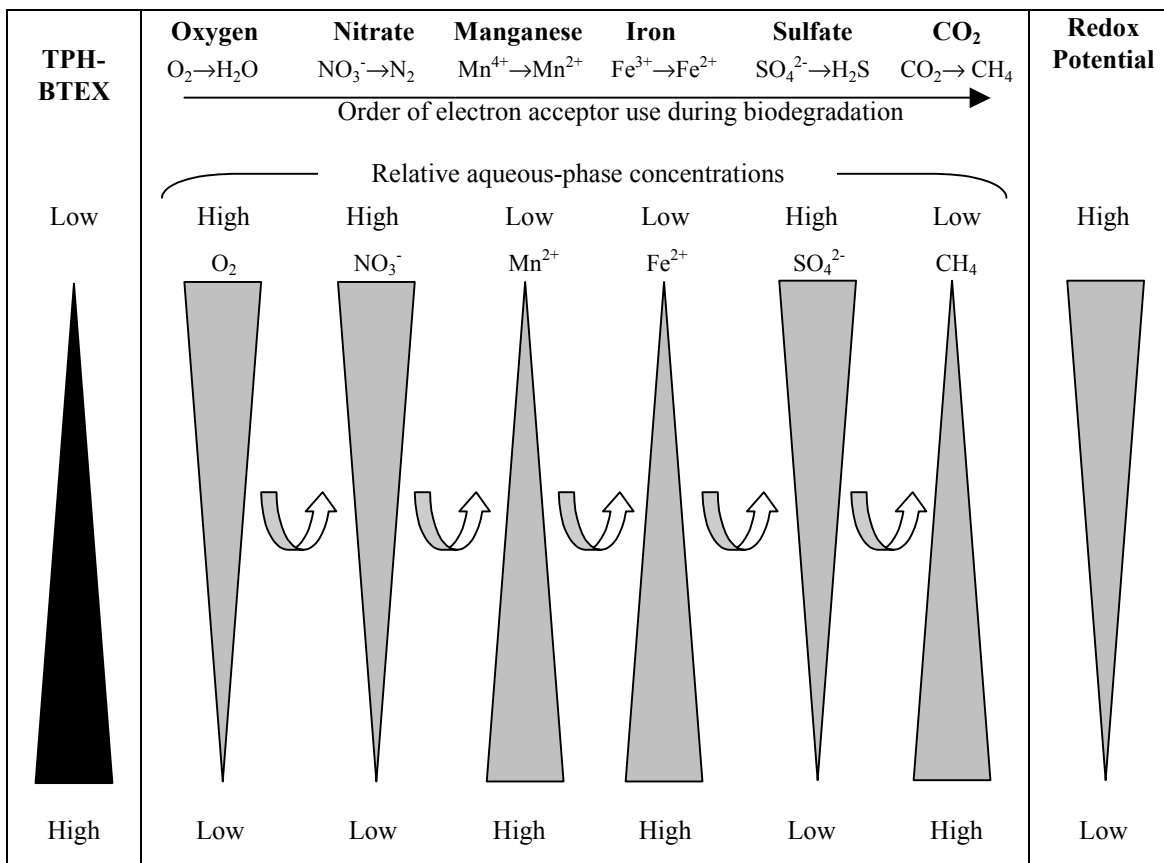
Figure 1.1 Relative relationships between TPH-BTEX concentrations and electron acceptor/reduction product concentrations and redox potential in ground water within a petroleum hydrocarbon plume.

area of affected ground water. For example, the absence of oxygen, presence of high levels of ferrous iron, and low ORP readings in the core of a BTEX plume at a site (relative to background locations) can suggest strong bioactivity and therefore indicate conditions that might be conducive to an aerobic bioremediation-based remedial strategy. Low Eh ground water with a high dissolved iron and manganese content (which can lead to clogging of pumping wells and above ground treatment systems) could signify greater maintenance attention should an ex-situ remedial strategy such as pump and treat be considered. Low Eh ground water with a high dissolved iron and manganese content could also present problems for in situ systems such as air sparging. The collection of redox information can thus be important in contributing to the initial screening and evaluation of candidate remedial technologies.

Redox parameters that should be measured both within and outside the plume in the initial stages of site characterization should at a minimum include dissolved oxygen, ferrous iron, and manganese. ORP measurements may also be considered, but should be used solely as a secondary line of evidence in support of these more reliable redox parameter measurements. If bioremediation is to be considered as a candidate remedy, then the redox parameter measurements should be expanded to include nitrate/nitrite, sulfate, and in some cases, alkalinity.

Measurement of dissolved oxygen, dissolved (ferrous) iron, and manganese within a hydrocarbon plume relative to background concentrations at the site will provide an indication of whether biodegradation processes are in effect and consequently whether the aquifer system is amenable to natural or enhanced bioattenuation. Measurement of these parameters will also provide an indication of design features that may need to be incorporated into candidate in situ and ex situ treatment systems to avoid potentially adverse reactions (e.g., precipitation). Measurement of nitrate/nitrite and sulfate/sulfide will provide an indication of additional electron acceptor availability/capacity within the aquifer while alkalinity measurements can be used as a

measure of microbial CO_2 production during biodegradation in the absence of other potential sources of alkalinity. In addition to these parameters, field measurements should generally include temperature, pH, and conductivity to further determine the extent to which the ground water may or may not be favorable to selected treatments.

Specific examples where redox parameter measurements may play a useful role in site characterization activities at petroleum hydrocarbon contaminated sites include the following.

Presence/Absence of Biodegradation Activity

The magnitude of biodegradation activity in ground water may be an important factor in the selection of remedial approaches such as enhanced bioremediation or monitored natural attenuation. Biodegradation by-products (e.g., degraded hydrocarbons, enzymes, residual inorganic constituents) of petroleum hydrocarbons are not easily quantified in ground water. Thus, there is a need to rely on alternative evidence such as the presence or absence of electron acceptors and reduction products to support the presence/absence of biodegradation activity at sites. For example, the absence of oxygen and presence of dissolved (ferrous) iron in a zone of ground-water contamination provides evidence that biodegradation is occurring. Increases in alkalinity may be indicative of carbon dioxide production associated with microbial respiration.

Petroleum Hydrocarbon Source Area Delineation

Decreasing dissolved oxygen, nitrate, and sulfate concentrations and increasing manganese and ferrous iron concentrations generally coincide with increasing proximity to hydrocarbon source areas. These measurements, as well as methane concentrations and ORP measurements, can be used as secondary lines of evidence to complement TPH and BTEX concentration measurements in verifying the locations of petroleum hydrocarbon source areas.

Dissolved Plume Delineation

Higher dissolved oxygen and nitrate concentrations and lower dissolved (ferrous) iron and manganese concentrations will generally be more characteristic of ground water outside the limits of a dissolved petroleum hydrocarbon plume. Within the limits of a dissolved plume, dissolved oxygen and nitrate concentrations will generally decrease and dissolved iron and manganese will increase with increasing proximity to the dissolved contaminant center of mass. These measurements can potentially be used to complement TPH and BTEX measurements in verifying the limits of dissolved plumes and the locations of dissolved contaminant center of masses.

Dissolved Contaminant Plume Behavior

Shrinking dissolved contaminant plumes would be expected to show gradually increasing oxygen and nitrate concentrations and decreasing dissolved (ferrous) iron and manganese concentrations around their peripheries with time. In contrast, expanding dissolved contaminant plumes would be expected to show gradually decreasing oxygen and nitrate concentrations and increasing dissolved (ferrous) iron and manganese concentrations at their peripheries with time. These measurements can potentially be used to complement TPH and BTEX measurements in determining whether source areas and dissolved plumes are shrinking, expanding, or at steady state.

1.4 Remedial Technology Applications

Measurement of selected redox parameters in ground water may have application in determining the feasibility of utilizing specific in-situ and ex-situ remedial treatments and in evaluating the performance of certain remedial systems once implemented. Technologies for remediating petroleum hydrocarbon impacted ground water currently include ex-situ treatments such as pump-and-treat and in-situ treatments focused on enhanced biodegradation or monitored natural attenuation. Technologies often considered for remediating residual phase and non-aqueous phase petroleum hydrocarbon contamination in the subsurface currently include in-situ surfactant/co-solvent flushing, in-situ thermal treatment, and in-situ oxidation. Examples of the potential applications of redox parameter measurements in determining the feasibility and evaluating the performance of remedial systems are presented below.

Determination of Natural Bioattenuation Potential

Dissolved oxygen, iron, nitrate, and sulfate concentrations can be used to indicate the presence/effect of natural bioattenuation processes on the ambient hydrochemical system. High dissolved (ferrous) iron concentrations

(e.g., > 1 ppm) coupled with low dissolved oxygen levels (e.g., < 1 ppm) near a source area or within a dissolved plume would generally indicate active bioattenuation. In contrast, sustained elevated dissolved oxygen levels and low dissolved (ferrous) iron levels near a source area or within a dissolved hydrocarbon plume could indicate the absence of natural bioattenuation processes. Estimation of the long-term capacity of an aquifer system to naturally attenuate petroleum hydrocarbons could be attempted by determining average up-gradient electron acceptor fluxes into the impacted zone and quantifying the aquifer solid phase "bioavailable" iron present within the impacted zone. The instantaneous BTEX biodegradation capacity of an aquifer system can be approximated based on the differences in up-gradient dissolved electron acceptor concentrations relative to dissolved electron acceptors and by-products near a petroleum hydrocarbon source area using the following relationship (U.S. EPA, 1996).

Biodegradation capacity (mg/L) =

$[(O_2$ concentration up-gradient - O_2 concentration in source area)/3.14)] +

$[(NO_3^-$ concentration up-gradient - NO_3^- concentration in source area)/4.9)] +

$[(SO_4^{2-}$ concentration up-gradient - SO_4^{2-} concentration in source area)/4.7)] +

$[Fe^{2+}$ concentration in source area/21.8] +

$[CH_4$ concentration in source area/0.78]

This relationship for BTEX biodegradation is the basis of EPA's BIOSCREEN model used as a screening tool to assess the potential role of natural bioattenuation at petroleum hydrocarbon contaminated sites.

It should be noted that although solid-phase "bioavailable" iron may serve as a major long-term electron acceptor source, it may become depleted with time. If the natural attenuation process is highly dependent on the presence of solid-phase ferric iron as an electron acceptor source, the eventual depletion of the iron source could result in further expansion of a hydrocarbon plume that might have initially been determined to be stable or receding. Quantification of "bioavailable" solid phase iron is addressed in the Session 6 Summary.

Performance Monitoring of Remedial Treatment Systems

Redox parameters such as dissolved oxygen measurements can be used to determine zones of influence for in situ bioenhancement treatments involving delivery of oxygen into an aquifer. Dissolved oxygen measurements coupled with pre-treatment and post-treatment redox potential and dissolved (ferrous) iron measurements, for example, can provide evidence of whether oxidizing conditions favorable for petroleum hydrocarbon biodegradation are being established and maintained. In cases where a monitored natural attenuation process has been implemented, redox parameter measurements (e.g., dissolved oxygen, dissolved (ferrous) iron) within and around the periphery of the plume can be used as supporting evidence to determine whether the plume is stable or is shrinking. This should be supplemented by solid phase ferric iron analysis to ensure adequate long-term electron acceptor capacity/longevity within the impacted aquifer.

Evaluation of Potential Impacts on Ex-situ Treatment Systems

Some ex-situ ground-water treatment systems may be adversely impacted by the presence of iron, manganese, and/or carbonates. This could be the case for any treatment system involving a significant change in redox potential, pH, or temperature during treatment of the ground water. Vulnerable components of treatment systems could include filters, air strippers, bioreactors, and re-injection systems. For example, an increase in redox potential of influent water during air stripping as a result of contact with oxygen can induce precipitation of dissolved (ferrous) iron and manganese, which may ultimately clog the stripper. Measurement of dissolved (ferrous) iron, manganese, alkalinity, and dissolved oxygen in ground water supplemented by redox potential measurements can provide essential information needed in the selection and proper design of ex-situ treatment systems.

Evaluation of Potential Impacts on In-situ Treatment Systems

Some in-situ treatment systems may be adversely impacted by various precipitation reactions or dissolution reactions that occur in response to changes in redox potential and pH. For example, the hydraulic conductivity of in-situ aquifer treatment zones that involve a change in redox potential or pH may decrease significantly over time as a result of specific precipitation or mineralization reactions that occur. Air sparging systems, for example, may induce precipitation of iron and manganese as a result of an increase in redox potential brought about by the introduction of oxygen into the aquifer. Measurement of parameters (see Session 4 Summary)

such as dissolved oxygen, dissolved (ferrous) iron, and manganese, and alkalinity in ground water can be used in conjunction with geochemical modeling to predict the nature and extent of precipitation/dissolution reactions that can be expected to occur during treatment.

1.5 Summary

The need for redox parameter measurements in the characterization and remediation of petroleum hydrocarbon impacted aquifer systems will vary based on the site-specific questions that need to be answered. A summary of potential site characterization and performance monitoring redox parameter needs for a number of different remediation technologies is presented in Table 1.1.

Table 1.1 Ground-water Redox Monitoring Guidance for Petroleum Hydrocarbon Site Characterization and Remediation

Remediation Technology[1]	Ground-water Redox Monitoring Requirements	
	Site Characterization[2]	Performance Monitoring
Ground-water extraction with treatment and/or re-injection[3]	Iron speciation[4], manganese. Additional parameters[5]: TSS, hardness	Variable[6]
Monitored natural attenuation (MNA)	Protocol parameters[7] (e.g., ASTM E-1943-98)	Variable[8]
Air sparging (mass removal in source zone)[9]	Variable[10]	DO and ferrous iron[11]
In-situ aquifer treatment zones (e.g., permeable reactive barriers)[12]	Ferrous iron and manganese	Variable depending on specific technology
Enhanced bioremediation – oxygen addition	Protocol parameters[13] Additional parameters: solid phase oxygen demand	DO, ferrous iron, TIC
Enhanced bioremediation – addition of other electron acceptors	Protocol parameters[13]	TIC, others[14]
In-situ chemical oxidation	Protocol parameters Additional parameters: TPH, solid phase COD, and solid phase iron mineralogy[15]	DO, ferrous iron, TIC Additional parameters: vadose zone CO_2
Surfactant flooding[16]	None Other parameters: TDS, major ions[17]	Variable[18]
Solvent flooding[16]	Variable[19]	Variable
Thermal methods (e.g., steam injection)	None	None
Phytoremediation	Research needed[20]	Research needed

1 Only saturated zone remedial technologies are considered. Surface soil and vadose zone remedial technologies (e.g., bioventing) are not addressed.
2 Includes data needed for remediation technology assessment and/or design.
3 Characterization of ground-water geochemistry is important to the design of virtually any remedial system involving extraction of ground water. Fouling of ground-water treatment and handling systems with iron precipitates, scale, and other solids is a significant design consideration. Potentially vulnerable systems include filters, strippers, bioreactors, re-injection systems (e.g., wells, french drains, etc.) and ancillary components (e.g., in-line monitors such as flow meters are particularly vulnerable).
4 Total iron loading is important, but it is also important to quantify dissolved (ferrous) iron to assess how much iron precipitation can be avoided by maintaining reduced conditions in the treatment system.
5 "Additional parameters" refers to important ground-water geochemical parameters not typically considered redox parameters.
6 Performance monitoring requirements will depend on system design, but will typically include analyses for one or more of the parameters specified under site characterization. However, performance monitoring is typically performed on extracted ground water rather than the in situ ground-water system.

7   A variety of protocols describe the range of redox parameters that should be included in characterization of natural attenuation at petroleum hydrocarbon sites. The first round of ground-water monitoring should typically involve monitoring for a relatively complete spectrum of redox parameters. The suite of analytical parameters used in subsequent monitoring can be optimized based on the initial findings.

8   This should be assessed on a site-specific basis.

9   Air sparging can also be used to create a "treatment wall" (with stripping and/or aerobic biodegradation providing the treatments) to minimize volatile hydrocarbon plume migration. For this air sparging application, also refer to the monitoring requirements associated with "in-situ aquifer treatment zones".

10   If the intent of the application is stripping of volatile constituents of concern, no redox characterization is required. If the intent is to promote aerobic biodegradation (for non-volatile constituents that will not be "stripped" from the ground water), it is prudent to confirm the premise of oxygen-limited conditions through analyses for MNA protocol parameters.

11   Performance monitoring will typically include assessment of the zone of sparging influence. This can be assessed through determination of spatial and temporal changes in dissolved oxygen (DO) and ferrous iron (a decrease in ferrous iron can be used as a supplemental indicator of aerobic conditions).

12   Includes any treatment technology relying on ground-water flow through a subsurface zone in which ground-water composition/conditions are altered (e.g., continuous wall systems, funnel and gate systems, sparging barriers, ground-water circulation wells, etc.)

13   When careful "mapping" of naturally occurring biological activity is critical to system design, use of hydrogen analyses in site characterization should be considered.

14   Performance monitoring requirements will be a function of the specific electron acceptor used. For example, performance monitoring for nitrate addition will typically include nitrogen speciation. See Session 2 Summary for definition of total inorganic carbon (TIC).

15   TPH measurement is used in calculating the upper boundary on aqueous phase oxygen demand. COD = chemical oxygen demand.

16   Focuses on the data needs associated with the *in situ* aspects of the technology. This technology typically includes ground-water extraction, treatment, and/or re-injection; also refer to the data needs specified for this category of remediation technologies.

17   Surfactant system design/effectiveness (e.g., interfacial tension reduction, potential surfactant precipitation) is a function of ground-water geochemistry. TDS = total dissolved solids.

18   Driven by the chemistry of the specific surfactant system being used.

19   There may be no need for redox data to assess the feasibility or design of a solvent flushing system. However, MNA will typically be used as a "polishing step" to deal with residual constituents of concern and the solvent. Also, use of biodegradable solvents may drastically lower the ground-water redox potential.

20   Given the focus of this document on ground-water geochemistry, the phytoremediation application of interest is the use of trees or other vegetation to serve as solar driven ground-water extraction systems. From a practical perspective, since this phytoremediation application is most often implemented as an "incremental boost" to natural attenuation processes, the ground-water redox will already have been characterized as part of the natural attenuation assessment. However, research is needed to allow interpretation of the effects of ground-water redox conditions on potential phytoremediation effectiveness.

References

American Society for Testing and Materials (ASTM). 1995. Standard guide for risk-based corrective action applied at petroleum release sites, ASTM E 1739-95. West Conshohocken, Pennsylvania.

American Society for Testing and Materials (ASTM). 1998. Standard guide for remediation of ground water by Natural Attenuation at petroleum release sites, ASTM E 1943-98. West Conshohocken, Pennsylvania.

Chapelle, F. H. 1999. Bioremediation of petroleum hydrocarbon-contaminated ground water: The perspectives of history and hydrology. *Ground Water*, v. 37, pp. 122-132.

U. S. Environmental Protection Agency. 1988. Cleanup of Releases from Petroleum USTs: Selected Technologies, EPA/530/UST-88/001.

U. S. Environmental Protection Agency. 1996. BIOSCREEN – Natural Attenuation Decision Support System, User's Manual Version 1.3, EPA/600/R-96/087.

Session 2 Summary:
Redox Processes for Remediation of Chlorinated Hydrocarbons and Methyl *tert*-Butyl Ether

Frank Chapelle, John Wilson, and Ralph Ludwig

2.1 Introduction

The purpose of this session was to develop recommendations concerning redox measurement parameters for remediation of ground water contaminated with chlorinated solvents and MTBE. Information on redox processes is necessary for site managers to plan and implement site characterization, select remedies, and optimize and monitor the performance of the selected remedies. The participants in the session made recommendations concerning the redox parameters that should be evaluated for various treatment technologies, and on the appropriate methods to collect the data.

The technologies include various techniques for destruction of the contaminants, including physical removal, chemical destruction, enhanced biological degradation, and monitored natural attenuation. The information needs for each technology are discussed within these categories.

2.2 Critical Redox Parameters Required for the Evaluation and Optimization of Different Treatment Technologies for Chlorinated Hydrocarbons

The information needed to characterize a site and select a remedy is often different from information needed to optimize a technology or monitor its performance. The tables in this section present a brief description of the major issues associated with redox parameters, grouped by major category of technology.

The "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (Wiedemeier et al., 1998) presents a comprehensive list of redox parameters that are useful for evaluating monitored natural attenuation in ground water. The parameters are listed in Table 2.1 of the Technical Protocol, and include alkalinity, arsenic, chloride, conductivity, ferrous iron, hydrogen, manganese, methane, nitrate, oxidation reduction potential (ORP), oxygen, pH, sulfate, sulfide, temperature, and total organic carbon in water.

Some of the parameters are useful for assessment of the system redox status, including dissolved oxygen, hydrogen, methane, sulfide, oxidation reduction potential, pH, and temperature. Some of the parameters are useful for assessment of the potential for microbial metabolism of contaminants. Oxygen can support microbial metabolism of certain chlorinated hydrocarbons including cis-dichloroethylene and vinyl chloride. In contrast, the presence of sulfate, nitrate, or oxygen can inhibit anaerobic biological processes such as reductive dechlorination of the chlorinated hydrocarbons. During reductive dechlorination, the contaminant serves as the electron acceptor in microbial metabolism. If sulfate, nitrate or oxygen are present they can compete with the contaminant for supplies of electron donors. Total organic carbon in water is a bulk parameter that can be used to estimate the supply of electron donors for reductive dechlorination.

Other redox parameters in the EPA Technical Protocol are measures of the degradation process. These include chloride and alkalinity. Chloride is an ultimate biodegradation product of chlorinated hydrocarbons. The analysis for alkalinity in the Technical Protocol was originally intended as an estimate of the amount of carbon dioxide that has been produced in the ground water by biological processes. In many aquifers, carbon dioxide produced by biological processes cannot be measured directly due to reactions with carbonate minerals in the aquifer matrix. Alkalinity measurements may also provide an overestimate of microbial CO_2 production in contaminant plumes with high concentrations of titrable organic acids. To address this later issue, a better estimate of the amount of carbon dioxide that has been produced is the change in total inorganic carbon (TIC) in ground water. The TIC can be measured directly, or calculated from measurements of alkalinity, pH, and dissolved carbon dioxide (see section 2.8).

Certain of the redox parameters can be used to establish the "footprint" of the contaminated water (National Research Council, 2000). If the geochemical "footprints" are similar between contaminated ground water in source areas and water produced from monitoring wells farther downgradient, they can be used to establish a hydrological connection between the source and the monitoring well. If the geochemical "footprints" in down gradient monitoring wells are distinctly different from the geochemistry of ground water at the source, they are not in the flow path from the source area of the plume. Geochemical "footprints" can also reveal the major biological and chemical oxidation/reduction processes that are responsible for removing chlorinated hydrocarbons from ground water. Chloride, methane, specific conductance, and TIC are particularly useful as "footprints."

Some of the redox parameters are required to evaluate risk from materials that were not the original contaminants of concern. Arsenic and manganese are included because the geochemical conditions that allow natural biodegradation of chlorinated hydrocarbons also allow biological reduction of natural aquifer materials that contain arsenic and manganese. Under conditions that promote natural anaerobic biodegradation of chlorinated hydrocarbons, the concentration of total arsenic and manganese produced from natural sources may exceed drinking water standards.

The appropriate regulatory authorities will determine on a site specific basis when it is necessary to analyze for arsenic and manganese. The circumstances where analysis for hydrogen is useful are discussed in Section 2.7. The following redox parameters should be routinely applicable to most sites, and will be referred to as the Routine EPA Protocol Parameters: dissolved oxygen, nitrate, sulfate, chloride, ferrous iron, sulfide, hydrogen, methane, oxidation/reduction potential, pH, temperature, specific conductance, total inorganic carbon, and total organic carbon.

Chlorinated hydrocarbons can be removed from aquifers by air sparging, bioventing or phytoremediation (see Table 2.1). They can be chemically destroyed by dithionite reduction, oxidation by the Fenton reaction, oxidation by permanganate, or by reduction by zero valence iron in a permeable reactive barrier (see Table 2.2). They can be biologically degraded through substrate additions, phytoremediation in the rhizosphere, and through monitored natural attenuation (see Table 2.3).

Air sparging is a process of stripping volatile compounds from ground water through the injection of air. Redox chemistry is not involved in this purely physical process. In theory precipitation of Fe (III) by oxidation of Fe (II) in ground water could plug the pore space in the aquifer. In practice this is not an important problem. The success of air sparging is controlled by the physics of flow of the injected air as controlled by the geology of the site.

Bioventing is technology applied to the unsaturated zone that is intended to treat ground water. It treats the residual hydrocarbons present as a NAPL that act as a long term source of contamination to ground water. It is successful at sites where the water table moves down during the time period of treatment to expose the oily phase at residual saturation to air in the unsaturated zone. Treatment is a combination of volatilization and in situ biodegradation. The recommended redox parameters are important to understand the biodegradation processes.

Phytoremediation has particular application to chlorinated hydrocarbons in shallow ground water in fine textured geological materials. Water is removed by evapotranspiration. The chlorinated hydrocarbons can be transpired with the water, or they can volatilize into air spaces created when the water is extracted. The relevant geochemical parameters determine whether plant roots can grow in the contaminated ground water (Pivetz, 2001).

In conventional practice for site characterization, the major emphasis is on sampling and analysis of ground water. Much less attention has been paid to characterization of aquifer solids. An analysis of aquifer solids is critical to the successful use of non-biological transformation technologies such as dithionite reduction, permanganate oxidation or the Fenton reaction to treat organic contaminants. The natural aquifer solids play an important role in the chemistry of the treatment process. The availability and reactivity of iron minerals in the aquifer are particularly important.

This is less true for passive reactive barriers using zero-valent iron in the treatment process. Only ground water is treated, and it is treated in the reactive wall as opposed to the aquifer. Passive reactive barriers are designed to allow adequate residence time of contaminated ground water to reduce the contaminant concentrations to the design goals. The design is constrained by the kinetics of reaction of the contaminants of concern with the reactive medium in the barrier, and with the seepage velocity of ground water through the barrier. In theory,

the geochemistry of the ground water should directly affect the long term capacity of a barrier to treat water. As an example, reaction with oxygen in ground water converts zero valent iron to higher oxidation states. The reaction of zero valence iron with oxygen and contaminants raises the pH. A variety of reaction products can form precipitates that may plug the pore space. These concerns are discussed in more detail in Powell et al. (1998) on pages 25 and 26. At present there is a research program coordinated between private industry and several federal agencies to evaluate the life cycle of passive reactive barriers. However, the present state of practice is to design them to work well, but not necessarily to design them to last for a predetermined time. As a consequence, geochemical considerations are less important to their design and implementation.

In technologies that add substrates (such as vegetable oil, lactate, molasses, or hydrogen) to support reductive dechlorination of chlorinated hydrocarbons, the success of the technology may be related to the availability of mineral nutrients for growth of bacteria, in particular phosphate and reduced fixed nitrogen in the form of ammonium ion. The primary source of reducing power is hydrogen, which is provided directly as dihydrogen, or as organic substrates that can be fermented to form dihydrogen. Organisms that use nitrate and nitrite as electron acceptors can effectively compete with organisms using chlorinated hydrocarbons for the available pool of dihydrogen. The presence of measurable nitrate or nitrite will preclude or strongly inhibit reductive dechlorination.

Chlorinated hydrocarbons can be biochemically degraded in soil or aquifer material in direct proximity to plant roots (the rhizosphere). The oxidation parameters are used to predict microbiological activity in the rhizosphere. In this application, total organic carbon is an indirect measure of plant root exudates that stimulate microbial activity against the chlorinated hydrocarbons.

Monitored Natural Attenuation is an important remedial technique for chlorinated hydrocarbons. The EPA protocol parameters have proved themselves useful as a qualitative tool to recognize geochemical environments where reductive dechlorination is possible (Wiedemeier et al., 1998). However, the role of alkalinity in the original EPA protocol should be replaced with an analysis or calculation of TIC (see section 2.8).

Table 2.1   Redox Parameters for Evaluation of Treatment by Physical Removal

Treatment Technology	Site Characterization	Performance Monitoring/ Remediation Optimization
Air Sparging	None	None
Bioventing to remove oily phase residuals of chlorinated hydrocarbons mixed with petroleum hydrocarbons.	Concentrations of oxygen and carbon dioxide in soil gas. Concentrations of methane in soil gas to define background conditions. An in situ respiration test to measure the instantaneous rate of oxygen consumption.	Same
Phytoremediation by evapo-transpiration of water.	Will plant roots grow in the contaminated ground water? Conductivity, pH, Dissolved Oxygen, Sulfide.	None

Table 2.2 Redox Parameters for Evaluation of Chemical Destruction

Treatment Technology	Site Characterization	Performance Monitoring/ Remediation Optimization
Dithionite	Inherent stability of Dithionite in the aquifer matrix. Dissolved Fe(III) extractable with 1 N HCl. Mineralogy of Iron.	ORP, reducing capacity of sediments measured as the demand for dissolved oxygen.
Other Oxidation Processes Fenton's reaction Permanganate	Routine EPA Protocol Parameters, Estimate volume of aquifer material in source area contaminated with organic materials. Permanganate demand of contaminated material.	Routine EPA Protocol Parameters, carbon dioxide in soil gas, Residual permanganate using colorimetric test.
Zero Valent Iron	Not Critical	Dissolved Fe (II), dissolved oxygen, sulfide, sulfate, ORP, conductivity, pH (measured either quarterly or semi-annually)

Table 2.3 Redox Parameters for Evaluation of Biological Degradation

Treatment Technology	Site Characterization	Performance Monitoring/ Remediation Optimization
Substrate Additions Vegetable Oil Lactate Molasses Hydrogen	Routine EPA Protocol Parameters hydrogen, nitrite, ammonium ion, phosphate.	(Have the redox processes changed as a result of the substrate addition?) Routine EPA Protocol Parameters, acetate, formate, propionate, hydrogen, nitrite, ammonium ion, phosphate.
Phytoremediation through biodegradation in the Rhizosphere	Routine EPA Protocol Parameters with emphasis on Total Organic Carbon.	Routine EPA Protocol Parameters with Emphasis on change in oxidation/reduction status.
Monitored Natural Attenuation of Chlorinated Ethenes Chlorinated Ethanes Chlorinated Benzenes	Routine EPA Protocol Parameters plus Potential Daughter Products. Hydrogen if necessary to interpret biodegradation processes.	Routine EPA Protocol Parameters plus Potential Daughter Products. Hydrogen if necessary to confirm continued biological activity.

2.3 Critical Redox Parameters for MTBE

Methyl-*tert*-butyl-ether (MTBE), an oxygenate added to petroleum hydrocarbon fuels to produce cleaner engine emissions, has been increasingly detected in ground water throughout the United States since the early 1990s. The increased presence of MTBE in ground water has been of particular concern due to the high mobility, relative recalcitrance, and suspected carcinogenic properties of this compound.

Although initially believed to undergo negligible or no biodegradation in the subsurface, there is an increasing body of evidence indicating that aerobic biodegradation can be used to remove MTBE from ground water. Salinitro et al. (2000) used bioaugmentation and aerobic in situ bioremediation to reduce MTBE in an aquifer to concentrations below 10 µg/liter. Redox parameters that are important for design of in-situ aerobic MTBE bioremediation systems include dissolved oxygen, sulfide and ferrous iron in ground water. Oxygen enhancement will stimulate biodegradation of MTBE if the original ambient oxygen concentration is less than 1 mg/liter. The presence of high concentrations of ferrous iron can cause problems with precipitates and plugging of pipes and distribution systems. The presence of ferrous iron or sulfide in ground water is often indicative of a high non-biological demand for oxygen associated with precipitates of iron and sulfide in the aquifer solids. Redox parameters important for monitoring in-situ aerobic bioremediation include dissolved oxygen, ferrous iron, and TIC. Dissolved oxygen concentrations should exceed a minimum concentration of 2 mg/liter to support degradation of MTBE, and should exceed 5 mg/liter for optimum performance. The increase in TIC over time can be used to monitor oxidation of the organic contaminants in the aquifer. In particular, redox parameters will be useful in monitoring the performance (e.g., zone of influence) of any in-situ enhanced bioremediation treatment system.

Bradley et al. (2001) have reported significant aerobic mineralization of MTBE in microcosm studies using MTBE and non-MTBE contaminated stream and lake bed sediments from eleven sites throughout the United States. The study indicated that even microbial communities indigenous to newly contaminated sediments exhibited some innate ability to mineralize MTBE under aerobic conditions. The magnitude of MTBE mineralization in the study was observed to vary inversely with the sediment grain size distribution. Landmeyer et al. (2001) showed that aerobic metabolism of MTBE in the bed sediments of a stream prevented transfer of MTBE from an anaerobic plume in ground water to aerobic surface water. Natural aerobic biodegradation of MTBE in surface waters and sediments probably make a substantial contribution to surface water quality.

Natural aerobic biodegradation of MTBE is probably not important for plumes of MTBE contamination in ground water. Kolhatkar et al. (2000) examined seventy-four MTBE plumes from spills of gasoline in the eastern United States. The ground water that contained MTBE contamination was strongly reducing. The most contaminated wells at forty-three of the seventy-four sites had no detectable sulfate and an accumulation of at least 0.5 mg/liter of methane. Only eighteen of the seventy-four sites had detectable concentrations of sulfate and methane concentrations less than 0.5 mg/liter. Nitrate was depleted in contaminated wells at every site. In the survey reported by Kolhatkar et al. (2000), water samples were collected according to the standard practice for sampling monitoring wells at underground storage tanks as approved by the local regulatory authority. In almost every case, the water samples were collected with bailers (see warnings in section 2.6). The water as sampled from the contaminated wells contained oxygen, even though the same water contained substantial concentrations of ferrous iron, sulfide, or methane. When water samples are collected with bailers, it is almost impossible to prevent contamination of the sample with oxygen. The widespread use of bailers for sampling wells at UST spills has created a mistaken impression at some MTBE spills that the ground water is aerobic, which can lead to a mistaken conclusion that aerobic natural degradation of MTBE in that particular aquifer is possible.

Other studies have indicated some biodegradation of MTBE under oxygen limiting conditions including methanogenic conditions (Wilson et al., 2000), iron reducing conditions, or nitrate reducing conditions (Bradley et al., 2001). However, it is unlikely that monitored natural attenuation will be an acceptable solution for MTBE in ground water at many sites. Kolhatkar et al. (2000) applied an objective test for natural attenuation of MTBE to the seventy-four stations they sampled in the eastern United States. Based on one round of sampling from existing monitoring wells, natural attenuation of MTBE was shown to be statistically significant at the 90% confidence level at only four of the seventy-four stations.

In many cases, an ex-situ approach may be preferred for addressing MTBE in ground water that is produced and distributed for water supply (Keller et al., 2000). As with any potential ex-situ ground-water treatment

Table 2.4 Appropriate Field and Laboratory Methods for Critical Redox Parameters

Parameter	Field Method	Laboratory Method
Dissolved Oxygen	Colorimetric methods are recommended. Electrodes can be used successfully in a flow-through or overflow cell. See discussion in section 2.4 below and Session 4 Summary.	Analysis on samples shipped to the laboratory is not recommended.
Ferrous Iron Fe (II)	Colorimetric analysis, use of field spectrophotometer is preferred. (See Session 4 Summary)	Analysis on samples shipped to the laboratory is not recommended.
Manganese	Colorimetric analysis, use of field spectrophotometer is preferred.	Analysis on samples shipped to the laboratory is not recommended.
Total Inorganic Carbon (TIC)	Determine alkalinity (endpoint titration to pH 4.5) and pH. For water with pH < 6.5, also use a colorimetric field kit for free carbon dioxide. Calculate TIC from the sum of carbonate and bicarbonate alkalinity plus free carbon dioxide. (See section 2.8)	The samples should be shipped without preservative, and sealed into the container without headspace. Laboratory analysis by purging TIC from an acidified sample and measuring CO_2 by infrared absorption.
Sulfide	Colorimetric analysis, use of field spectrophotometer is preferred.	Analysis on samples shipped to the laboratory is not recommended. If analysis on samples shipped to the laboratory is necessary, the samples should be shipped with an appropriate preservative, such as zinc acetate.
Methane	Preserve in the field, ship to the laboratory for analysis. (See Session 5 Summary)	Headspace analysis using gas chromatography with a flame ionization detector (GC/FID)
Oxidation/ Reduction Potential	Platinum electrode in a flow- through cell or an overflow cell. Readings should be corrected to the standard hydrogen electrode. (See Session 4 Summary)	Analysis on samples shipped to the laboratory is not recommended.
Specific Conductance	Electrode in a flow-through cell or an overflow cell. The electrode may not automatically correct for temperature; measure and report temperature.	Electrode in a water sample that has not been preserved. The samples should be sealed into the container without headspace to prevent the oxidation and precipitation of iron.
pH	Electrode in a flow-through cell or an overflow cell. The electrode should be calibrated in the field prior to use.	Electrode in a water sample that has not been preserved. The samples should be sealed into the container without headspace.
Temperature	Thermometer in a flow-through cell or an overflow cell.	Not Possible.
Hydrogen	Collect using bubble Stripping Technique. Analysis in a field laboratory is preferred, using gas chromatography with a reducing gas detector. (See Session 5 Summary)	Analysis using gas chromatography with a reducing gas detector. A flame ionization detector is not sufficiently sensitive to hydrogen.
Nitrate	Not recommended. Adequate field methods exist for these parameters; however, they are not cost-effective compared to analysis in a laboratory.	Ion Chromatography. The following preservation and holding times are recommended: nitrate, 4 °C with 48 hour holding time; sulfate, 4 °C with 28 day holding time; chloride, ambient temperature with 28 day holding time (see U.S. EPA, 1999).
Sulfate		
Chloride		

process, the geochemistry of the ground water (e.g., iron and manganese content) can be an important factor in determining which ex situ treatment process is likely to be most cost-effective. Low redox ground waters containing high levels of dissolved iron and manganese may pose problems (e.g., precipitate clogging or coating) for treatment systems in which increases in redox potential occur during treatment. In such cases, a pre-treatment or modified treatment process may be required to achieve effective overall treatment. Thus, in cases where an ex-situ treatment process is under consideration, the measurement of redox parameters such as dissolved iron/manganese may be beneficial in evaluating the feasibility of using selected above ground treatment technologies.

2.4   Relationship of Redox Processes to Phytoremediation

In the root zone (rhizosphere) of plants, especially trees, it has been shown that exudates from roots supply organic carbon, especially organic acids, that stimulate bacterial growth (Lee et al., 2000; Schnoor et al., 1995). In addition, the decay of root biomass can also add organic carbon to the vadose zone and shallow ground water. Where near-reducing conditions have been established in ground water near phreatophytes such as cottonwood trees, reductive dechlorination of TCE has been observed in the rhizosphere (Lee et al., 2000). Alternatively, some plants can provide some oxygen to roots, or create avenues for atmospheric oxygen to enter ground water or the deep vadose zone through root holes, perhaps enhancing the aerobic environment in shallow ground water.

Thus, biodegradative processes can occur in the rhizosphere of plants, especially phreatophytes in addition to the well known removal of contaminated ground water by transpiration and degradation of the contaminants within the plant biomass (Schnoor et al., 1995).

2.5   Appropriate Field and Laboratory Methods for Critical Redox Parameters

Many redox parameters are unstable; they start to change as soon as the ground water is exposed to the atmosphere (see Session 4 Summary and Appendix A). As a consequence, many of these redox analyses must be done at the well head. The following recommendations are based on the combined experience of the participants at the session. They represent a group consensus on methods and techniques that can be expected to provide data of adequate quality at hazardous waste sites.

2.6   General Considerations for Ground-Water Sampling

The method used to collect a sample of ground water is often more important for data quality than the method used to analyze the sample. Recommendations for improved practice are discussed in detail in Puls and Barcelona (1996). If ground water is exposed to the atmosphere while it is being collected into the sampling well, or when it is pumped from the well, the sample can be seriously compromised. The ground water may gain oxygen from the atmosphere. The oxygen introduced into the sample may chemically react with ferrous iron or sulfide and transform these materials. Oxygen will also disturb measurements of oxidation reduction potential.

The standing water in a well is exposed to the atmosphere; it is usually oxygenated with respect to the native ground water in the aquifer. In most applications, the standing water within the well is purged and replaced with ground water that has not been altered. To avoid aeration, water should be pumped from the well using a gentle device such as a peristaltic pump or bladder pump. Bailers should only be used when there is no other option for geochemical sampling. If a bailer must be used, the bailer should be slowly immersed in the standing column of water in the well to minimize aeration. After sample collection, the water should be drained from the bottom of the bailer through tubing into the sampling container.

Ground water can also be aerated if the well is pumped down too far. The ground water will enter the well, then cascade down the inside of the screen as the water level in the well drops. To avoid aeration, wells that are screened below the water table should not be pumped at a rate which lowers the standing water in the well to a level below the top of the screen. If practical, wells screened across the water table should be pumped at a rate that lowers the total height of the water column in the well no more than five to ten percent.

An overflow cell or a flow-through cell should be used for the measurement of well-head parameters such as pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential. Experts in the area of field sampling of ground water differ in their preference for flow-through cells or overflow cells. Flow-through cells effectively prevent contact of a water sample with oxygen, particularly when they don't trap a bubble in the cell. Depending on the position of the outlet tube and flow restrictions in the outlet tube, water in

the flow-through cell can be under positive pressure. This will preclude the proper use of certain electrodes that depend on gravity flow of electrolyte to a salt bridge in the electrode. The user's manual for an electrode should be consulted to determine if this may be a problem. Overflow cells can function as well as flow-through cells when the flow from the pump is presented directly to the sensor surface of the electrodes, and then flows up past the body of the electrode before it overflows. The position of an electrode can be adjusted in the overflow cell to make the elevation of the reservoir of electrolyte higher than the overflow of water being monitored.

The "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water" (Wiedemeir et al., 1998, EPA/600/R-98/128) depicts a flow-through cell on page A4-17. The authors of the Technical Protocol used an Erlenmeyer flask as an overflow cell because the wide base of the flask kept the leads to the electrodes from tipping the flask over. However, this configuration provides a reservoir for mixing of the ground water in the flask and does not provide directed flow of ground water across the sensor surface of the electrodes. The overflow cell should be a cylinder that is only slightly larger than the space needed to contain the electrodes. A graduated cylinder works well. It can be held in place with clamps or a lead doughnut.

2.7 When to Measure Hydrogen in Ground Water

Measurement of hydrogen in ground water should be considered when the redox processes cannot be interpreted from the more conventional Protocol Parameters. As an example, a trichlorethylene plume may show a marked reduction in the concentration of trichloroethylene downgradient of the source, with accumulation of minor concentrations of the first reduction transformation product, cis-dichloroethylene, and no detectable vinyl chloride. This distribution can be easily interpreted in two ways. Reductive dechlorination may be weak, resulting in transformation of a minor amount of trichloroethylene to cis-dichloroetheylene. The reduction in concentrations of trichloroethylene are caused by physical processes such as dilution and dispersion. In the second interpretation, reductive dechlorination is strong, and is the cause of the loss of trichloroethylene. The transformation product cis-dichloroethylene does not accumulate because it is further transformed to carbon dioxide, without going through vinyl chloride as an intermediate. If concentrations of hydrogen are low, less than 1 nanomolar, the second interpretation is excluded and the first interpretation is supported. If hydrogen concentrations are high, greater than 1 nanomolar, the second interpretation is supported, although not necessarily proven. Hydrogen concentrations should be measured when they are necessary to understand the redox processes. When the redox processes can be interpreted from the more conventional parameters, measurement of hydrogen is not necessary. A recent publication compares two techniques for sampling hydrogen (McInnes and Kampbell, 2000).

2.8 Determination or Calculation of Total Inorganic Carbon (TIC)

Microorganisms degrade chlorinated hydrocarbons through a variety of mechanisms including aerobic respiration, iron and manganese reduction, or use as the electron acceptor in reductive dechlorination. MTBE has been shown to be degraded under aerobic, nitrate reducing, iron reducing, sulfate reducing and methanogenic conditions. The most universal end product of biodegradation of chlorinated hydrocarbons or MTBE is carbon dioxide that is produced from the contaminant itself, or from the compound used as an electron donor in reductive dechlorination. This biogenic carbon dioxide can be seen in plumes of contaminated ground water as an increase in the TIC above the background TIC in uncontaminated water in the aquifer. It is often one of the most revealing "footprints" of ground water that has been remediated by natural biological processes.

This geochemical parameter is termed TIC because it is measured on water samples that have not been filtered. In most cases the measured TIC is equivalent to the dissolved inorganic carbon (DIC) in the ground water. It is best not to filter ground water samples before analysis for inorganic carbon. Often ground water is not in equilibrium with the atmosphere, and it is difficult to avoid exchange of carbon dioxide between the water samples and the atmosphere during filtering.

The concentration of TIC can be determined directly by adding acid to the water sample, partitioning carbon dioxide to a head space and measuring the carbon dioxide directly with an infrared detector (see methods for total inorganic carbon in U.S. EPA, 1999). This is the preferred method. The concentration of TIC can also be calculated from measurements of alkalinity, free carbon dioxide, and pH as described later in this section. Methods for alkalinity are described in U.S. EPA (1999), and for free carbon dioxide in APHA (1999) and ASTM (1996).

These calculations are generally accurate; however, there are important categories of plumes where these calculations can produce major errors. The calculations assume that there is no hydroxide alkalinity associated

with strong bases. Occasionally an unnaturally high pH is caused by disposal of caustic waste materials in the subsurface. A high pH can also be caused by improper grouting or cementing of monitoring wells. The calculations also assume that there is no alkalinity associated with other weak acids. Ground waters often contain organic acids that contribute to alkalinity (Hemond, 1990). Plumes of leachate from solid municipal waste landfills often have large amounts of alkalinity associated with organic acids such as acetate and butyrate.

The correspondence between carbon dioxide produced during metabolism and the increase in TIC is not one-for-one. In acid ground water, some of the carbon dioxide may be lost across the water table. This effect is probably not important in most plumes, but it should be considered and evaluated. In aquifers that contain carbonate minerals in the aquifer matrix, the biogenic carbon dioxide can ultimately react with calcium or magnesium carbonate minerals to dissolve them as calcium or magnesium hydrogen carbonate. In this reaction there are two moles of TIC produced in ground water for each mole of biogenic carbon dioxide consumed. Once formed, TIC can precipitate with ferrous iron as siderite, or sorb to the anion exchange complex. In many ground waters these reactions do not appear to be in equilibrium. As a consequence, it is usually impossible to directly convert a change in TIC to an amount of carbon dioxide produced by biological activity. However, it is often possible to calculate a range of carbon dioxide concentrations that could have produced the measured TIC.

There are two calculations that can be used to estimate the total inorganic carbon (TIC) from pH, alkalinity, and free carbon dioxide.

Method 1: Calculate TIC from the sum of measured alkalinity and measured free CO_2

Dissolved inorganic carbon is the sum of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate. For convenience we will express the sum of dissolved carbon dioxide and carbonic acid as carbonic acid $[H_2CO_3^*]$.

$$[TIC] = [H_2CO_3^*] + [HCO_3^{-1}] + [CO_3^{-2}]$$

Alkalinity is conventionally determined as the amount of acid required to titrate water to a colorimetric end point near pH 4.8. It is conventionally expressed as the amount of $CaCO_3$ that would be consumed by that amount of acid. The meq/liter of acid required is the alkalinity in mg/liter of $CaCO_3$ divided by 50.

$$\text{Alkalinity as } [H^+] \text{ consumed} = [HCO_3^{-1}] + 2[CO_3^{-2}]$$

Each 100 mg/liter of $CaCO_3$ alkalinity accepts 2 meq/liter of H^+.

$$CaCO_3 \text{ alkalinity (mg/liter)}/50 = 0.5 [HCO_3^{-1}] + [CO_3^{-2}]$$

Free carbon dioxide is calculated from the amount of base needed to convert all the $H_2CO_3^*$ and HCO_3^{-1} to CO_3^{-2}. It is usually expressed in mg/liter of CO_2.

$$\text{Free carbon dioxide as } [H^+] \text{ provided} = 0.5 [HCO_3^{-1}] + [H_2CO_3^*]$$

$$\text{Each 44 mg/liter of Carbon Dioxide provides 2 meq/liter of } H^+$$

$$\text{Free Carbon Dioxide (mg/liter)}/ 22 = 0.5 [HCO_3^{-1}] + [H_2CO_3^*]$$

$$CaCO_3 \text{ alkalinity}/50 + \text{free } CO_2 /22 = [H_2CO_3^*] + [HCO_3^{-1}] + [CO_3^{-2}] = [TIC]$$

$$\text{TIC (mg Carbon/liter)} = 12 *(CaCO_3 \text{ alkalinity}/50 + \text{Free } CO_2/22)$$

Method 2. Calculation of TIC from Alkalinity and pH

This method should only be applied to waters with pH > 6.5 and easily measurable $CaCO_3$ alkalinity.

$$[TIC] = [H_2CO_3^*] + [HCO_3^{-1}] + [CO_3^{-2}]$$

The calculation proceeds in three steps:

(1) Calculate $[HCO_3^{-1}]$ from measured alkalinity and pH.
(2) Then calculate $[H_2CO_3^*]$ and $[CO_3^{-2}]$ from the pH, the $[HCO_3^{-1}]$ as calculated previously, and the governing pKa.
(3) Then add the calculated $[H_2CO_3^*] + [HCO_3^{-1}] + [CO_3^{-2}]$ and multiply by 12,000 to convert to TIC (mg C/liter).

Alkalinity is conventionally determined as the amount of acid required to titrate water to a colorimetric end point near pH 4.8. It is conventionally expressed as the amount of $CaCO_3$ that would be consumed by that amount of acid. The meq/liter of acid required is the alkalinity in mg/liter of $CaCO_3$ divided by 50.

$$CaCO_3 \text{ alkalinity as } [H^+] \text{ consumed} = [HCO_3^{-1}] + 2[CO_3^{-2}]$$
$$CaCO_3 \text{ alkalinity (mg/liter)/50} = [HCO_3^{-1}] + 2[CO_3^{-2}]$$

Calculation of $[HCO_3^{-1}]$

The ratio of $[HCO_3^{-1}]$ and $[CO_3^{-2}]$ can be predicted from the pKa of $[HCO_3^{-1}]$ and the pH.

The pKa of $[HCO_3^{-1}]$ to $[CO_3^{-2}]$ and $[H^+]$ is 10.49 at 10 °C.

In other words: $([H^+][CO_3^{-2}])/[HCO_3^{-1}] = 10^{-10.49}$ and $[CO_3^{-2}] = [HCO_3^{-1}]/10^{(10.49-pH)}$

Substituting $[HCO_3^{-1}]/10^{(10.49-pH)}$ for $[CO_3^{-2}]$ in equation (1) yields

$$CaCO_3 \text{ alkalinity (mg/liter)/50} = [HCO_3^{-1}] + 2([HCO_3^{-1}]/10^{(10.49-pH)}).$$

Solving for $[HCO_3^{-1}]$ yields

$$[HCO_3^{-1}] = (\text{mg/liter } CaCO_3/50)* 10^{(10.49-pH)} / (2+ 10^{(10.49-pH)}).$$

Calculation of $[CO_3^{-2}]$

Again the pKa of $[HCO_3^{-1}]$ to $[CO_3^{-2}]$ and $[H^+]$ is 10.49 at 10 °C.

In other words: $([H^+][CO_3^{-2}])/[HCO_3^{-1}] = 10^{-10.49}$ and $[CO_3^{-2}] = [HCO_3^{-1}] * 10^{-10.49 + pH}$

Calculation of $[H_2CO_3^*]$

The pKa of $[H_2CO_3^*]$ to $[HCO_3^{-1}]$ and $[H^+]$ is 6.42 at 10 °C.

In other words: $([H^+][HCO_3^{-1}])/[H_2CO_3^*] = 10^{-6.42}$ and $[H_2CO_3^*] = [HCO_3^{-1}]/10^{-6.42 + pH}$

References

American Public Health Association, American Water Works Association, Water Environment Federation (APHA). 1999. *Standard Methods for the Examination of Water and Wastewater*, Titrimetric method for free carbon dioxide 4500- CO_2 C, American Public Health Association, Washington, D.C.

American Society for Testing and Materials (ASTM). 1996. Standard Test Methods for Total and Dissolved Carbon Dioxide in Water, ASTM D 513-92. Philadelphia, Pennsylvania.

Bradley, P. M., Landmeyer, J. E., and Chapelle, F. H. 2001. Widespread potential for microbial MTBE degradation in surface-water sediments. *Environmental Science and Technology*, v. 35, pp. 658-662.

Hemond, H. F. 1990. Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids. *Environmental Science and Technology*, v. 24, p. 1486-1489.

Keller, A. A., Sandall, O. C., Rinker, R. G., Mitani, M. M., Bierwagen, B., and Snodgrass, M. J. 2000. Evaluation of physicochemical treatment technologies for water contaminated with MTBE. *Ground Water Monitoring and Remediation*, v. 20, pp. 114-126.

Kolhatkar, R., Wilson, J., and Dunlap, L. 2000. Evaluating natural attenuation of MTBE at multiple UST Sites.

In *Proceedings of NGWA/API Conference and Exposition on Petroleum and Organic Chemicals in Ground Water: Prevention, Detection and Remediation.* Anaheim, California, November 15-17, 2000, pp. 32-49.

Landmeyer, J. E., Chapelle, F. H., Herlong, H. H., and Bradley, P. M. 2001. Methyl *tert*-butyl ether biodegradation by indigenous aquifer microorganisms under natural and artificial oxic conditions. *Environmental Science amd Technology*, v. 35, pp. 1118-1126.

Lee, R. W., Jones, S. A., Kuniansky, E. J., Harvey, G., Sherwood-Lollar, B, and Slater, G. F. 2000. Phreatophyte influence on reductive dechlorination in a shallow aquifer contaminated with trichloroethene (TCE). *International Journal of Phytoremediation*, v. 2, pp. 193-211.

McInnes, D. M. and Kampbell, D. 2000. The bubble stripping method for determining dissolved hydrogen (H_2) in well water. *Field and Analytical Chemistry and Technology*, v. 4, pp. 283-296.

National Research Council. 2000. *Natural Attenuation for Groundwater Remediation*, National Academy Press, p. 11.

Pivetz, B. 2001. *Phytoremediation of Contaminated Soil and Ground Water at Hazardous Waste Sites*, EPA/540/S-01/500. U. S. Environmental Protection Agency, Cincinnati, OH. [http://www.epa.gov/ada/download/issue/epa_540_s01_500.pdf].

Powell, R. M., Blowes, D. W., Gilham, R. W., Schult, T., Puls, R. W., Vogan, J. L., Powell, P. D., and Landis, R. 1998. *Permeable Reactive Barrier Technologies for Contaminant Remediation*, EPA/600/R-98/125. U. S. Environmental Protection Agency, Cincinnati, OH. [http://www.epa.gov/ada/download/reports/reactbar.pdf].

Puls, R .W. and Barcelona, M. J. 1996. *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, EPA/540/S-95/504. U. S. Environmental Protection Agency, Cincinnati, OH. [http://www.epa.gov/ada/download/issue/lwflw2a.pdf].

Salanitro, J. P., Johnson, P.C., Spinnler, G. E., Maner, P. M., Wisniewski, H. L., and Bruce, C. 2000. Field-scale demonstration of enhanced MTBE bioremediation through aquifer bioaugmentation and oxygenation. *Environmental Science and Technology*, v. 34, pp. 4152-4162.

Schnoor, J. L., Licht, L. A., McCutcheon, S. C., Wolfe, N. L., and Carreira, L. H. 1995. Phytoremediation of organic and nutrient contaminants. *Environmental Science and Technology*, v. 29, pp. 318-323A.

U. S. Environmental Protection Agency. 1999. EPA Methods and Guidance for Analysis of Water, June 1999, Office of Water, Washington, D.C, Version 2.0, EPA 821-C-99-004.

Wiedemeier, T. H., Swanson, M. A., Moutoux, D. E., Gordon, E. K., Wilson, J. T., Wilson, B. H., Kampbell, D. H., Haas, P. E., Miller, R. N., Hansen, J. E., and Chapelle, F. H. 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. EPA/600/R-98/128. U. S. Environmental Protection Agency, Cincinnati, OH. [http://www.epa.gov/ada/download/reports/protocol.pdf].

Wilson, J. T., Cho, J. S., Wilson, B. H., and Vardy, J. A. 2000. *Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions*, EPA/600/R-00/006. U. S. Environmental Protection Agency, Cincinnati, OH. [www.epa.gov/ada/reports].

Session 3 Summary:
Redox Processes in Inorganic Remediation

Robert W. Puls and William J. Deutsch

3.1 Introduction

The purpose of this session was to develop recommendations concerning reduction/oxidation (redox) measurement parameters for inorganic hazardous waste site remediation. It is hoped that the information provided will be useful to site managers to guide site characterization, data collection efforts, and, in particular, performance evaluation of in-situ remedial approaches. The following issues and/or questions were addressed in the session:

1) What remediation processes specific to inorganic contaminants require the need for redox measurements during site characterization and/or remediation (e.g., MNA, zero valent metal treatment, in-situ redox manipulation, etc.)?

2) What parameters must be measured during site assessment and remediation? Are the required parameter measurements universal or contaminant-specific? Is there a universal set of parameters that is sufficient for all remedial strategies?

3) What specific redox measurements are required (e.g., Eh, DO, Fe, etc.), how are redox measurements best made, and how are the measurements used? Is there a need to evaluate redox characteristics of the solid matrix in addition to the mobile phase?

The overall findings and conclusions from this session were:

- Geochemical models are recommended for use at all sites. Site data are needed to support the geochemical model.

- A set of core aqueous-phase redox measurement parameters are recommended for initial characterization at all sites to understand the redox status of the aquifer. Supplemental measurement parameters may be needed on a site-specific basis.

- There are commonalities for site characterization across treatment types and contaminant types.

- Eh measurement is included in the recommended core parameters, even though this measurement is controversial and may only provide qualitative information.

- Site diversity and differences in treatment applications preclude a "hard" list of redox measurement parameters applicable to every site. Measurement parameters will change from site-to-site.

- Solid-phase redox measurements are generally not performed. The solid-phase should be tested for metals to determine the form of the metal contaminant before and after treatment and to look at metal stability.

- Solid-phase sample preparation and analytical methods are lagging behind aqueous-phase methods and need more development.

- We need to be able to predict the performance of a selected site remedy (treatment) and its influence on the risk assessment. A decision tree for guidance on site evaluation would be useful.

- We need to define parameters/criteria for site closure (post-treatment monitoring).

3.2 Redox Processes Impacting Inorganic Contaminants

Redox processes are chemical reactions that include a transfer of electrons and consequently a change in valence state of elements that are either oxidized to a higher valence state or reduced to a lower valence state. This change in valence state of the elements impacts remediation through three mechanisms:

- Change in speciation to a lower/higher toxicity
- Solubility decrease to immobilize contaminants or increase in solubility to mobilize contaminants
- Adsorption/desorption impacts on contaminant mobility

Change in Valence and Toxicity

By definition, redox processes involve a change in valence state of the elements whereby one or more elements are oxidized and one or more are reduced. If the inorganic contaminant participates in these electron transfer reactions, then its valence state will change. The toxicity of an element is a function of its valence state because different valence states of the elements react to a greater or lesser degree with biological functions. For example, the acute toxicity of As(III) is substantially greater than that of As(V) (Franke and Moxon, 1936). Furthermore, As(III) is the initial substrate in the methylation of arsenic (Thomas, 1994); thus, changes in the arsenic valence state will have an effect on the production of the methylated arsenic species.

The relative toxicities of the different valence states of other redox-sensitive elements appear to be related to both availability and toxic effects. For example, the trivalent form of chromium [Cr(III)] is considered much less toxic than Cr(VI), however, this may be due as much to the lower solubility of Cr(III) solids in aquifer environments compared to Cr(VI) solids as to the inherent toxicity of the two valence states of chromium (Losi et al., 1994). In the case of selenium, availability and toxicity appears to be related to the presence of the more oxidized, soluble selenate [Se(VI)] and selenite [Se(IV)] redox states compared to the reduced, less soluble forms of elemental selenium (Se^o) and selenide [Se(-II)] (Neal, 1990).

Mineral Solubility Impacts on Remediation

Under equilibrium conditions, the solubility of a mineral limits the dissolved concentration of one of its constituent elements. The solubility of minerals containing the redox-sensitive elements can vary by orders of magnitude depending on the valence state of the element in the mineral, the redox status of the aquifer and in particular, the pH of the ground water. For example, the solubility of the Cr(III) mineral $Cr(OH)_3$ under typical ground-water conditions is in the part per billion range whereas the solubilities of Cr(VI) minerals under these same conditions are in the part per million range (Richard and Bourg, 1991). As a consequence, reducing Cr(VI) to Cr(III) either by adding a reductant to the aquifer or by allowing the natural system sufficient time to reduce the chromium valence state and reach equilibrium has the potential for achieving a ground-water cleanup level by precipitation of the relatively insoluble $Cr(OH)_3$ mineral.

The use of precipitation of low solubility minerals as a remediation measure is directly related to the concept of geochemical barriers in natural systems (Perelman, 1986). A geochemical barrier is a zone in the subsurface characterized by a sharp change in physical or chemical environment along the flowpath and is often associated with the precipitation of elements from solution. Redox barriers are classified as a type of physico-chemical barrier, which also includes alkaline, acidic, and adsorption barriers. Because barriers represent a change in environmental condition, each type of barrier must be considered in the context of the types of water with different redox characteristics that might enter the barrier. In addition to being a major control on solubility, the pH of the aquifer will affect the type of element immobilized by the geochemical barrier.

Methods of Immobilizing Inorganic Contaminants

Applied techniques for immobilizing inorganic contaminants are generally based on the well-documented natural processes that impact element mobility, particularly at geochemical barriers. If manganese concentrations in mildly oxidizing water downgradient from a landfill must be lowered, then either increasing the redox potential to precipitate a less soluble Mn(IV) oxide or reducing the redox potential and adding sulfide to form a less soluble sulfide mineral might be considered. Some of the issues to consider in the applied redox approach are the type and amount of reactant, means of emplacement, reaction kinetics, unwanted byproducts, solubility of contaminant-containing mineral, and geochemical stability of the imposed barrier environment. Some of the complexity of the situation has been shown by Seaman et al. (1999) who found that in situ immobilization of Cr(VI) by using Fe(II) solutions was complicated by the hydrolysis of Fe(III) which lowered the pH and mobilized Cr(VI) in column experiments.

The types of oxidizing and reducing compounds that have been tested or suggested to lower inorganic contaminant concentrations in an aquifer are listed in Table 3.1. Most of these compounds can be dissolved in water and injected into the aquifer. Air and ozone are added to the subsurface in a vapor phase. Elemental iron (Fe^o) is a solid that can be emplaced in a trench or as a slurry that intercepts the contaminated water. It has been shown to be effective not only at reducing the concentrations of inorganic contaminants (particularly chromate and uranium), but also chlorinated volatile organic compounds such as PCE and TCE. This type of remediation is expected to expand as its effectiveness becomes more widely known and the injection of reagents to achieve remediation becomes more commonly accepted by regulatory agencies.

Table 3.1 Potential Oxidants and Reductants for Inorganic Remediation

Oxidants/elements treated*	Reductants/elements treated*
Dissolved oxygen / Fe	Fe^0(PRB) / Cr, As, U, Tc, Se, Mo
Air / U, As	Colloidal Fe^0 / Cr, As, U, Tc
Oxygen Release Compound / As	Dithionite / Cr, U, Tc
Potassium permanganate	Sodium sulfide / Cr, U
Fenton's reagent	Hydrogen sulfide / Cr
	Fe^{2+} / Cr
	Ferrous sulfate / Cr
	Hydrogen Release Compound / Cr
	Organic materials / sulfate, nitrate, ARD

* known elements treated or proposed following successful lab testing

The adsorption capacity of an aquifer can be increased to immobilize contaminants by adding dissolved ferrous [Fe(II)] iron to an aquifer and then oxidizing the ferrous iron to precipitate ferric (oxy)hydroxide. The large surface area of this solid and its strong affinity for both dissolved cations and anions has the potential for substantially lowering dissolved contaminant concentrations.

Methods of Mobilizing Inorganic Contaminants

It is preferable to leave a contaminant in place if its mobile concentration can be reduced to below a cleanup level and rendered non-toxic; however, in some instances immobilization may not be possible and removal is necessary. Removal of an inorganic contaminant requires not just extraction of contaminated ground water, but also dissolution of contaminant-containing minerals and perhaps desorption of the contaminant from the surface of solids. If an element is concentrated under reducing conditions (e.g., Cr, U, Mo, Se), then creating oxidizing conditions in the aquifer should mobilize the contaminant. This is exactly the process used to mine uranium by in-situ leach methods. Oxygen is added to the subsurface where uranium has been concentrated by natural processes in the reduced U(IV) mineral uraninite (UO_2). Uraninite is soluble under the imposed oxidizing conditions leading to its dissolution and the removal of dissolved uranium in production wells.

Mobilization of contaminants can be complicated by the strong adsorption and high capacity of iron and manganese oxyhydroxides for other metals. If oxidizing conditions are generated in a reducing environment to mobilize metals, iron and manganese solids may precipitate and remove from solution some of the metals that are the target of remediation. This occurrence may require a stepwise mobilization process to first oxidize the elements in the minerals and then reduce and dissolve iron and manganese oxyhydroxides to release adsorbed contaminants. The kinetics of these reactions will also control the oxidation/reduction of the elements and can greatly impact any remedial scheme.

Adsorption/Desorption Impacts on Contaminant Mobility

Adsorption is the attachment of dissolved ground-water constituents to the surfaces of the aquifer solids and desorption is the release of the constituents back into the water. Redox reactions that affect the affinity or the capacity of the solid surfaces for dissolved constituents can impact contaminant mobility. Adsorption is very pH dependent because cations (or anions) of the same charge will adsorb at very different pH values depending on the element (Jain et al., 1999; Langmuir, 1997). Any remedial scheme which involves a redox manipulation that affects the pH of the system or alters the nature of sorbent surfaces can have profound impacts on element adsorption/desorption reactions and thus contaminant mobilization/immobilization.

3.3 Site Characterization Requirements

It is necessary to collect data during site characterization on the aqueous and solid phase geochemistry of the system, model the data, and construct a site conceptual model. This is an iterative, evolutionary process.

Aqueous Chemistry

Numerous redox measurement parameters required to characterize site geochemistry and to evaluate treatment were discussed in the session. Table 3.2 shows which parameters were considered to be core measurements that are recommended for all sites, as well as additional site-specific parameters that may be useful.

There was considerable debate about the usefulness and necessity of the Eh measurement. It is considered by some to be more of a qualitative measurement because it can give inconclusive results. The electrode will often not stabilize in oxygenated waters, or in reduced waters without sulfur being present. Many members of the panel felt that Eh determinations using electrodes were of limited usefulness in mixed waters (different ground-water sources). Discrepancies between Pt electrode measurements and Eh calculated from redox couples have been well documented (Lindberg and Runnells, 1984). The time required for stabilization of the electrode can also make the measurement impractical in the field. It was noted that because of this, Eh probably should not be a stabilization parameter for low-flow ground-water sampling. Others felt that in some settings the measurement has been shown to be of value (acid rock drainage) and research involving long-term performance of permeable reactive barriers has focused on Eh as a potential indicator of system performance. Eh can be helpful in context with other data, such as iron speciation. Some participants felt that it is a good idea to collect Eh data even though it may be a questionable measurement.

Finally, several members felt that the most valid approach to evaluate redox was collection of multiple parameters, including Pt electrode measurements, such as iron speciation and other site-specific redox couples (e.g., arsenic, sulfur). Table 3.3 lists some important characteristics of many redox-sensitive elements.

Table 3.2   Core and Site-Specific Redox Measurement Parameters

Core Parameters	Site-Specific Parameters	
Ground Water	*Ground Water*	*Solid-Phase*
Temperature	Dissolved Inorganic Carbon	Oxidizing Capacity
Eh, pH, alkalinity	Total Dissolved Solids	Reducing Capacity
Turbidity	Fluoride	Neutralization Capacity
Total and Ferrous Iron	Hydrogen	Adsorption Capacity
Dissolved Oxygen	Methane	Cation Exchange Capacity
Specific Conductance	Sulfide	Acid Generation Capacity
Dissolved Organic Carbon	Priority Metal Contaminants (As, Cd, Cr, Cu, Hg, etc.)	Total Metal(s) Concentration
Major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, S^{2-}, SO_4^{2-}, NO_3^-, Ammonium, Phosphate)		Iron/Aluminum Extraction
Aluminum, Silica, Manganese		Mineralogy (XRD)
		Total Organic Carbon
		Sulfur Extraction

Table 3.3 Sampling Parameters for Inorganic Characterization

Parameter	Comments
Field Measurements -	
Temperature	Must be done in the field; downhole (monitoring wells) preferred
pH	Must be done in the field, robust, easily measured, flow cell recommended
Eh	Must be done in the field, variable, more standard checks recommended, flow cell recommended
Dissolved Oxygen	Must be done in the field, variable, accuracy of probes limited at less than 1 mg/L
Turbidity	Must be done in the field
Specific Conductance	Recommended for field
Alkalinity	Recommended for field
Redox Indicators	S^{2-}, H_2
Laboratory Analyses – Water	
Major Cations	Ca, Mg, Na and K
Major Anions	HCO_3/CO_3, Cl, SO_4, NO_3/NO_2
Redox Indicators	Mn, Fe, S^{2-}, As(III)/As(V), CH_4, DOC,
Minor/Trace Constituents	Al, Si, PO_4, Br, F
Metals of Potential Concern	As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Tl, Zn

Collection of turbidity data was seen as important for a variety of reasons including its usefulness as a sampling equilibration parameter using low-flow techniques where metals are contaminants of concern, and to explain data anomalies (e.g., high total iron concentrations under oxidizing conditions) and evaluate the influence of particulates on metals concentrations.

The collection of major anion and cation data is important in order to properly evaluate the aqueous geochemistry of the system and perform accurate geochemical modeling in support of a site conceptual model. Additional information on this topic is covered in the next section. Fluoride was seen as important in some hydrogeologic settings because of its high complexing capacity and thus, its importance in adequate determination of ion balances for geochemical modeling purposes.

Solid Phase Geochemistry

There was a general consensus among the group that more solid phase characterization was required for site characterization and performance assessment of in-situ technologies for remediation of inorganic-contaminated sites. Some of these are listed in Table 3.2. The solid phase should be tested to confirm the form of the metal associated with the solid phase (mineralogy) to determine its stability or mobilization potential; this is particularly important for monitored natural attenuation (MNA) assessments. If immobilization is invoked for MNA, then it is imperative to know what the immobilization mechanism is and under what conditions it may be reversed (i.e., mobilized). Assessment of the oxidation and reduction capacities of sediments can be important for several in-situ remedial technologies including monitored natural attenuation and the creation of 'redox barriers' using injections of liquid reductants (Palmer and Puls, 1994; Fruchter et al., 2000). Sulfur extractions are useful to assess the nature of the redox environment and also the stability of precipitated solid phases. Similarly, extractions for amorphous and crystalline iron oxides are important in terms of metal stability and iron bioavailablity.

Field versus Laboratory Analyses

There was consensus among the group that certain parameters must be measured in the field due to stability issues and other measurements are recommended for the field but could be done in the laboratory. Table 4

attempts to address these concerns and provides at least a partial listing of some of the more commonly measured parameters.

Site Conceptual Model Development

The development of a site conceptual model is imperative for any site characterization effort, particularly as a project moves closer toward remedial selection. It involves the incorporation of a comprehensive assessment of physical, chemical, and biological processes operative within a defined geologic framework at a site. The group felt strongly that an iterative evolutionary process be employed to develop and refine a site conceptual model regarding ground-water flow, hydrogeochemical setting or definition, and contaminant fate and transport. The developing model must continually be tested against new data and be consistent with data collected throughout the site characterization process.

3.4 Geochemical Modeling

There are two primary reasons for using geochemical computer models at a site. The first is to better understand the processes active at the site and be able to explain observed compositions of the various phases and trends in composition across the site. The second reason is to aid in the remedial design for cleanup of a contaminated site. Accurate geochemical modeling of a contaminated site can be used to estimate the outcome of various remedial actions. The model can be used to select the best remediation technologies and to optimize application of the technology. This applies to the evaluation of both natural and applied redox processes as well as to other geochemical-based remediation measures such as pH neutralization.

The development of a geochemical model of a system starts with the compilation of available information on water composition, presence of solid phases, hydrogeology, etc. The existing site conditions are evaluated in terms of the known types of geochemical and physical processes that occur in the environment. These processes include mineral dissolution/precipitation, oxidation/reduction, adsorption/desorption, ground-water recharge, and mixing of ground waters from two or more aquifers. The combination of site specific conditions and known, common geochemical/physical processes leads to the development of a conceptual model of how the site operates. The conceptual model can be combined with a computer code to calculate the impacts of the various processes and provide quantitative estimates of these impacts on the composition of the various phases. The result is a geochemical computer model consisting of the conceptual model and the computer code that together can simulate existing conditions and predict the impact on the system of changes in environmental conditions.

3.4 Modeling Capabilities and Applications

The presence of dissolved constituents in water is a result of chemical interactions between water and the vapor and solid phases in contact with the water. A competent geochemical model of a site must be able to simulate the processes that occur between these phases. They include gas dissolution and exsolution from ground water, aqueous speciation, mineral dissolution/precipitation, oxidation/reduction, and adsorption/desorption. Two of the most commonly used equilibrium mass transfer codes are MINTEQA2 (Allison et al., 1991) and PHREEQC (Parkhurst, 1995). MINTEQA2 is available on the EPA website at ftp://ftp.epa.gov/epa_ceam/ wwwhtml/softwdos.htm and PHREEQC at the USGS website http://h2o.usgs.gov/software/geochemical.html.

The ability to simulate changing environmental conditions opens up the entire realm of remediation design to geochemical modeling. Once an accurate model of an existing contaminated site has been developed, it is relatively simple to vary site parameters and evaluate the impact of the new condition on contaminant concentrations in the solution and solid phases. The parameters that might be varied include pH, redox potential, ionic strength, and concentrations of complexing compounds. For remediation purposes, it is possible to evaluate both in-situ fixation and immobilization of contaminants as well as enhanced mobility and removal of contaminants from a system. For example, arsenic is strongly adsorbed onto iron oxyhydroxide minerals in shallow, oxidizing aquifers. If the dissolved arsenic concentration must be reduced in order to attain a cleanup goal, then adding additional iron minerals to the aquifer might enhance adsorption of arsenic and its removal from ground water. Alternatively, arsenic might be removed from the aquifer by circulating a reducing solution through the aquifer that dissolves the iron mineral adsorbents and releases arsenic to ground water so that it can be flushed more easily from the aquifer. Both of these remediation alternatives can be simulated with a geochemical model.

Table 3.4 Characteristics of Redox-Sensitive Inorganic Contaminants

Element	Redox States	Water Mobility
Antimony	III, V	Sb solids of both valence states are very soluble.
Arsenic	III, V	As (III) sulfide minerals insoluble at low Eh, As(V) minerals soluble.
Chromium	III, VI	Relatively immobile due to low solubility of Cr (III) hydroxides. Cr(VI) minerals highly soluble.
Copper	I, II	$Cu(OH)_2$ formation limits ground-water concentration; Cu solubility limited by hydroxysulfate, hydroxycarbonate.
Iron	II, III	Fe oxyhydroxides (HFO) form at pH $>$ 2.5 under oxidizing conditions and Fe (II) is limited by sulfides and carbonate under reducing conditions depending on pH and solution composition.
Manganese	II, III, IV	Mn (III, IV) oxides and oxyhydroxides relatively insoluble when pH $>$ 5 and oxidizing; Mn (II) carbonate more soluble but stable in reducing conditions.
Mercury	0, I, II	Soluble solids when pH $>$ 4 and oxidizing; relatively insoluble sulfide minerals under reducing conditions.
Nitrogen	-III, 0, III, V	No concentration limiting solid phases; dentrification may limit nitrate.
Selenium	-II, 0, IV, VI	Soluble selenite/selenate minerals; selenide less soluble than selenite which is less soluble than selenate.
Sulfur	-II to VI	Soluble sulfate minerals; insoluble sulfide minerals.
Vanadium	III, IV, V	May substitute for Fe in ferric oxide lattices; mobile in reducing conditions.
Uranium	IV, VI	Soluble VI minerals; insoluble IV oxides.

One of the additional benefits of modeling remediation is that secondary reactions that might not be immediately obvious to the investigator may become clear in reviewing the modeling results. For example, adding iron to an aquifer to precipitate as iron oxyhydroxide and provide additional adsorption sites may change the pH of the solution because iron precipitation is a hydrolysis reaction that produces hydrogen ions. If the system is not well buffered, the pH will decrease, which, in turn, may mobilize other metals. The aqueous speciation computer codes used to develop the geochemical models can take into account the formation of hydrogen ions during iron precipitation and will allow for buffering by carbonate/bicarbonate ions in solution. If carbonate minerals are also present in the system, the modeler may want to allow them to interact with the solution as iron carbonate precipitates.

Limitations

The utility of a geochemical model for a particular site is limited by errors introduced during development of the model and our ability to model certain processes. The first opportunity for introducing error into the process is data collection. The model developed is highly dependent on accurate physical and chemical data from the site. We need to know flow direction to determine whether concentrations are increasing or decreasing along the flow path and we need accurate measurements of temperature, pH, Eh, and concentrations

of dissolved constituents. For example, an incorrect Eh will affect the speciation of all redox-sensitive species that are allowed by the modeler to equilibrate with the measured value. If nonequilibrium conditions exist for some of the allowed redox pairs, then the model calculations will be incorrect. This will, in turn, affect calculations of mineral equilibrium and solubility. Therefore it is important to collect speciation data on iron and other redox-sensitive elements which may be present in the aquifer to increase confidence in the approximate redox poising of the system.

Most of the major inorganic geochemical processes impacting natural systems are well known and incorporated into the modeling codes. However, certain systems may be relatively unique and some of the processes occurring may not be standardized in the available computer codes. For example, some of the elements that may be of interest for evaluating radionuclide migration (such as plutonium and americium) are not in the standard databases of MINTEQA2 or PHREEQC. Also, a rare mineral or amorphous solid may limit solution concentrations of a contaminant that does not normally reach high concentrations in the natural environment. If this solid phase is not in the code database, its formation cannot be simulated. Most of the available computer codes allow the user to input new thermodynamic data for elements, solution complexes and solid phases. This allows the user to develop an appropriate model if concentration and thermodynamic data are available.

The computer code used to make the calculations required by the model has its own limitations. Many of the equilibrium thermodynamic codes do not have a method of calculating reaction rates. If a mineral forms or dissolves slowly in a system, the model developed from these codes will not account for these kinetic effects. This is not a major limitation for most aquifer systems where residence times are measured in years; however, kinetic effects can become more important in modeling surface water systems or reactions anticipated to occur during applied remediation methods such as the injection of reactants into an aquifer. PHREEQC is one of the few models which does have kinetic data as part of the code.

These limitations should be considered in developing a geochemical model, however they will rarely be sufficient reason for not developing a model for a site. Considering the number of useful applications for a geochemical model in site characterization, contaminant transport and remediation design, it is often beneficial to collect sufficient data for modeling and develop a geochemical model for each site.

3.5 Applications to Remediation Methods

A number of in-situ remedial methods were discussed where redox processes are key to implementation and success. These included the following: physical emplacement (permeable reactive barriers), reagent injection (potassium permanganate, Fenton's reagent, colloidal iron, sodium dithionite, sodium sulfide), and natural attenuation. The group chose to focus on permeable reactive barriers due to a preponderance of experience with this in-situ technology by members of the group. Additional discussions involved the issue of acid rock drainage (ARD) because of the magnitude of the problem and recognition of ARD as an emerging environmental isssue.

Permeable Reactive Barriers

In terms of initial site assessment for permeable reactive barrier application, the core list referenced above in Table 3.2 was deemed adequate by the group. The following additional measurement parameters specific to PRBs were also recommended by the participants:

- verify site ground water/barrier interaction - rate of loading of contaminant (e.g., Cr) onto reactive media (e.g., iron)
- microbiological activity (biomass estimates and populations [e.g., iron oxidizers, sulfate reducers, etc.]) upgradient, downgradient and within the PRB
- longevity (examination of precipitation and clogging within reactive zone over time)
- metal speciation
- solid-phase analysis (see Table 3.2)
- hydrology
- conservative tracer to track movement into, and through barrier (bromide, chloride, iodide, etc.)

It is imperative to know the extent of source area contamination to design an appropriate remedial system. Will/can the source area be removed/treated? If left in place, how long will the source area contribute to

contamination of the ground water? Identification of the plume boundaries in three-dimensional space as well as temporal variation is important in siting and designing the PRB. Verification monitoring to demonstrate treatment effectiveness is also needed. For long-term usage, one needs to determine how quickly mineral precipitates are accumulating on the iron surface, which will decrease porosity over time and will also passivate the reactive surfaces. Coatings may accumulate faster in some geochemical environments compared to others (e.g., high sulfate or high alkalinity waters). Regulators want to know how long the PRB is going to work.

In the specific case of chromium remediation using PRBs, the following list of parameters has been measured:

- Cr speciation, aqueous
- Cr speciation, solid phase (sequential extractions, surface analyses)
- Oxidation capacity, adsorption capacity of aquifer solids
- Permeability assessment of PRB over time (water levels, flow meters, tracer tests)
- Microbiological assessments (phospholipid fatty acid analyses)

Cost-effective methods for long-term performance monitoring of these systems are currently being evaluated by a number of groups. It is hoped that some direct and inexpensive methods may be employed to accurately and safely predict performance and longevity.

3.6 Acid Rock Drainage

This group discussed numerous technologies used to remediate Acid Rock Drainage (ARD) and many more that are proposed but not used. Many of these techniques, however, apply to cleanup of surface waters, not ground waters. Interactions between surface waters and ground waters are important, but the nature of these interactions and their environmental impacts are not well understood. Redox chemistry is what ARD production, remediation, and performance assessment is all about. All remediation technologies need to address neutralization and many utilize reductive processes. ARD can be categorized into six types:

- Underground workings
- Tailings
- Waste Rock
- Contaminated Aquifers
- Heap leach pads
- Pit lakes/Open pits (not necessarily acid, but redox is definitely important)
- Slag
- Backfill

Necessary redox parameters are the same as those outlined for other inorganic contaminant situations. Iron speciation [Fe(II)/Fe(III)] is necessary instead of optional and prioritization of other parameters will be site-specific. For example, some sites require measurement of As(III)/As(V), but not H_2S and vice versa.

Three groups of mineral assemblages are needed to undergo solid phase analyses: oxidizable (sulfide) minerals, gangue minerals, and country rock minerals. Solid phase analyses are needed to evaluate 1) the amounts/types of acid-generating sulfide minerals, 2) the amounts/types of acid-neutralizing minerals (carbonates, alumino-silicates), and 3) the reactivity of these minerals (function of crystal form, size, and composition).

An important aspect of remedial technologies for ARD is that there are very few, clear-cut success stories with cleanup, long-term maintenance, and with monitoring for decades demonstrating compliance. Hence, it is difficult to look to case histories for guidance.

3.7 Summary

The members of this group were acknowledged experts in the area of environmental assessment and remediation for inorganics in the environment. Members were employed in industry, universities and the government sector. Many had extensive field experience in monitoring and remediation. Strong consensus was reached on a number of issues including the following:

- Use of geochemical models is strongly recommended for all sites and sufficient data for model usage needs to be collected.

- Certain core geochemical parameters need to be measured at all sites.
- Supplemental parameters are also needed for all sites.
- The diversity of contaminant behavior and potential remedial technologies precludes a one-size-fits-all list of parameters.
- Metals are persistent in the environment. If immobilization technologies are considered, the solid phase must be analyzed to determine/verify the form of the contaminant and evaluate whether conditions will persist to contain the contaminant.
- Development and application of analytical methods (extractions) for solid phase analyses lags those for the aqueous phase and more research is needed in this area.

References

Allison, J. K., Brown, D. S., and Novo-Gradac, K. J. 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems*, U.S. Environmental Protection Agency.

Franke, K. W. and Moxon, A. L. 1936. A comparison of the minimum fatal dose of selenium, tellurium, arsenic and vanadium. *Journal of Pharmacology and Experimental Therapeutics*, v. 58, pp. 454-459.

Fruchter, J. S., Cole, C. R., Williams, M. D., Vermeul, V. R., Amonette, J. E., Szecsody, J. E., Istok, J. D., and M. D. Humphrey. 2000. Creation of a subsurface permeable treatment zone for aqueous chromate contamination using in situ redox manipulation. *Ground Water Monitoring & Remediation*, v. 20, pp. 66-77.

Jain, A., K. P. Raven and R. H. Loeppert. 1999. Arsenite and arsenate adsorption on ferrihydrite: Surface charge reduction and net OH$^-$ release stoichiometry. *Environmental Science and Technology*, v. 33, pp.1179-1184.

Langmuir, D. *Aqueous Environmental Geochemistry.* Prentice Hall, 600p.

Lindberg, R. D. and Runnells, D. D. 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science*, v. 225, pp. 925-927.

Losi, M. E., Amrhein, C., and Frankenberger, W. T. Jr. 1994. Factors affecting chemical and biological reduction of hexavalent chromium in soil. *Environmental Toxicology and Chemistry*, v. 13, pp. 1727-1735.

Neal, R. H. 1990. Selenium. In *Heavy Metals in Soils*, ed. B. J. Alloway. Blackie, Glasgow, pp. 237-270.

Palmer, C. D. and Puls, R. W. 1994. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils*, EPA/540/S-94/505. U. S. Environmental Protection Agency, Cincinnati, OH.

Parkhurst, D. L. 1995. *User's guide to PHREEQC, a computer model for speciation, reaction path, advective transport and inverse geochemical calculations.* U.S. Geological Survey.

Perelman, A.I. 1986. Geochemical barriers: theory and practical applications. *Applied Geochemistry*, v. 1, pp. 669-680.

Richard, F. C. and Bourg, A. C. M. 1991. Aqueous geochemistry of chromium: a review. *Water Resources*, v. 25, pp. 807-816.

Seaman J.C., P.M. Bertsch and L. Schwallie. 1999. In situ Cr(VI) reduction within coarse-textured, oxide-coated soil and aquifer systems using Fe(II) solutions. *Environmental Science and Technology*, v. 33, pp. 938-944.

Thomas, D. J. 1994. Arsenic toxicity in humans: research problems and prospects. *Environmental Geochemistry and Health*, v. 16, pp. 107-111.

Session 4 Summary:
Field Measurement of Geochemical Redox Parameters

Richard T. Wilkin and Carol J. Ptacek

4.1   Introduction

Conceptual models of contaminant transport and fate in ground water critically depend on geochemical measurements and their interpretation. Transport and fate processes are often dependent on redox processes because in many cases oxidation-reduction reactions cause changes in speciation that have a marked effect on contaminant mobility and toxicity. The importance of reliable field characterization is especially significant when evaluating redox-sensitive speciation because of the potential for sample alteration (oxidation) during sample collection and handling.

This group considered methods used by environmental scientists to characterize the redox chemistry of ground water in support of site characterization and remedial performance monitoring. The group recognized that a wide variety of analytical techniques are available to quantitate redox-sensitive elements (e.g., Fe, S, N). Selection of the appropriate technique for a given parameter will depend on specific project objectives. It was recognized that project objectives and principal data uses collected in monitoring programs change with time as more site-specific information is obtained and conceptual models evolve. Although a wide variety of techniques are available for redox characterization (see Appendix A), members of this group agreed that standards for improved field practices are needed (see, for example, U.S. Geological Survey, 1997). Methods of analysis identified during the group discussion are briefly reviewed in this chapter, and include Eh, dissolved oxygen, iron speciation, sulfur speciation, nitrogen speciation, and alkalinity.

4.2   Sampling and Measurement Objectives

Sample collection programs are designed around goals associated with specific project objectives. Data Quality Objectives (DQOs) define the types, quality, and quantity of data that are required by the various aspects of a project. With DQOs in place, appropriate sampling methodologies, analytical protocols, and specific methods may be considered and selected. For example, DQOs may be different if project goals put emphasis on detection and monitoring of contaminant concentrations or whether geochemical speciation and the development of site conceptual models are targeted goals.

The principal objective of geochemical characterization in site assessment and remedial performance monitoring is to obtain water quality information, with no alteration of water chemistry, from a chosen sampling point. Such uncompromised data are critical in developing accurate conceptual and quantitative models of contaminant transport and fate. There was strong agreement among the group that sample collection practices and measurement techniques are among the greatest challenges to developing reliable site conceptual models. Several categories of ground-water sampling methods were recognized: accumulation or diffusion samplers, purge techniques with flow-through cells, and bailing. The generally recommended and most commonly practiced method is low-flow, minimal draw-down purging and sampling. Low-flow methods minimize chemical and hydrological disturbances in and around the well. In some situations, multiple-tube bundle piezometers or diffusion samplers may provide the best method for collecting ground-water samples without chemical alteration. Bailing techniques were not recommended for purposes of redox characterization because of the likelihood of changing water chemistry by unavoidable reaction with air.

Measurements of geochemical parameters can be divided into three categories: laboratory, in situ, and purging or field measurements. Laboratory analyses are carried out on preserved samples for characterization of total or selected metals, anions, and organic constituents. In some cases redox integrity of dissolved components can be

preserved by acidification (e.g., for NO_3^-/NH_4^+) because oxidation rates generally decrease substantially with decreasing pH. In situ measurements such as down hole probes or contained sampling devices are desirable for the measurement of unstable parameters that are ideally made at well conditions. In-situ measurements are potentially advantageous for the determination of dissolved oxygen, temperature, and oxidation-reduction potential. Project objectives may or may not require the extra cost and effort required to collect data using in-situ techniques.

Measurements carried out in the field include electrode measurements of DO, pH, specific conductance, Eh, and other ions using ion-selective electrodes. Field-deployable techniques for ions also include UV-Vis spectrometry and ion chromatography. Field analyses are made to gather information in the field to guide activities and/or because the measured parameters are considered to be too unstable to transport samples without compromising their chemical integrity. There was general agreement that unstable parameters, best measured in the field at the time of sample collection, include pH, turbidity, DO, ferrous iron, alkalinity, sulfide, and oxidation-reduction potential. Measurements of these parameters are ideally made during well purging. Members of the group reported a variety of demonstrated techniques for preserving the redox integrity of samples pumped to the surface, such as: minimizing tubing length, use of high-quality tubing with low oxygen diffusion coefficients, use of syringes with luer-lok fittings, preventing direct exposure of tubing and all electronic equipment to sunlight, and ensuring air-tight seals. Specific methods are discussed below for the measurement of Eh, DO, and speciation of iron, sulfur, and nitrogen (Table 4.1).

Table 4.1 Redox Parameters and their Common Methods of Measurement

Parameter	Common Field Methods	Standards for Performance Assessments	References
Oxidation-Reduction Potential (ORP)	Combination Platinum electrode with Ag/AgCl reference electrode; KCl filling solution	Zobell's solution; Light's solution	Langmuir (1971) Nordstrom (1977) Standard Methods for the Examination of Water and Wastewater (1999)
Dissolved Oxygen (DO)	Membrane-covered electrode Colorimetric (high range, indigo carmine) Colorimetric (low range, rhodazine D) Modified Winkler titration	Air-saturated water	Hitchman (1978) Gilbert et al. (1982) White et al. (1990) Standard Methods for the Examination of Water and Wastewater (1999)
Iron Speciation	Ferrous iron colorimetric indicators (1,10 phenanthroline; ferrozine)	Prepared ferrous solutions	Tamura et al. (1974) Stookey (1970)
Sulfur Speciation	Sulfate (turbidimetric); Sulfide (methylene blue colorimetric method)	Prepared sulfate and sulfide solutions	Standard Methods for the Examination of Water and Wastewater (1999) Cline (1969)
Nitrogen Speciation	Nitrate+Nitrite (cadmium reduction) Ammonia (Nessler method; Salicylate method)	Prepared nitrate, nitrite, or ammonia solutions	Standard Methods for the Examination of Water and Wastewater (1999)
Alkalinity	Acid titration	Prepared bicarbonate or carbonate solutions	Standard Methods for the Examination of Water and Wastewater (1999)

4.3 Geochemical Parameters

Eh

The Eh measurement is the most commonly used technique to characterize the oxidation-reduction state of ground water. Eh is the measured potential of a platinum electrode corrected to the Standard Hydrogen Electrode (SHE). Eh is not the same as the oxidation-reduction potential (ORP), which is the direct, uncorrected potential reading of the reference electrode. It was recognized during the group discussion that although measured Eh values usually do not correspond to Eh values calculated using the Nernst Equation with measured concentrations of aqueous redox pairs, e.g., N(V)/N(-III) or S(-II)/S(VI), there is benefit to measuring this parameter in the field. Eh measurements are a relatively easy approach for determining overall redox conditions. Eh measurements should be thought of as qualitative indicators of the state of oxidation or reduction of a natural system (Langmuir, 1971). In rare situations, such as acid-mine waters, high activities of both Fe(III) and Fe(II) provide a dominant and reversible couple that poises Eh measurements (Nordstrom et al., 1979).   Many ground waters are not well poised and speciation calculations for ground waters have shown that redox couples typically exist in a state of disequilibrium (e.g., Stumm, 1966; Lindberg and Runnells, 1984). Such systems in disequilibrium yield mixed potentials that may or may not represent the redox distribution of any specific redox couple. The reasons for this include disequilibria in low-temperature ground water (Lindberg and Runnells, 1984; Thorstenson, 1984), poisoning or coating of Pt electrodes (Jackson and Patterson, 1982; Whitfield, 1974), potential measurements reflect mixed potentials with little thermodynamic significance (Morris and Stumm, 1967).

The recommended procedure for measurement of Eh involves the use of a small-volume flow-through cell into which a temperature and Eh electrode is inserted. The type of electrode recommended for ease of use is a high-quality combination Pt electrode typically with a Ag/AgCl reference electrode. After purging the flow-through cell with several volumes of ground-water, Eh readings are recorded until they stabilize or a minimum value is obtained. Often 30 minutes or longer is required for electrode stabilization, but the group generally agreed that waiting >30 minutes for electrode stabilization was not a time-effective practice. Proper preparation and mainte-nance of the Pt electrode is required, including frequent polishing of the electrode surface, changing of the internal filling solution, and frequent checks with standard solutions that are maintained at ground-water temperature (American Public Health Association et al., 1999). The most common standard solution for reference checks is Zobell's solution (Nordstrom, 1977). Additional check solutions include Light's solution (Light, 1972), and others recommended by electrode manufacturers (i.e., Orion ORP standard). The importance of correcting field measure-ments of ORP to reference the values to the Standard Hydrogen Electrode was emphasized. To properly reference measured values, correction factors must be available as a function of temperature for the specific type of reference electrode and reference solution used in the measurement assembly. To determine Eh of a sample relative to the Standard Hydrogen Electrode, measure the ORP of both sample and standard solution (at the same temperature). Eh of the sample may then be calculated:

$$\text{Eh} = \text{ORP (mV)} - \text{ORP}_{\text{reference solution}}\,(\text{mV}) + \text{Eh}_{\text{reference solution}}\,(\text{mV}) \qquad [1]$$

The group discussed the limitations on the use of corrected Eh readings. It was recommended that the readings be used in three ways: 1) as a general guide to interpret other redox data, 2) for speciation of Fe(II) and Fe(III) in acidic mine drainage waters, and 3) for geochemical speciation calculations to determine mineral stability for selected Fe and Mn phases that are stable under intermediate Eh conditions. Views from the session participants varied, but it was recognized that in the absence of a field Eh reading, there was no widely available method of calculating saturation indices for phases such as Fe(oxy)hydroxides, Mn oxides, and Mn and Fe carbonates. It was further recommended that Eh values should not be used to determine saturation indices for phases such as FeS, which incorporate species (HS^-) that are not generally responsive to measurement by Pt electrodes (Whitfield, 1974; Walton-Day et al., 1990).

Dissolved Oxygen

Dissolved oxygen (DO) is often the principal oxidizing chemical component in ground water; consequently, DO can be a key parameter governing the mobility of redox-sensitive contaminants, including organic compounds, transition metals, and transuranic metals.   DO is also important in governing the nature and level of microbial activity. It is therefore directly tied to the fate of dissolved nutrients and organic contaminants consumed through metabolic processes (e.g., Baedecker and Back, 1979). The concentration of DO in ground water is controlled by local inputs of oxygen-rich meteoric water, microbial respiration, biodegradation of organic matter, and reaction with reduced mineral phases in the aquifer (Champ et al., 1979; White et al., 1990).

The group recognized four major methods for determining DO concentrations: 1) the Winkler titrimetric method, 2) the membrane-covered electrode method, 3) the indigo carmine colorimetric method, and 4) the rhodazine D colorimetric method. Of these methods, the Winkler method (and its modifications) was regarded as the most accurate and precise technique for determining DO. This method has served as a benchmark for laboratory comparisons and calibration of the electrochemical and colorimetric techniques (e.g., Reynolds, 1969; Hitchman, 1978; Gilbert et al., 1982). From the field perspective, the Winkler method is cumbersome and it uses reagents that can be hazardous to manage in the field. Seven different Winkler modifications exist and selection of the appropriate modification requires prior knowledge of a sample that is often not available during field investigations.

Because of the difficulties associated with carrying out Winkler titrations in the field, alternative methods such as membrane-covered polarographic electrodes are widely used (Hitchman, 1978). Membrane-covered electrodes are simple to use and calibration checks are usually limited to determining oxygen concentrations in water-saturated air (American Society for Testing Materials, 1992). Electrodes are ideally suited for in-situ measurements of DO concentrations and for continuous monitoring of oxygen levels. Dissolved oxygen electrodes do not function at temperatures greater than about 50 °C, which is not a limitation for most ground waters. Membrane fouling can be a common cause of difficulty, and electrode measurements can be inaccurate without any indication that poor results are being obtained. Hydrogen sulfide, thio-organic, and other organic compounds are the most problematic to continued reliable electrode performance. These species react irreversibly at the electrode surface and detrimentally affect electrode response and accuracy.

Several colorimetric methods have been developed for the measurement of DO. The indigo carmine (blue) and rhodazine D (reddish violet) methods are the most prominently used techniques (Gilbert et al., 1982; White et al., 1990; American Society for Testing Materials, 1995a). These colorimetric procedures provide quick and convenient methods for accurate field measurements of dissolved oxygen. Colorimetric reagents utilize oxidation-reduction indicators that upon reaction with dissolved oxygen in water transform from reduced, colorless forms to oxidized, colored forms. The extent of color formation is proportional to the concentration of dissolved oxygen and can be measured by visual comparison to sets of liquid color standards or with a spectrophotometer. Color development by reaction with dissolved oxygen is independent of salinity so that a wide range of sample types from seawater to fresh water can be analyzed with these methods without correction (Gilbert et al., 1982).

Because the colorimetric reagents involve oxidation-reduction reactions to indicate the concentration of DO, other redox species in ground water can influence the result of colorimetric determinations (Gilbert et al., 1982). Concentrations of the easily reduced species Fe(III), Cr(VI), and Cu(II) can lead to erroneously high DO values when rhodazine D is used (White et al., 1990). A potential cause of false-positive readings using the rhodazine-D reagent in ground-water studies may be the presence of very fine-grained ferric hydroxide colloids. Both Fe(II) and Fe(III) as well as nitrite were shown to lead to inaccurate determinations of DO using the indigo carmine reagent (Gilbert et al., 1982). Hydrogen sulfide does not interfere with either colorimetric technique. The effects of dissolved organic carbon (DOC) on the use of the rhodazine D and indigo carmine reagents are incompletely understood.

Winkler, electrode, and colorimetric methods for determining DO have different strengths and weaknesses. For projects requiring the highest available quality (in terms of accuracy and precision over a wide range of DO concentrations), the extra effort associated with the Winkler methods is warranted. Where data quality objectives are not as strict, both electrode and colorimetric methods are acceptable. Electrodes are generally reliable at DO levels above 1 mg/L, but are less accurate at levels below 1 mg/L. Multiple methods are preferred if high quality data are required to meet project objectives (Wilkin et al., 2001). Figure 4.1 shows a decision tree discussed by the group that may be useful for selecting an appropriate method or methods for DO determination.

The most common and convenient quality check for field measurements of DO is air-saturated water. Air-saturation is achieved using an aerator or through manual agitation. Members of the group pointed out that using such methods can cause water to become supersaturated with respect to air. Air-saturated DO values are mainly dependent on temperature and less so on salinity (Figure 4.2). Thus, when quality check values are reported the temperature must be specified for the check to be meaningful.

Iron Speciation

Iron is present in ground water as dissolved ferrous iron (Fe(II)), colloidal particles containing either ferric or ferrous iron, and as dissolved ferric iron (Fe(III)). The relative and absolute abundances of these iron forms vary widely depending mainly on pH and redox state of ground water. Dissolved forms may be unassociated or
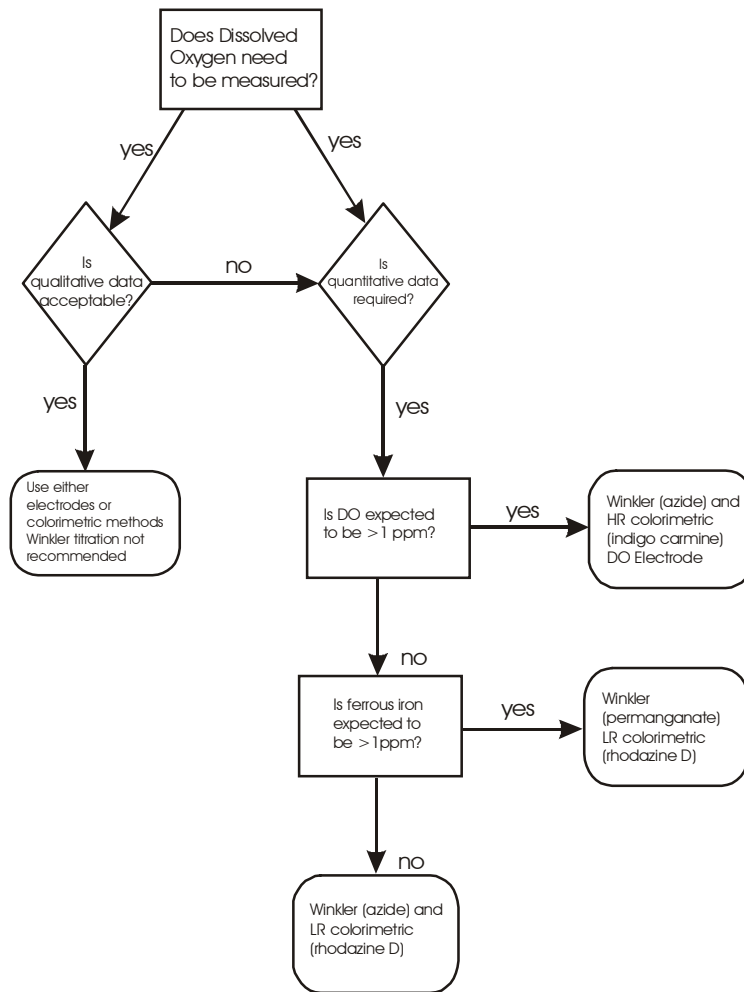
Figure 4.1 Decision tree for selecting method for determining concentration of DO.
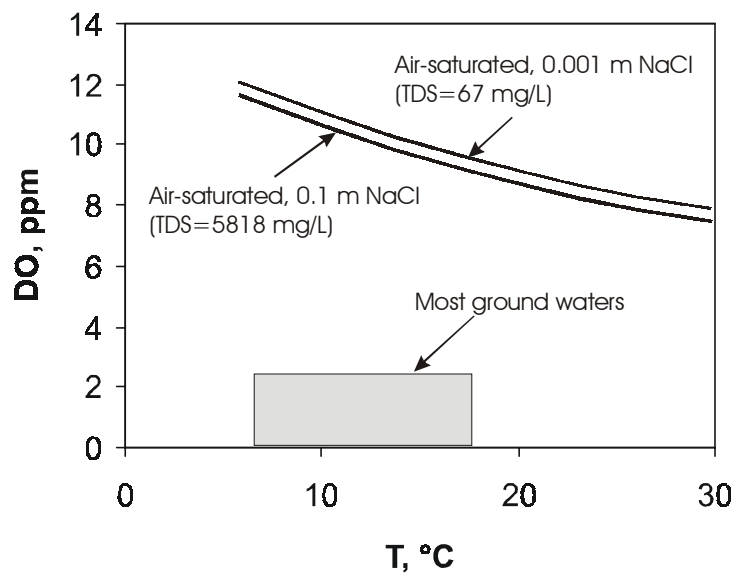

Figure 4.2 Air-saturated DO concentration in water.

complexed with organic or inorganic ligands. Dissolved iron is generally considered to be that fraction passing through a 0.45 μm filter paper, however, water filtered in this way may still contain colloidal iron that will dissolve upon addition of an acid.

Ground waters containing dissolved oxygen at concentrations above 1 mg/L will seldom contain concentrations of dissolved iron above 1 mg/L. Exceptions to this general rule are more acidic ground waters (pH<4) in which the solubility of ferric oxyhydroxides is sufficiently high to be detected using standard methods of analysis. The solubility of ferrous iron increases under reducing conditions, where oxygen is depleted and Eh values are low (<0 mV). In zones of intense iron reduction, concentrations of ferrous iron may reach levels as high as several hundred mg/L.

Dissolved Fe(II) concentrations in ground waters are commonly measured using colorimetric techniques with complexing reagents, such as 1,10 phenanthroline (Tamura et al., 1974), ferrozine (Stookey, 1970 as modified by Gibbs, 1976; To et al., 1999), and bipyridine (e.g., Baedecker and Cozzarelli, 1992). There was general agreement among the group that ferrous iron measurements using colorimetric reagents should be completed soon after sample collection. Minimizing the amount of time between sample collection and Fe(II) measurement is necessary because of the relatively fast oxidation rate of ferrous iron at near-neutral pH. Ferrous iron oxidizes following the overall reaction

$$Fe^{2+} + 5/2H_2O + 1/4O_2 = Fe(OH)_3 + 2H^+$$

The abiotic rate of ferrous iron oxidation is principally controlled by the partial pressure of O_2, pH, and alkalinity. At pH<3.5, the oxidation rate of ferrous iron is slow and independent of pH. At pH below about 5, however, iron-oxidizing bacteria greatly increase the rate of iron oxidation. For purposes of sample preservation biotic ferrous iron oxidation is avoided by filtration and acidification. At pH>3.5, a pH-dependent rate equation is given by Eary and Schramke (1990):

$$-d[Fe^{2+}]/dt = k[Fe^{2+}]P O_2[OH^-]^2$$

Figure 4.3 shows the rate of ferrous iron consumption via oxidation as a function of pH (6-8) and $P O_2$ (0.02 and 0.2 bars) estimated using this equation. Note that at pH 7, ferrous iron concentrations will decrease by a factor of two in < 15 minutes at air-saturated conditions. A sample recovered from a well and brought to the surface does not necessarily experience the full atmospheric $P O_2$ of 0.2 bars unless it is continuously agitated. A more realistic value of $P O_2 = 0.02$ bars still imparts a fast loss of Fe(II), especially at pH > 7 (Figure 4.3). These calculations illustrate the importance of carrying out Fe(II) measurements immediately after sample collection.

A common practice for estimating Fe(III) is to measure total iron (ΣFe) on filtered and acidified samples and subtract from that quantity the concentration of ferrous iron from measurements made in the field. The group agreed that no assumptions should be made about the speciation of the iron fraction represented by ΣFe-Fe(II). At near-neutral pH and in the absence of significant concentrations of DOC there should be reasonable agreement between total iron and Fe(II). However, ΣFe on filtered samples should not be assumed to be equal to Fe(II) due to the potential formation of soluble Fe(III) - DOC complexes. Measurement of total iron can in many instances be a useful quality check for Fe(II) measurements made in the field.

Acid mine drainage represents a special case with respect to iron measurements because at low pH the solubility of Fe(III) increases significantly. An accurate determination of the abundances of Fe(II) and Fe(III) is especially important because such waters are typically rich in iron and charge balance calculations strongly depend on the Fe(II)/Fe(III) ratio (see To et al., 1999). When dealing with low pH waters it is desirable to directly measure Fe(III) concentrations (To et al., 1999).

Field quality checks can be carried out using purchased or prepared iron solutions. Mohr's salt (ferrous ammonium sulfate) can be used as a standard ferrous solution. Standard solutions should be prepared daily and ideally should be made from deoxygenated water, prepared by purging with nitrogen gas.

Sulfur Speciation

Dissolved sulfur may be present in ground water as sulfate (most oxidized form), sulfide (most reduced form), or as species with oxidation states intermediate between sulfate and sulfide including polysulfides, sulfite, and thiosulfate. Concentrations of the intermediate sulfur species are typically low in ground water and their occurrence is believed to be restricted to redox interfaces that separate reducing hydrogen sulfide-bearing waters from oxygenated waters. Such interfaces can occur within aquifers or in mixing zones between ground and surface waters. Sampling techniques and methods for determining the concentration of intermediate sulfoxyanions can be
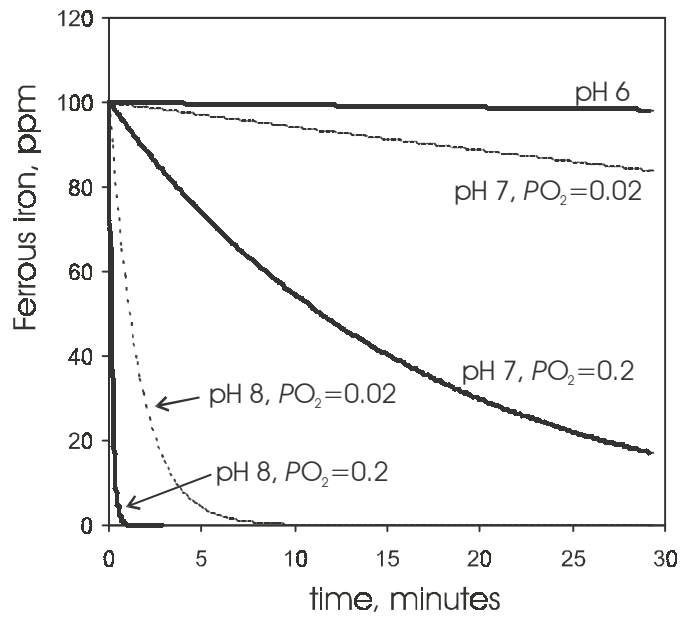
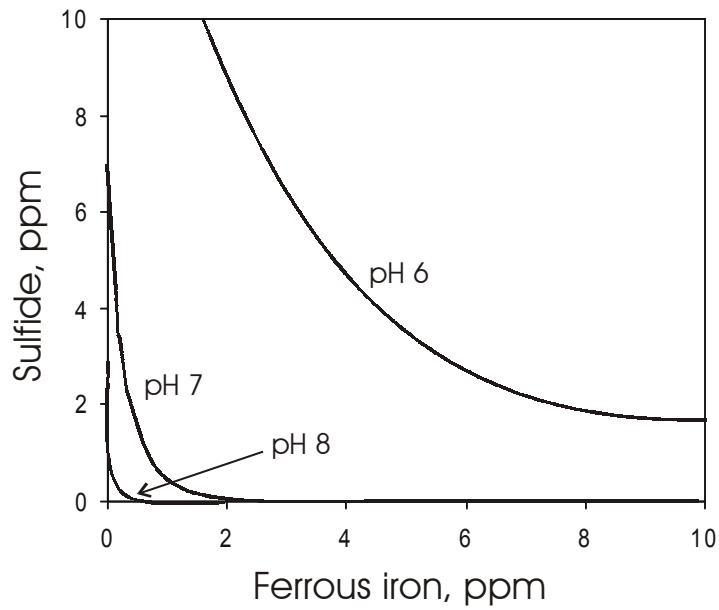**Figure 4.3** Ferrous iron oxidation kinetics at pH 6-8 and PO_2 at 0.02 and 0.2 bars.

Figure 4.4 Iron monosulfide solubility at pH 6-8 (Ionic strength = 0.0).

found in Moses et al. (1984). Sulfate concentrations in ground water vary widely from below 1 to several thousand milligrams per liter. The highest concentrations of sulfate are typically found associated with acidic surface drainage produced from the oxidative weathering of metal sulfides. Sulfate concentrations in ground water are measured using gravimetric methods (precipitation as barium sulfate), the barium dichloride turbidimetric method, or using laboratory techniques such as ion chromatography or capillary electrophoresis. Preservation is generally not a problem for sulfate unless samples are especially rich in DOC that can be respired by sulfate reducing bacteria. Because samples collected for anions are typically not acidified, ferrous iron-rich samples may be problematic if sulfate becomes incorporated into iron hydroxide precipitates that form prior to sample analysis.

Hydrogen sulfide is produced in anoxic systems through the bacterial reduction of sulfate. Measurements of total sulfide in ground water include $H_2S(aq)$, HS^-, and acid-soluble metal sulfides present in colloidal suspended materials. These species can react rapidly in the presence of oxygen so samples must be collected with a minimum of aeration. Methods for determining hydrogen sulfide concentrations include electrode, gravimetric, iodometric, and colorimetric techniques.

The handling and storage methods are critical for water samples containing concentrations of dissolved sulfide. Ideally, measurements are carried out immediately after sample collection. Preservation of samples will otherwise be necessary to prevent losses through volatilization or oxidation. At pH less than ~6, volatilization of H_2S can be a problem, i.e., $H_2S(aq) \rightarrow H_2S(gas)$. Sulfide anti-oxidant buffers (SAOB) are alkaline solutions that contain complexing agents such as EDTA and a reductant such as ascorbate. Hydrogen sulfide is then released from the alkaline solutions by acidification and purging with an inert gas such as nitrogen or argon.

The most commonly used methods for determining dissolved sulfide concentrations are modifications of the methylene blue technique described by Cline (1969). In this method, reduced sulfur species (H_2S, HS^-, S^{2-}) react with diamine (N,N-dimethylphenyl-1,4-diamine) in the presence of ferric chloride to form a blue complex that is measured spectrophotometrically at a wavelength of 670 nm. Visual colorimetric comparison kits are also available. Detection limits down to 0.01 ppm sulfide are obtainable. Standard solutions can be prepared by dissolving into deoxygenated water quantities of sodium sulfide ($Na_2S \times 9H_2O$). The concentration of sulfide is then measured by adding excess iodine and back-titrating with thiosulfate. To minimize oxidation of sulfide species, reagents should be added to samples immediately after sample collection followed by spectrophotometric measurement.

Sulfide electrodes that use silver sulfide as the sensing element are generally not used in field studies. Specific ion electrodes are better suited for laboratory studies conducted under controlled conditions. Long response times and poisoning of the reference electrode by sulfide have limited the use of sulfide-selective electrodes (Lawrence et al., 2000). Gravimetric determinations of sulfide concentrations are appropriate in situations where concentrations of dissolved sulfide are > 5 mg/L. Solutions can be directly collected into bottles containing quantities of Zn acetate or Cd acetate solutions. A 1 L sample of solution containing 5 mg/L dissolved sulfide will produce a mass of 15.2 mg or 22.5 mg of ZnS or CdS precipitate, respectively.

In ground-water systems containing dissolved sulfide, dissolved oxygen concentrations will be generally 0 or < 1 mg/L. If hydrogen sulfide is present in ground water above 1 mg/L, concentrations of ferrous iron will generally be negligible. The concentrations of ferrous iron and hydrogen sulfide in surface and subsurface environments are generally governed by the solubility of iron monosulfide minerals, such as mackinawite, i.e.,

$$FeS + H^+ = Fe^{2+} + HS^-$$
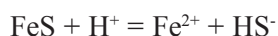
The equilibrium constant (K_{sp}) for this reaction is $10^{-3.1}$ where FeS is taken to be crystalline mackinawite (Davison, 1991). In Figure 4.4 the solubility curves of mackinawite are plotted at three pH values from 6 to 8. Note that solubility decreases as pH rises, and that when concentrations of either iron or sulfide are low the other is necessarily high.

Nitrogen Speciation

The common nitrogen species present in ground water include nitrate (NO_3^-), nitrite (NO_2^-), and ammonia (NH_3). At near-neutral pH typical of most ground water, ammonia is present predominantly as the ammonium ion (NH_4^+). Although colorimetric methods are available to quantitate nitrate, nitrite, and ammonia, field determination using these methods is not generally needed as long as laboratory measurements can be made within specified holding times.

The cadmium-reduction method can be used to determine the amount of nitrate+nitrite in ground water. In this method, cadmium metal is used to reduce nitrate to nitrite. The nitrite ions then react with sulfanilic acid and gentistic acid to form an amber-colored compound (American Society for Testing Materials, 1995b). Strong oxidizing and reducing substances are possible interfering components; ferric iron, in particular, will cause high results.

Ammonia is produced during the microbiological decay of organic matter. Two colorimetric methods for ammonia are the Nessler method and the Salicylate method. The Nessler method is probably the most commonly used method and develops a yellow color proportional to the concentration of ammonia. High concentrations of calcium and magnesium may cause interferences. Ferrous iron and dissolved sulfide can also interfere with ammonia determinations using this method.

Samples collected for nitrogen speciation should be preserved by keeping cold (4°C) and measured within specified holding times, generally < 48 h. Longer holding times are possible by acidifying samples with sulfuric acid and keeping them cold. Before analysis the samples should be brought back to room temperature and neutralized by adding base.

Alkalinity

Alkalinity is a measure of the acid neutralizing capacity of dissolved solutes in a water sample and is reported as equivalents per liter or as mg/L of $CaCO_3$. Alkalinity is not typically included as a redox parameter. The group included this parameter because alkalinity production often accompanies oxidation-reduction reactions, e.g., in sulfate or iron reduction. The alkalinity concentration consists of the sum of titratable carbonate and titratable non-carbonate species in a water sample, including proton-accepting organic compounds. Proton-accepting species include CO_3^{2-}, HCO_3^-, OH^- (and metal-OH complexes), HS^-, PO_4^{3-}, ammonium, silicate, and borate. The alkalinity measurement is important for evaluating charge balance of a solution and is a critical component of modeling approaches using geochemical speciation computer packages. Because particulate materials can be an important sink for acid, alkalinity determinations should be made in filtered or low-turbidity waters (turbidity < 5 NTU).

The most accurate determinations of alkalinity are made in the field at the time of sample collection. Fixed end-point titrations to pH 4.3 are suitable for ground waters with negligible concentrations of dissolved organic matter or titratable species other than inorganic carbon. For more complex ground waters, especially those rich in dissolved organic material, fixed end-point titrations will give inaccurate results (see Hemond, 1990). Total alkalinity should then be determined by measuring pH as a function of titrated acid to a pH of 3.0. Using this method, alkalinity is calculated from the volume of acid added to reach the end-point pH. The end-point is determined graphically by plotting pH as a function of titrant volume and locating the inflection point. The importance of protecting the sample from oxidation was also discussed. In high Fe(II) waters, the oxidation of Fe(II) to Fe(III) can produce sufficient acid to bias the titration, resulting in an underestimation of actual alkalinity. Rapid analysis is recommended, and protection of the sample from aeration is needed for accurate measurements of alkalinity in iron-rich water.

4.4 Summary

A variety of measurement options are available for monitoring the most important redox parameters in ground water. The core list of parameters identified by this group was Eh, dissolved oxygen, iron speciation, sulfur speciation, and nitrogen speciation. Selection of the appropriate technique for a given parameter will depend on specific project objectives. It was recognized that project objectives and principal data uses collected in monitoring programs change with time as more site-specific information is obtained and conceptual models evolve. There was general agreement that there exists a need for improved standards for routine field practices. There was strong agreement among the group that sample collection practices and measurement techniques are among the greatest challenges to developing reliable site conceptual models.

References

American Public Health Association (APHA), American Water Works Association, Water Environment Federation. 1999. *Standard Methods for the Examination of Water and Wastewater, 20th Edition*. American Public Health Association, Washington, D.C.

American Society for Testing Materials (ASTM). 1992. Standard test methods for dissolved oxygen in water, ASTM D 888-92. Philadelphia, Pennsylvania.

American Society for Testing Materials (ASTM). 1995a. Standard test methods for low-level dissolved oxygen in water, ASTM D 5543-94. Philadelphia, Pennsylvania.

American Society for Testing Materials (ASTM). 1995b. Nitrate-Nitrite in water, Test method B, ASTM D 3867-90. Philadelphia, Pennsylvania.

Baedecker, M. J. and Back, W. 1979. Hydrogeological processes and chemical reactions at a landfill site. *Ground Water*, v. 17, pp. 429-437.

Baedecker, M. J. and Cozzarelli, I. M. 1992. The determination and fate of unstable constituents of contaminated groundwater. In *Groundwater contamination and analysis at hazardous waste sites*, eds. S. Lesage and R. Jackson, Marcel-Dekker, New York, pp. 425-461.

Cline, J. D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography*, v. 14, pp. 454-458.

Champ, D. R., Gulens, J., and Jackson, R. E. 1979. Oxidation-reduction sequences in ground water flow systems. *Canadian Journal of Earth Sciences*, v. 16, pp. 12-23.

Davison, W. 1991. The solubility of iron sulphides in synthetic and natural waters at ambient temperature. *Aquatic Sciences*, v. 53, pp. 309-329.

Eary, L. E. and Schramke, J. A. 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. In *Chemical Modeling of Aqueous Systems, II, Chapter 30*, eds. D. C. Melchior and R. L. Bassett, American Chemical Society, Washington, D.C., pp. 379-396.

Gibbs, C. R. 1976. Characterization and application of ferrozine iron reagent as a ferrous iron indicator. *Analytical Chemistry*, v. 48, pp. 1197-1200.

Gilbert, T. W., Behymer, T. D., and Castaneda, H. B. 1982. Determination of dissolved oxygen in natural and wastewaters. *American Laboratory*, v. 14, March, pp. 119-134.

Hemond, H. F. 1990. Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids. *Environmental Science and Technology*, v. 24, pp. 1486-1489.

Hitchman, M. L. 1978. *Measurement of Dissolved Oxygen*, John Wiley & Sons, New York, 255 p.

Jackson, R. E. and Patterson, R. J. 1982. Interpretation of Eh and pH in a fluvial-sand aquifer. *Water Resources Research*, v. 18, pp. 1255-1268.

Lawrence, N. S., Davis, J., and Compton, R. G. 2000. Analytical strategies for the detection of sulfide: a review. *Talanta*, v. 52, pp. 771-784.

Langmuir, D. 1971. Eh-pH determination. In *Procedures in Sedimentary Petrology, Chapter 26*, ed. R. E. Carver, Wiley-Interscience, New York, pp 597-635.

Light, T. S. 1972. Standard solution for redox potential measurements. *Analytical Chemistry*, v. 44, pp. 1038-1039.

Lindberg, R. D. and Runnells, D. D. 1984. Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science*, v. 225, pp. 925-927.

Morris, J. C. and Stumm, W. 1967. Redox equilibria and measurements of potentials in the aquatic environment. In *Equilibrium Concepts in Natural Water Systems*, ed. R. F. Gould, American Chemical Society, Washington, D.C., pp. 270-285

Moses, C. O., Nordstrom, D. K., and Mills, A. L. 1984. Sampling and analyzing mixtures of sulphate, sulphite, thiosulphate, and polythionate. *Talanta*, v. 31, pp. 331-339.

Nordstrom, D. K. 1977. Thermochemical redox equilibria of Zobell's solution. *Geochimica et Cosmochimica Acta*, v. 41, pp. 1835-1841.

Nordstrom, D. K., Jenne, E. A., and Ball, J. W. 1979. Redox equilibria of iron in acid mine waters. In *ACS Symposium Series 93, Chapter 3*, ed. E. A. Jenne, American Chemical Society, Washington, D.C., pp. 51-79.

Reynolds, J. F. 1969. Comparison studies of Winkler vs oxygen sensor. *Journal Water Pollution Federation*, v. 41, pp. 2002-2009.

Stookey, L. L. 1970. Ferrozine-A new spectrophotometric reagent for iron. *Analytical Chemistry*, v. 42, pp. 779-781.

Stumm, W. 1966. Redox potential as an environmental parameter; conceptual significance and operational limitation. In *3rd International Conference on Water Pollution Research, Section 1, No. 13,* Water Pollution Control Federation, Washington D.C., pp. 1-16.

Tamura, H., Goto, K., Yotsuyanagi, T., and Nagayama, M. 1974. Spectrophotometric determination of iron (II) with 1,10 phenanthroline in the presence of large amounts of iron (III). *Talanta*, v. 21, pp. 314-318.

Thorstenson, D. C. 1984. The concept of electron activity and its relation to redox potentials in aqueous geochemical systems. U.S. Geological Survey Open-File Report 84-072, 45 p.

To, T. B., Nordstrom, D. K., Cunningham, K. M., Ball, J. W., and McCleskey, R. B. 1999. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. *Environmental Science and Technology*, v. 33, pp.807-813.

U.S. Geological Survey. 1997. *National Field Manual for the Collection of Water-Quality Data*. U.S. Geological Survey Techniques of Water-Resources Investigations, book 9. [http://water.usgs.gov/owq/FieldManual/mastererrata.html]

Walton-Day, K., Macalady, D. L., Brooks, M. H., and Tate, V. T. 1990. Field methods for measurement of ground water redox chemical parameters. *Ground Water Monitoring Review*, v. 10, pp. 81-89.

White, A. F., Peterson, M. L., and Solbau, R. D. 1990. Measurement and interpretation of low levels of dissolved oxygen in ground water. *Ground Water*, v. 28, pp. 584-590.

Wilkin, R. T., McNeil, M. S., Adair, C. J., and Wilson, J. T. 2001. Field Measurement of Dissolved Oxygen: A Comparison of Methods. *Ground Water Monitoring and Remediation*, v. 21, pp. 124-132.

Whitfield, M. 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnology and Oceanography*, v. 19, pp. 857-865.

Session 5 Summary:
Measurement of Dissolved Gases

Donald Kampbell and Frank Chapelle

5.1 Introduction

A dissolved gas refers to a chemical element in a gaseous phase at ambient temperature. The dissolved gas is absorbed by a liquid, in this case water, without a chemical interaction occurring. Dissolved gases such as oxygen, hydrogen, and aliphatic hydrocarbons such as methane, are important components to determine the status of biodegradation processes in ground water. For example, when dissolved oxygen is present, microorganisms will preferentially use oxygen as the primary electron acceptor and aerobic metabolism will tend to dominate the system. When dissolved oxygen is not present, however, the microbial population must use alternative electron acceptors such as nitrate, ferric iron, sulfate, carbon dioxide, or, in some contaminated aquifers, chlorinated ethenes in order to carry on respiration. When carbon dioxide serves as the primary electron acceptor (methanogenic respiration) methane is produced. Thus, concentrations of dissolved oxygen and methane can be useful in determining the kinds of microbial metabolism occurring in a ground-water system.

In general, decreasing concentrations of oxygen along ground-water flow paths are indicative of aerobic metabolism. Similarly, increasing concentrations of methane along ground-water flow paths indicate the presence of active methanogenesis in an aquifer. Frequently, the anaerobic process becomes functional after oxygen becomes depleted. Then nitrates and sulfates can become electron acceptors. Finally, methane can become a major component characteristic of an anaerobic medium. Although the assay of dissolved gases is important to characterize biodegradation, other conditions need to be favorable for a given xenobiotic such as the presence of compatible microorganisms and favorable environmental settings. Plume ground-water that has a decrease in oxygen and an increase in methane is an important characteristic that should be monitored.

Hydrogen is an important intermediate product of anaerobic microbial metabolism. Under anaerobic conditions, the oxidation of organic matter requires food chains of symbiotic microorganisms. First, complex organic matter is partially oxidized by fermentative bacteria with the production of intermediate compounds such as acetate and molecular hydrogen. Secondly, these fermentative products are fully oxidized by respirative microorganisms coupled to reduction of mineral electron acceptors such as nitrate, sulfate, ferric iron, and carbon dioxide. Importantly, chlorinated ethenes such as perchloroethene (PCE) and trichloroethene (TCE) can also serve as electron acceptors during the metabolism of hydrogen. Concentrations of dissolved hydrogen can be an indication of the efficiency of reductive dechlorination in ground-water systems. Generally, high concentrations of dissolved hydrogen favor efficient reductive dechlorination. The rate of reductive dechlorination at particular field sites is useful in assessing the viability of employing monitored natural attenuation. Because of this, concentrations of hydrogen can be a useful indicator parameter.

The complete reductive dechlorination of PCE and TCE results in the formation of ethene. Furthermore, ethene can then be further reduced to ethane under strongly reducing methanogenic conditions. Thus, the presence of ethene and ethane can be indicators that reductive dechlorination of PCE and TCE is occurring in a ground-water system. For these reasons, it is important to measure concentrations of dissolved ethene and ethane at sites where reductive dechlorination may be occurring.

Abiotic and biological transformations are important mechanisms controlling natural attenuation as a plume management strategy. Plume management requires monitoring of the transformation processes to confirm protection of the environment and human health. Thus, measuring concentrations of oxygen, H_2, ethene, ethane, and methane provide important information about the kinds of microbial processes occurring in ground-water systems.

5.2 Measurement Methods

The measurement of dissolved gases in ground water can aid in understanding what biochemical processes are active, or have been active, in ground-water systems. If oxygen has been depleted, then most likely anaerobic processes have predominated. The presence of hydrogen is useful to stimulate dechlorination of chlorinated hydrocarbon pollutants.

Gases such as oxygen, hydrogen, and methane are slightly soluble in water. Thus, their concentrations are directly proportional to their partial pressure as formalized by Henry's Law. Because the Henry's Law constant for each gas is highly temperature-dependent, the solubility of each may be used to calculate the amount present at saturation for given temperatures. The solubility varies greatly with temperature. For example, the solubility of oxygen in fresh water at 1 atm. pressure ranges from 14.6 mg/L and 7 mg/L at $0^{\circ}C$ and $35^{\circ}C$, respectively. The solubility of H_2 and methane are similarly variable with temperature. At high temperature conditions where oxygen is least soluble, biological oxidation increases along with oxygen demand. These critical conditions can limit the purification capacity to remove waste pollutants.

Because oxygen, hydrogen, and methane are so slightly soluble in water, sampling methods must rigorously exclude exposure to the air. This is particularly problematic with oxygen, since air is about 21 percent oxygen. Measurements of dissolved oxygen must always be done in a closed air-free environment, and measurements should be made as soon after sample collection as possible. In general, all measurements of dissolved oxygen should be made in the field at the time of sample collection. Similarly, hydrogen measurements are most accurate when made in the field at the time of sample collection. However, storage methods are now available for transporting hydrogen samples to the laboratory. Because methane is relatively stable, and because methane is not a major component of air, methane samples are relatively easy to collect and store for later analysis in the laboratory. Care must be used when collecting water samples for dissolved gases, especially oxygen and hydrogen. Exposure to the air will lead to a potential loss or gain of these components. Water sampling and analyses should be done in a closed air-free system and as soon as possible. Because air is about 21 percent oxygen, it can be a critical factor of contamination when collecting low level oxygen water samples. Hydrogen and methane are constituents of air, but in the ppm range. Generally, exchange of these components with air can be overcome by care during sampling. The expected concentration ranges of dissolved methane and hydrogen in contaminated ground water are in the ppm range.

The primary factor for quality assurance, besides careful sampling to avoid sample contamination by air, is instrument calibration. Pressurized cylinders containing known hydrogen or methane, ethane, and ethene can be used. Concentrations of oxygen in water can be obtained from standard oxygen solubility versus temperature tables. Generally, 10 percent of the collected samples should be duplicated to measure precision.

5.3 Hydrogen

A routine technique developed to analyze water samples for dissolved hydrogen has been described by McInnes and Kampbell (2000). This is an adaptation of a method originally developed by Chapelle et al. (1997) and is called the "bubble strip" technique. This method is an application of Henry's Law. After the sample is collected in a 20 mL bubble inside a 250 mL gas sample vessel, a 2 mL aliquot of the bubble is removed for analysis using a reduction gas analyzer/chromograph. A typical calibration range for hydrogen is 0.5 to 10.0 ppm.

5.4 Oxygen

Several decades ago, the dominant procedure for determining dissolved oxygen in water was the Winkler, Full Bottle technique (U.S. EPA, 1979b; Method 360.2). The test depended on oxygen oxidizing divalent manganese to a higher state of valence under alkaline conditions. The higher valence state manganese would then oxidize iodine to free iodine in an acid solution. The free iodine released was equivalent to dissolved oxygen. Standard sodium thiosulfate then measured the free iodine. Interferences from nitrates were reduced by use of sodium azide.

Dissolved oxygen can also be analyzed by electrode probe (U.S. EPA, 1979a; Method 360.1, see Appendix A). On the end of the probe is a thin organic film over two metallic electrodes in a media of liquid electrolyte. The oxygen that diffuses through the film is reduced electrochemically. A current is generated proportional to oxygen in the sample. These electrodes are well suited for analyses in water because their portability, ease of operation, and maintenance make them convenient for field applications. They are less amenable to interferences than the Winkler test. The principal disadvantage of electrodes for measuring dissolved oxygen relates to the diffusion-dependent mode of operation. When concentrations of dissolved oxygen are low, oxygen diffusion is very low and

the current generated by the electrode is correspondingly low. It is thus difficult for electrodes to accurately measure dissolved oxygen concentrations below 0.5 mg/L. Because many ground-water systems contain low concentrations of dissolved oxygen, the use of electrodes can be problematic in some systems (see Session 4 Summary).

More recent chemical methods for measuring dissolved oxygen concentrations were developed by CHEMetrics, Inc. One method, the indigo carmine method (ASTM D 888-87), is used for dissolved oxygen concentrations in the 1-10 ppm range. The chemistry of this method relies on the reaction of reduced indigo carmine with oxygen to produce a blue product. Another method, the rhodazine D method (ASTM D 5543-94), is used to measure dissolved oxygen concentrations in the 0.1 to 1.0 ppm range. The chemistry of this method relies on the reaction of rhodazine D with oxygen to form a bright pink reaction product. Neither of these methods is subject to interferences from temperature, salinity, or dissolved gases, which often do interfere with dissolved oxygen electrodes. For both the high range (indigo carmine) and low range (rhodazine D), the reagents are sealed in ampules designed to fit into a plastic beaker. The beaker is attached to a stream of water pumped from the well (sealed from the air) and is allowed to overflow. After a brief period of flushing (~30 seconds), an ampule is inserted into the stream of water and the tip cracked. This draws water into the ampule where it reacts with the reagents. The intensity of the color development is directly proportional to the dissolved oxygen concentration, which can be compared visually to standards supplied with the reagents. This method is fast, reproducible, and minimizes sample exposure to atmospheric oxygen.

5.5 Methane, Ethane, and Ethene

Glass serum bottles are filled with ground-water samples at the field site, preserved with diluted sulfuric acid, and capped with air-tight septa. Ten percent of the water is then removed to create a gaseous headspace. After equilibrium by shaking the bottles, an aliquot of the headspace is removed by a gas-tight syringe for analysis by gas chromatography. Dissolved methane, ethane, and ethene in the water sample can then be completed using Henry's Law as explained by Kampbell and Vandegrift (1998). Quantitation limits for methane, ethane, and ethene by this method were 0.001, 0.002, and 0.003 mg/L, respectively.

5.6 Summary

Methods used for field site characterization studies to determine the status of biodegradation processes in ground water as related to dissolved gases were discussed. Emphasis was directed toward dissolved oxygen, hydrogen, and aliphatic hydrocarbons such as methane, ethane, and ethene. A method for each of these parameters is listed that has been used over a number of years to aid in identifying processes of natural attenuation.

References

Chapelle, F. H., Vroblesky, D. A., Woodward, J. C., and Lovley, D. R. 1997. Practical considerations for measuring hydrogen concentrations in groundwater. *Environmental Science and Technology*, v. 31, pp. 2873-2877.

Kampbell, D. H. and Vandegrift, S. A. 1998. Analysis of methane, ethane, and ethylene in ground-water by a standard gas chromatographic technique. *Journal* of *Chromatographic Science*, v. 36, pp. 253-256.

McInnes, D. M. and Kampbell, D. H. 2000. The bubble stripping method for determining dissolved hydrogen (H_2) in well water. *Field Analytical Chemistry and Technology*, v. 4, pp. 283-296.

U.S. Environmental Protection Agency. 1979a. Dissolved Oxygen by the Membrane Electrode Technique. Methods for Chemical Analysis of Water and Wastes, EPA Method 360.1, EPA 600/4-79-020. U.S. EPA, Government Printing Office, Washington, DC.

U.S. Environmental Protection Agency. 1979b. Dissolved Oxygen by the Modified Winkler Full-Bottle Technique. Methods for Chemical Analysis of Water and Wastes, EPA Method 360.2, EPA 600/4-79-020. U.S. EPA, Government Printing Office, Washington, DC.

Session 6 Summary:
Solid Phase Redox Characterization

Robert G. Ford

6.1   Introduction

Monitoring oxidation-reduction (redox) processes for ground-water remediation must be applied both to the liquid and solid phases in the remediation zone. Many of the redox sensitive elements that participate in chemical reactions during subsurface remedial processes are cycled between these two phases during the reaction lifecycle. Examples of important redox sensitive elements include carbon, iron, nitrogen, and sulfur. Site characterization and monitoring may require the development of a site-specific database for the composition of the aquifer solid matrix and the capacity of the matrix with respect to remedial performance measures.

The level of effort for solid phase characterization will depend on the specific remedial technology employed. Two examples include in-situ redox manipulation of the aquifer matrix versus emplacement of a new solid matrix to serve as a reactive barrier. Both treatment technologies require knowledge of the mechanisms and capacity of specific redox reactions to achieve the treatment goals. For the first example, one must identify the mass and distribution of the reactive components naturally occurring within the contaminated aquifer. This may require an extensive level of effort to characterize both the abundance and distribution of redox-sensitive phases as well as their reactivity during the remedial process. For the second example, characteristics of the reactive solid components are typically known prior to barrier installation. However, it may be necessary to carry out field measurements to characterize changes in the reactive phase(s) during remedial monitoring activities.

6.2   Session Objectives

The overall goal of this breakout session was to identify the key solid phase parameters relevant to redox-controlled processes active during *in-situ* remediation of ground water. As part of this discussion, the group was to identify: 1) a list of solid phase parameters that addressed a variety of remedial technologies, 2) appropriate methods of sample collection specific to characterization needs, and 3) available analytical methods for estimating solid phase parameters. Throughout this discussion, the group was tasked with identifying characterization issues with the greatest level of uncertainty and making recommendations concerning technical areas where the U. S. Environmental Protection Agency should focus investment of resources.

6.3   Case-Specific Evaluation

A remedial case study was evaluated to provide a specific frame of reference for discussion of solid phase characterization analyses that may be required as part of remedial design and monitoring. The case study was the remedial effort implemented by the U. S. Department of Energy to treat chromate-contaminated oxic ground water via in-situ redox manipulation of aquifer sediments at the Hanford Site in southeastern Washington (Williams et al., 2000). The goal of this remedial effort was to reduce naturally occurring ferric iron, $Fe(III)$, in aquifer sediments to soluble and solid forms of ferrous iron via injection of a buffered solution of a strong reductant, dithionite. The ferrous iron, $Fe(II)$, subsequently reacted with dissolved chromium; reducing $Cr(VI)$ to insoluble $Cr(III)$-bearing precipitate phases (Amonette, 2000). While the reaction of $Fe(II)$ with $Cr(VI)$ was the specific process controlling chromium stabilization, the overall success of the remedial process was dependent on the efficiency of the initial reduction of native $Fe(III)$ via dithionite injection. Thus, solid phase characterization was focused towards evaluating the production and longevity of $Fe(II)$ within the treatment zone.

Design of the remedial process required analysis of the mass and distribution of reactive iron in aquifer sediments and the rates of iron reduction/oxidation and non-beneficial reactions involving dithionite. Non-beneficial reactions included those that consumed dithionite without production of $Fe(II)$ and the release of potentially toxic elements during dissolution of iron oxide minerals. Sediment cores were collected within the proposed treatment zone for mineralogical characterization and to evaluate rates and products for beneficial and non-beneficial reactions. All tests were carried out using the <4 mm sediment fraction, with the assumption that the largest

proportion of reactive iron would be contained in this size fraction. Following is a list with test description and purpose used for site characterization and remedial performance evaluation.

Site Geology and Hydrology

Procedures that were performed included establishing the uniformity of site geology through well-site boring logs and characterization of physical properties on split tube samples, including porosity, bulk density, and particle size distribution.   In addition, pre- and post-dithionite injection hydraulic tests were performed to establish treatment design criteria and to evaluate potential changes in formation hydraulic properties following dithionite injection.

Sediment Iron Mineralogy

The distribution of iron in sediment minerals was examined for the <4 mm size fraction for pre- and post-treatment samples. The predominant phases identified for pre-treatment samples included iron adsorbed to mineral surfaces, amorphous and crystalline Fe(III) oxides, Fe(II) carbonate, and Fe-bearing clay minerals. Post-treatment samples had a decreased fraction of amorphous Fe(III) oxide and increased fractions of adsorbed Fe(II) and Fe(II) carbonate. Mass balance calculations suggested that dithionite reduction primarily converted amorphous Fe(III) oxides to adsorbed Fe(II). Separate experiments indicated that adsorbed Fe(II) provided the greatest reactivity for Cr(VI) reduction. Thus, the observed changes in iron mineralogy provided verification of the success of dithionite reduction.

Reagent (Dithionite) Stability

Ferric iron reduction in the presence of dithionite ($S_2O_4^{2-}$) occurs via a chemical reaction between Fe(III) and a sulfoxyl free radical ($SO_2^{-}*$) that exists in equilibrium with $S_2O_4^{2-}$ (Amonette, 2000). However, dithionite is also subject to pH-dependent disproportionation reactions resulting in other dissolved forms of sulfur ($S_2O_3^{2-}$ and SO_3^{2-}) that reduce Fe(III) at a much slower rate. These latter reactions are non-beneficial and occur in solution or may be catalyzed at mineral surfaces. Tests were carried out to evaluate the optimal reaction pH and the rate at which aquifer sediments catalyzed dithionite disproportionation. These parameters were required to establish the extent to which the injection solution pH had to be buffered and the optimal rate of injection into the aquifer in order to minimize the impact of dithionite disproportionation.

Sediment Oxidation Capacity

Oxidation capacity was defined for this study as the degree of dithionite consumption during the reduction of Fe(III) in aquifer sediments. These results were corrected for disproportionation reactions that resulted in dithionite oxidation without concurrent Fe(III) reduction. An operational definition for oxidation capacity was required, since not all Fe(III) was accessible to reduction due to physical constraints or slow rates of reduction for certain mineral phases. This result highlights the need to tailor characterization methods for consistency with the remedial technology.

Sediment Reduction Capacity

Sediment reduction capacity for post-treatment sediment samples was characterized by exposure of reduced sediments to oxygen-saturated synthetic ground water. Rates of Fe(II) oxidation in 1-D column studies, calculated from oxygen consumption, were used to estimate the lifetime of Fe(II) within the in-situ reaction zone. These tests were run on sediments collected prior to and following dithionite injection. Reduction capacity for pre-treatment sediments was evaluated in the laboratory following dithionite treatment. Comparable reduction capacities were measured for pre- and post-treatment sediment samples, providing a performance measure for success of the reduction stage of the remedial effort. The rate of Fe(II) oxidation was also used to provide an estimate of in-situ reaction zone longevity.

Contaminant Stabilization and Trace Metal Mobilization

The stability of reduced chromium was evaluated during sediment re-oxidation with oxygen-saturated water to simulate field conditions (Fruchter et al., 2000; Williams et al., 2000). No leaching of chromium occurred as a result of re-oxidation. In addition, the potential mobilization of native trace metals in the aquifer sediments that are sensitive to changes in ground-water redox was examined during reduction with dithionite. Release of metals such as arsenic did occur, but soluble concentrations were elevated only in reduced sediments. Soluble metal concentrations decreased significantly during sediment re-oxidation. These results indicated that sediment reduction effectively stabilized chromium and did not negatively impact water quality due to concurrent trace metal leaching. In order to minimize soluble trace metal concentrations in the treated aquifer, the spent dithionite

injection reagent and several additional injection volumes of ground water were withdrawn following the predetermined iron reduction period.

This example illustrates the rationale and procedures that may be a necessary component of remedial evaluation and monitoring. Procedures such as assessment of site geology may be common to a wide range of remedial strategies. Assessment of aquifer sediment capacity parameters may also be common, but may require tailored procedures that are more consistent with remedial objectives. In summary, it is clear that solid phase characterization procedures will likely be required at all stages of remedial design, implementation and monitoring. In order to provide a broader scope to encompass other remedial technologies, the discussion panel developed a more universal list of potential characterization procedures and evaluated their utility for a wider range of remedial technologies. These observations are discussed in the following section.

6.4   Solid Phase Characterization: Evaluation of Information Needs

The discussion group developed a list of potential solid phase measurements to be applied as part of site assessment and monitoring. Some measurements would be required as part of the initial remedial assessment, while other measurements would primarily be implemented as part of remedial monitoring. Measurement of the listed parameters may require field- and/or laboratory-based tests. A general description is provided in Table 6.1 for each of the discussed parameters. There may be additional parameters that require characterization for specialized remedial technologies, but the list in Table 6.1 is generally comprehensive.

The list in Table 6.1 was then used as a reference point for evaluating data requirements for assessment, design, and monitoring of a select number of remedial technologies. The outcome of this activity is illustrated in Table 6.2. The remedial technologies that were evaluated included oxidant injection (permanganate), reductant injection (dithionite), reactive barrier installation (zero valent iron), enhanced biological degradation, and monitored natural attenuation (MNA). Several general trends were observed:

1) The reactive barrier technology requires the least amount of solid phase characterization, since it was assumed that properties of the barrier material would be fully characterized. This also assumes sufficient knowledge of the influence of ground-water geochemical parameters on the (bio)chemical reactions controlling contaminant remediation within the barrier. However, some characterization of the native aquifer material may be required to address potential deleterious effects from alteration of the ground-water redox state.

2) Injection (oxidant/reductant), enhanced biological, and MNA technologies require more extensive solid phase characterization, since the aquifer matrix (mineralogy and microbial population) is an integral reactant in the remedial technology.

3) Use of MNA as a remedial technology for an inorganic contaminant will necessitate the greatest extent of solid phase characterization. This observation is due to the importance of inorganic contaminant immobilization onto aquifer solids as the remedial endpoint.

Analysis of this select group of remedial technologies indicates that a single list of required solid phase characterization parameters will not apply for all technologies. Of the listed parameters, only solubilized non-target contaminant and aquifer permeability were considered universal for all technologies. In addition, a determination must be made whether solid phase characterization is performed on the entire sample or a specific size fraction. Parameters that pertain to a reaction capacity, such as acid neutralizing capacity, should be assessed for the entire sample. However, determinations of mineralogy may only be feasible following initial isolation of a specific size fraction, e.g., determination of the clay mineral content. Thus, it was generally recommended that a preliminary case-specific assessment should be made to identify solid phase parameter measurements critical to successful implementation of the proposed remedial technology.

6.5   Recommended Procedures: Sample Collection and Characterization

Collection and Preservation of Solid Phase Material

Recommendations for collection and preservation of solid phase material and its derived components were solicited from the discussion group. In general, collection and preservation methods were grouped based on the desired parameter to be characterized. The recommendations listed below were specific to the retrieval of subsurface material from the saturated zone. This type of sample will generally display the greatest instability during above-ground processing.

Mineralogy. The greatest concerns for preservation of mineralogy in aquifer materials were the prevention of contact with oxygen and removal of pore water. For example, iron- and manganese-bearing minerals may exist in a reduced state within the saturated zone. Minerals that are stable under a reducing environment are subject to significant alteration upon exposure to oxygen. In addition, solid phase structural and chemical transformations are commonly mediated or facilitated by the pore water. Thus, removal of pore water may act to retard or impede transformation. If dewatering is required to minimize sample alteration, it was recommended that non-aggressive techniques, such as draining by gravity, be employed for removal of pore water.

General methods for sample handling were grouped into those employed in the field and laboratory. In the field, sample cores should be immediately capped and frozen. Sample freezing can be accomplished either by submersing in liquid nitrogen or placement in a portable freezer located in the field. Following transport to a laboratory setting, frozen materials should be thawed under an oxygen-free or inert atmosphere, e.g. within a glove box. Residual pore water may then be displaced using a non-reactive solvent such as acetone. However, while this treatment will leave the mineralogy intact, it will likely alter the solid organic matter. Drying at ambient temperature in air or an inert atmosphere should be employed in order to minimize alteration of amorphous minerals. Significant changes in reactivity may result from changes in mineral structure and surface area due to drying at even slightly elevated temperatures (e.g., Stanjek and Weidler, 1992). Some of the group participants have had success storing materials in de-oxygenated water. However, extended periods of storage should be avoided, since sample mineralogy will alter with time during approach to a new equilibrium with the fresh de-oxygenated water.

Microbiology. The method used to preserve the microbial community within the core depends on the goal of characterization. If characterization requires quantification of bacterial counts, then the solids should be maintained at a reduced temperature, e.g. 4 °C, but not frozen. However, if there is no need to maintain a viable microbial population, then samples can be frozen in the field. No other recommendations were made with regard to microbial characterization, since the general group consensus was that this is a less problematic issue than mineralogical preservation.

Pore Water. It was recommended that pore water be isolated from the core material in the field prior to preservation of core solids. This may be accomplished for coarse-grained material by allowing the pore water to drain into a collection container. Pore water may be extracted from fine-grained material by manual pressure filtration using a syringe. Alternatively, pore water may be isolated by centrifugation if the location for sample collection is close to laboratory facilities. Pore water should not be isolated in the laboratory after the core has been subjected to freezing and thawing. Preservation of isolated pore water should be consistent with the desired analytical measurements.

Characterization Methods

Insufficient time was available to make recommendations for methods to be employed to characterize all of the solid phase parameters listed in Table 6.1. Discussion was thus directed towards a select number of parameters. In all cases, the subsurface material bulk density should be measured so that the chemical parameters listed in Table 6.1 can be reported on a mass basis. In addition, any testing protocol must include evaluation of the performance of the analytical procedures. Methods referenced in Tables 6.3 and 6.4 should be initially evaluated to assess their appropriateness for site materials. The capacities of materials derived from impacted environments may exceed the analytical range for which the methods were originally developed.

Oxidation Capacity. Methods for the determination of an 'oxidation capacity' for solids are listed in Table 6.3. The most aggressive approach involves digestion of the solid with a strong chemical reductant, i.e., aqueous Cr(II). This approach may overestimate the effective oxidation capacity of the solid material. A more targeted approach may be achieved via dithionite titration, but this may only be useful for evaluation of dithionite injection as a remedial technology. Likewise, methods designed to target iron oxides will only be valid for aquifer sediments in which the oxidation capacity is dominated by these minerals. Development of a tailored method may prove most useful, but this will necessitate additional research and development.

Reduction Capacity. Several methods are documented for the determination of a 'reduction capacity' for the solid material. A selection of these methods is listed in Table 6.4. Methods for determining chemical oxygen demand (COD) and organic matter content were not developed for the purpose of collecting data relevant towards implementation of a remedial technology. The reducing capacity may be under- or overestimated relative to the remedial target. However, these methods are well documented and have been commonly employed for solid phase characterization in soil and waste treatment studies. The method for measuring dissolved oxygen demand

developed at the Pacific Northwest National Laboratory was designed to provide data specific to the remedial technology employed (Williams et al., 2000). This method involves measuring oxygen demand in a continuous

Table 6.1   Solid Phase Parameters Requiring Measurement as Part of Remedial Assessment, Design, and Monitoring

Solid Phase Parameter	Parameter Description
Oxidation Capacity	Capacity of sediment to oxidize a reduced chemical (contaminant or introduced remedial reagent)
Reduction Capacity	Capacity of sediment to reduce an oxidized chemical (contaminant or introduced remedial reagent)
Neutralization Capacity	Capacity of solid phase to buffer change in pH (acid or alkaline)
Contaminant Sorption Capacity	Total mass of contaminant that can be partitioned to solid phase by various mechanisms
Ion Exchange Capacity	Total mass of charged ions that can be partitioned to solid phase via an electrostatic mechanism
Sorbed Contaminant	Mass of contaminant that is partitioned to solid phase
Solubilized Non-Target Contaminant	Mass of non-target contaminant associated with solid phase that may be solubilized as a result of remediation
Reagent Stability	Identification of undesirable by-products produced during reaction between remedial reagent and contaminant/ solid phase
Mineralogy (Bulk and Trace)	Identity of mineral phases present in various size fractions of solid phase
Non-Target Solid Phase Contaminant	Non-target contaminant that may negatively interact with remedial technology
Extractable Fe/Al/Mn	Mass of Fe/Al/Mn extracted from solid phase using reagents designed to attack specific mineral phases
Extractable Sulfide	Mass of sulfide extracted from solid phase using reagents designed to attack specific sulfidic mineral fractions (see Appendix A)
Total Organic Carbon	Mass of carbon associated with organic solid phases in sediment (see Appendix A)
Total Inorganic Carbon	Mass of carbon associated with inorganic solid phases in sediment
Reduction/Oxidation Reaction Rate	The rate at which solid phase will reduce/oxidize (consume) oxidizing/reducing reagent
Microbial Activity or Physiology	Characterization of the microbial processes/characteristics controlling contaminant degradation/stabilization
Microbial Population	Identification of the species of microbes that inhabit contaminated solid phase
Aquifer Permeability	The ability of aquifer material to transmit ground water based on measurement of porosity

Table 6.2 Solid Phase Measurements Applied as Part of Site Assessment and Monitoring for a Selected Number of Remedial Technologies.

Measured Parameter	Remedial Technology				
	Oxidant Injection (Permanganate)	Reductant Injection (Dithionite)	Reactive Barrier (ZVI)	Enhanced Biological Degradation	MNA Inorganic Contaminant
Oxidation Capacity	X	X		X	X
Reduction Capacity	X	X		X	X
Neutralization Capacity	X	X		X	X
Contaminant Sorption Capacity				(X)	X
Ion Exchange Capacity					X
Sorbed Contaminant					X
Solubilized Non-Target Contaminant	X	X	X	X	X
Reagent Stability	X	X			
Mineralogy (Bulk and Trace)		X	(X)		X
Solid Phase Contaminant	X	X		X	
Extractable Fe/Al/Mn		X		X	X
Extractable Sulfide		(X)			X
Total Organic Carbon	X			X	X
Total Inorganic Carbon			X		
Reduction/Oxidation Reaction Rate	X	X			
Microbial Activity or Physiology				X	[X]
Microbial Population			[X]	[X]	[X]
Aquifer Permeability	X	X	X	X	X

The symbols used to indicate required technology-specific measurements are as follows: X = site assessment and monitoring, (X) = post-remediation characterization only, and [X] = measurement not always required. ZVI = Zero Valent Iron, MNA = Monitored Natural Attenuation.

Table 6.3   Methods That May Be Employed for Estimating an Oxidation Capacity for Solid Materials

Method	Source	Comments
Cr(II)	(Barcelona and Holm, 1991a) (Barcelona and Holm, 1991b) (Barcelona and Holm, 1992)	Most aggressive but oxygen-free atmosphere recommended; high estimate
Digestion with Ti(III)-EDTA	(Ryan and Gschwend, 1991)	Developed for extraction of Fe oxides; applicability limited to iron oxide dominated solids
Titration/digestion with dithionite solution	(Loeppert and Inskeep, 1996) (Williams et al., 2000)	Valid for only specific remedial technology; targets Fe oxides
Exposure to treatment reagent	Not Documented	Case specific evaluation; requires preliminary research and development effort
Estimate based on mineralogy	Not Documented	No consensus values for reference minerals; unreliable value

Table 6.4   List of Methods That May Be Employed for Estimating a Reduction Capacity for Solid Materials

Method	Source	Comments
Chemical Oxygen Demand by digestion with acid dichromate	(U.S. EPA, 1979) (Barcelona and Holm, 1991a) (Barcelona and Holm, 1991b) (Barcelona and Holm, 1992)	Precipitate coatings if pH not buffered; high estimate
Digestion in hydrogen peroxide solution	(Nelson and Sommers, 1996)	Developed for quantifying organic matter content
Dissolved oxygen consumption in air-saturated water	(Williams et al., 2000)	Dynamic column test with mathematical simulation; test design must minimize gas diffusion from external sources; time-consuming, but realistic
Exposure to treatment reagent	Not Documented	Case specific evaluation; requires preliminary research and development effort
Estimate based on mineralogy	Not Documented	No consensus values for reference minerals; unreliable value

flow column configuration. Variation of column flow parameters and mathematical simulation may be required to arrive at a reliable estimate. Implementation of this method would strongly depend on the level of heterogeneity of the aquifer solids within the treatment zone and the relative value of the data for successful implementation of the remedial technology. As with recommendations for oxidizing capacity measurements, method development or modification may be required to optimize the usefulness of the derived data.

Acid-Base Neutralizing Capacity. The ability of the aquifer solids to buffer changes in ground water pH is a critical parameter for the success of a remedial technology dependent on redox reactions. Many redox reactions involve the production/consumption of protons/hydroxyl, and the reaction rates may be optimal only within a restrictive pH range. Thus, the acid-base neutralizing capacity of the aquifer material must be known in order to evaluate the efficiency of the desired redox reaction(s). It may prove necessary to supplement the aquifer neutralizing capacity depending on the remedial technology that is employed (e.g., Williams et al., 2000). Determination of the acid-base neutralizing capacity may be readily achieved through use of a standardized acid/base solution. The primary decision with regard to quantification of the capacity is the time for equilibration at the desired pH endpoint, since part of the neutralizing capacity of a soil is derived from rate-dependent mineral dissolution reactions. A reaction-based determination consistent with anticipated site conditions provides the most reliable estimate. It is inappropriate to base neutralizing capacity estimates on bulk mineralogical content (e.g., total carbonate analysis), since a fraction of the mineral content of the aquifer may not be reactive under site conditions.

Microbially Reducible Iron. The recognition that degradation of organic contaminants in ground water can be coupled to the microbial reduction of ferric iron in aquifer sediment minerals has prompted the development of screening methods for the estimation of solid phase microbially reducible iron (e.g., Lovley and Phillips, 1987). Quantification of the reducible ferric iron fraction by this type of method typically involves the determination of dissolved iron. The inherent assumption behind such a test is that solid phase ferric iron that is easily reduced under mild conditions by a chemical reductant can be correlated to the fraction of microbially reducible iron. However, there was no consensus within the group concerning the iron mineralogy associated with this type of extraction. In addition, there is evidence that iron bound in clay minerals may serve as a terminal electron acceptor in the absence of iron dissolution (Ernstsen et al., 1998). Thus, estimates from this type of extraction should be viewed with caution. There was group consensus that observed changes in the 'reducible' solid phase iron fraction within an aquifer sediment may be used as an indicator of iron serving as a terminal electron acceptor. However, this conclusion is only valid if the absence of abiotic iron reduction reactions can be verified. There is also evidence for reduction of solid phase iron in soils through biologically controlled reactions for which no terminal electron acceptor process is active (Schwertmann, 1991).

6.6   Session Conclusions

It was clear from this discussion that a single, clear-cut approach towards characterization of solid phase redox parameters is not feasible. While technical consensus may be reached for a select number of analytical approaches, a complete characterization effort will require a high degree of technical expertise. However, there was consensus that this type of analysis is critical towards the successful implementation of many *in-situ* remedial technologies. Thus, the discussion group arrived at the following overall conclusions:

1. Solid phase characterization will play a significant role for some remedial technologies.

2. More solid phase characterization will be required for technologies that rely on the inherent or enhanced treatment capacity of the aquifer matrix versus installation of a barrier technology.

3. Evaluation of several solid phase characteristics may be of common importance to a variety of remedial technologies, but specificity based on site, contaminant, or remediation technique prevents a universal approach.

4. Recommendations can be made for best practices relative to characterization of solid phase redox parameters, but it is not technically feasible to issue specific (restrictive) requirements.

5. Synthesis and documentation of existing methods and development of new methods is required to fulfill data needs.

Solid phase characterization issues have generally been avoided from the standpoint of regulatory guidance due to the complexity of the technical issues. However, the need for a consistent framework for evaluating solid phase redox processes is significant with increased implementation of remedial technologies that manipulate or monitor solid phase processes.

References

Amonette, J. E. 2000. Iron Redox Chemistry of Clays and Oxides: Environmental Applications. In *Electrochemistry of Clays*, ed. A. Fitch, Clay Minerals Society, Aurora, Colorado.

Barcelona, M. J. and Holm, T. R. 1991a. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology*, v. 25, pp. 1565-1572.

Barcelona, M. J. and Holm, T. R. 1991b. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology*, v. 25, 2540.

Barcelona, M. J. and Holm, T. R., 1992. Oxidation-reduction capacities of aquifer solids. *Environmental Science and Technology*, v. 26, pp. 2538-2539.

Ernstsen, V., Gates, W. P. and Stucki, J. W. 1998. Microbial reduction of structural iron in clays - A renewable source of reduction capacity. *Journal of Environmental Quality*, v. 27, pp. 761-766.

Fruchter, J. S., Cole, C. R., Williams, M. D., Vermeul, V. R., Amonette, J. E., Szecsody, J. E., Istok, J. D., and M. D. Humphrey. 2000. Creation of a subsurface permeable treatment zone for aqueous chromate contamination using in situ redox manipulation. *Ground Water Monitoring & Remediation*, v. 20, pp. 66-77.

Loeppert, R. H. and Inskeep, W. P. 1996. Iron. In *Methods of Soil Analysis: Part 3 - Chemical Methods*, ed. D. L. Sparks, Soil Science Society of America Book Series, Soil Science Society of America, Inc., Madison, Wisconsin, pp. 639-664.

Lovley, D. R. and Phillips, E. J. P. 1987. Rapid assay for microbially reducible ferric iron in aquatic sediments. *Applied and Environmental Microbiology*, v. 58, pp. 1536-1540.

Nelson, D. W. and Sommers, L. E. 1996. Total Carbon, Organic Carbon, and Organic Matter. In *Methods of Soil Analysis: Part 3 - Chemical Methods*, ed. D. L. Sparks, Soil Science Society of America Book Series, Soil Science Society of America, Inc., Madison, Wisconsin, pp. 961-1010.

Ryan, J. N. and Gschwend, P. M. 1991. Extraction of iron oxides from sediments using reductive dissolution by titanium(III). *Clays and Clay Minerals*, v. 39, pp. 509-518.

Schwertmann, U. 1991. Solubility and dissolution of iron oxides. *Plant and Soil*, v. 130, pp. 1-25.

Stanjek, H. and Weidler, P. G. 1992. The effect of dry heating on the chemistry, surface area, and oxalate solubility of synthetic 2-line and 6-line ferrihydrites. *Clay Minerals*, v. 27, pp. 397-412.

U.S. Environmental Protection Agency. 1979. Chemical Oxygen Demand. Methods for Chemical Analysis of Water and Wastes, EPA Method 410.4, EPA 600/4-79-020. U.S. EPA, Government Printing Office, Washington, DC.

Williams, M. D., Vermeul, V. R., Szecsody, J. E. and Fruchter, J. S. 2000. 100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater, PNNL-13349, Pacific Northwest National Laboratory, Richland, Washington.

Appendix A

A list of EPA documented analytical methods for redox sensitive elements is included in Table A1. Abbreviated descriptions for these methods are provided in Table A2. The full references in Table A1 should be consulted for details on these methods. There are no EPA documented methods for the determination of ferrous iron or oxidation-reduction potential in aqueous solutions. Summary Chapter 4 should be consulted for these methods. Included in Tables A1 and A2 are methods for the determination of total organic carbon, total inorganic carbon and acid-volatile sulfur in solids. There are no EPA documented methods for total sulfur and acid-digestible iron in solids. Multiple procedures listed in Tables A1 and A2 for a given element are due to either differences in analytical range or method of detection. The most appropriate method will be based on the total analyte mass and specific matrix characteristics of the sample. The listed methods were developed for implementation in a laboratory setting, though many of the colorimetric and potentiometric methods for aqueous solutions have been adapted to field-based procedures by several commercial vendors.

Table A1. EPA Methods for Selected Redox Parameters

Chemical or Method Name	Number	EPA	ISSUE DATE
Alkalinity - Colorimetric, Automated	0310.2	600/4-79-020	
Alkalinity - Titrimetric, pH 4.5	0310.1	600/4-79-020	
Ammonia in Estuarine by Gas Segmented CF/CA	0349.0	600/R-97-072	09/01/1997
Ammonia-N / automated colorimetry / prelim distill	1690		02/01/1999
Ammonia-N /ion-selective electrode potentiometry	1689		02/01/1999
Ammonium in Wet Deposition by Electrometric	0350.6	600/4-86-024	03/01/1986
Ammonium in Wet Deposition/Automated Colorimetric	0350.7	600/4-86-024	03/01/1986
Bomb Preparation Method for Solid Waste/Metallic	5050	SW-846 Ch 5	09/01/1994
Carbon & Nitrogen in sediments & particulates	0440.0	600/R-97-072	09/01/1997
Extractable Sulfides	9031	SW-846 Ch 5	07/01/1992
Inorganic Anions by Ion Chromatography	0300.0	600/R-93-100	08/01/1993
Inorganic Anions by Ion Chromatography	9056	SW-846 Ch 5	09/01/1994
Inorganic Anions by Ion Chromatography	9056A	SW-846 Ch 5	
Inorganic Anions in Aqueous Matrices - CIE	6500	SW-846 Ch 3.3	01/01/1998
Nitrate - Ion-Selective Electrode	9210	SW-846 Ch 5	12/01/1996
Nitrate - Ion-Selective Electrode	9210A	SW-846 Ch 5	
Nitrate & Nitrite by Gas Segmented CF/CA	0353.4	600/R-97-072	09/01/1997
Nitrate/nitrite-N in biosolids - auto photometry	1685		02/01/1999
Nitrate/nitrite-N in biosolids/ manual colorimetry	1686		02/01/1999
Nitrate-N by IC	0300.0	600/4-79-020	
Nitrate-Nitrate by Automated Colorimetry	0353.2	600/R-93-100	08/01/1993
Nitrate-Nitrite by Automated Colorimetric	0353.6	600/4-86-024	03/01/1986
Nitrite by IC	0300.0	600/4-79-020	
Nitrogen, Ammonia - Colorimetric	0350.1	600/4-79-020	
Nitrogen, Ammonia - Colorimetric, Titrimetric	0350.2	600/4-79-020	
Nitrogen, Ammonia - Potentiometric	0350.3	600/4-79-020	
Nitrogen, Kjeldahl, Total - Colorimetric	0351.2	600/4-79-020	
Nitrogen, Kjeldahl, Total - Colorimetric/Automated	0351.1	600/4-79-020	
Nitrogen, Kjeldahl, Total - Colorimetric/Titrimetric	0351.3	600/4-79-020	
Nitrogen, Kjeldahl, Total - Potentiometric	0351.4	600/4-79-020	
Nitrogen, Nitrate - Colorimetric, Brucine	0352.1	600/4-79-020	
Nitrogen, Nitrate-Nitrite - Colorimetric/Cadmium	0353.2	600/4-79-020	
Nitrogen, Nitrate-Nitrite - Colorimetric/Hydrazine	0353.1	600/4-79-020	
Nitrogen, Nitrate-Nitrite - Manual Cadmium	0353.3	600/4-79-020	
Nitrogen, Nitrite - Spectrophotometric	0354.1	600/4-79-020	
Organic Carbon, Total - Combustion or Oxidation	0415.1	600/4-79-020	
Organic Carbon, Total - UV Promoted	0415.2	600/4-79-020	
Oxygen, Dissolved - Membrane Electrode (Probe)	0360.1	600/4-79-020	
Oxygen, Dissolved - Modified Winkler	0360.2	600/4-79-020	
Sulfate	0300.0	600/4-79-020	
Sulfate - Colorimetric, Automated, Chloranilate	0375.1	600/4-79-020	
Sulfate - Colorimetric, Automated, Chloranilate	9035	SW-846 Ch 5	09/01/1986
Sulfate - Colorimetric, Automated, Methylthymol	0375.2	600/4-79-020	
Sulfate - Colorimetric, Automated, Methylthymol	9036	SW-846 Ch 5	09/01/1986
Sulfate - Colorimetry, Automated	0375.2	600/R-93-100	08/01/1993
Sulfate - Gravimetric	0375.3	600/4-79-020	
Sulfate - Turbidimetric	0375.4	600/4-79-020	
Sulfate - Turbidimetric	9038	SW-846 Ch 5	09/01/1986
Sulfide - Colorimetric, Methylene Blue	0376.2	600/4-79-020	
Sulfide - Ion-Selective Electrode	9215	SW-846 Ch 5	12/01/1996
Sulfide - Titrimetric, Iodine	0376.1	600/4-79-020	
Sulfides, Acid-Soluble & Insoluble - Titrimetric	9034	SW-846 Ch 5	12/01/1996
Sulfides, Acid-Soluble & Insoluble -Distillation	9030B	SW-846 Ch 5	12/01/1996
Total Kjeldahl Nitrogen - Semi-Automated	0351.2	600/R-93-100	08/01/1993
Total Kjeldahl nitrogen / preliminary	1687		02/01/1999
Total Kjeldahl nitrogen / preliminary	1688		02/01/1999
Total Organic Carbon	9060	SW-846 Ch 5	09/01/1986

SOURCES OF EPA TEST METHODS

Index to EPA Test Methods, May 2000 Revised Edition, U.S. EPA Region 1 Library at http://www.epa.gov/region01/oarm/testmeth.pdf

EPA 530/SW-846 Test Methods for Evaluating Solid Waste: Physical/Chemical Methods 3rd ed - 4 vols. November 1986. (Subscription from GPO / SN955-001-00000-1; one-time print purchase from NTIS; also on CD ROM from NTIS and Solutions) All methods including Update IVA and Update IVB and other pre-releases online at www.epa.gov/epaoswer/hazwaste/test/sw846.htm

EPA 600/R-93-100 Methods for the Determination of Inorganic Substances in Environmental Samples. August 1993 (NTIS / PB94-120821)

EPA 600/R-97-072 Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices. 2nd edition. September 1997. (NSCEP or NTIS /PB97-127326 or www.epa.gov:80/nerlcwww/ordmeth.htm or CD ROM)

EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes. Revised March 1983 (NTIS / PB84-128677 for paper; CD ROM; NEPIS/ http://www.epa.gov/cincl)

EPA 600/4-86-024 Development of Standard Methods for the Collection and Analysis of Precipitation. May 1986 (NTIS / PB86-201365)

Table A1. EPA Methods for Selected Redox Parameters

Analyte	Method	Detection Limits	Preservation	Description
Alkalinity	310.1	In a single laboratory using surface water samples at an average concentration of 122 mg $CaCO_3$ /L , the standard deviation was 3.	The sample should be refrigerated at 4˚C and run as soon as practical. Do not open sample bottle before analysis. The sample must not be filtered, diluted, concentrated, or altered in any way.	Titrimetric: An unaltered sample is titrated to an electrometrically determined end point of pH 4.5.
Alkalinity	310.2	The applicable range is 10 to 200 mg/L as $CaCO_3$. In a single laboratory, using surface water samples at concentrations of 15, 57, 154, and 193 mg/L as $CaCO_3$ the standard deviation was 0.5.	Sample should be refrigerated at 4˚C and run as soon as practical. Do not open sample bottle before analysis.	Automated Colorimetric Titration Methyl Orange indicator
Carbon, Total Organic	415.1	The method is most applicable to measurement of organic carbon above 1 mg/L.	Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure. Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4˚C) and protected from sunlight and atmospheric oxygen. In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified to pH< 2) with HCl or H_2SO_4.	Combustion or oxidation. This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector.

Analyte	Method	Detection Limits	Preservation	Description
Carbon, Total Organic	415.2	The applicable range is from approximately 50µg/L to 10mg/L. Higher concentrations may be determined by sample dilution. In a single laboratory, using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07mg/L total organic carbon respectively, the standard deviations from ten replicates were 0.13, 0.03, 0.02, and 0.02mg/L, respectively.	Sampling and storage of samples must be done in glass bottles. Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics. Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4˚C) and protected from sunlight and atmospheric oxygen. When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH < 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.	UV-promoted oxidation. This method covers the determination of total organic carbon in drinking water and other waters. This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method. This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2µm or less.
Carbon (& Nitrogen)	440.0	Method detection limits (MDLs) of 10.5 µg/L and 62.3 µg/L for Particulate Nitrogen and Particulate Carbon, respectively, were obtained for a 200mL sample volume. Sediment MDLs of PN and PC are 84 mg/kg and 1300mg/kg, respectively, for a sediment sample weight of 10.00mg. The method has been determined to be linear to 4800µg of C and 700µg of N in a sample.	Whenever possible, immediately filter the samples. Store the filtered sample pads by freezing at -20˚C or storing in a desiccator after drying at 103-105˚C for 24 hr. No significant difference has been noted in comparing the two storage procedures for a time period of up to 100 days. If storage of the water sample is necessary, place the sample into a clean amber glass bottle and store at 4˚C until filtration is done.	Analysis of particulates by combustion at 975˚C using an elemental analyzer. The combustion products are passed over a copper reduction tube to convert the oxides of N into molecular N. Carbon dioxide, water vapor and N are homogeneously mixed at a known volume, temperature and pressure. The mixture is released to a series of thermal conductivity detectors/traps, measuring in turn by difference, hydrogen (as water vapor), C (as carbon dioxide) and N (as N). Inorganic and organic C may be determined by two methods which are also presented.
Carbon, Total Organic	9060	Precision and accuracy data are available in Method 415.1 of Methods for Chemical Analysis of Water and Wastes.	Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the time between sample collection and the start of analysis should be minimized. Also, samples should be kept cool (4˚C) and protected from sunlight and atmospheric oxygen. In instances where analysis cannot be performed within 2 hr from time of sampling, the sample is acidified (pH < 2) with HCl or H_2SO_4. Samples should be collected in glass bottles.	Method 9060 is used to determine the concentration of organic carbon in ground water, surface and saline waters, and domestic and industrial wastes. Method 9060 is most applicable to measurement of organic carbon above 1 mg/L.

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen (Ammonia)	349.0	A method detection limit (MDL) of 0.3µg N/L has been determined by one laboratory from spiked surface water of three different salinities.	After collection and filtration or centrifugation, samples should be analyzed as soon as possible. If samples will be analyzed within 3 hours then keep refrigerated in tightly sealed, glass or high density polyethylene bottles in the dark at 4˚C until the analysis can be performed. At low concentrations of ammonia (< 20 µg N/L), no preservation technique is satisfactory. *Samples must be analyzed within 3 hours of collectio*n. At moderate and high concentrations of ammonia (> 20 µg N/L) samples can be preserved by the addition of 2 mL of chloroform per liter of sample and refrigerated in the dark at 4˚C. Samples can be stored in either glass or high density polyethylene bottles. A maximum holding time for preserved estuarine and coastal water samples with moderate to high concentrations of ammonia is two weeks.	Gas segmented CF/CA. The method is based upon the indophenol reaction, here adapted to automated gas-segmented continuous flow analysis.
Nitrogen (Ammonia)	350.1	Range of 0.01 to 2.0mg/L NH3 as N. In a single laboratory, using surface water samples at concentrations of 1.41, 0.77, 0.59 and 0.43mg NH_3 -N/L, the standard deviation was 0.005.	Preservation by addition of conc. H_2SO_4 to pH < 2 and refrigeration at 4˚C.	Colorimetric, Automated Phenate. This method covers the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen (Ammonia)	350.2	Range from about 0.05 to 1.0mg NH_3-N/L for the colorimetric procedure, from 1.0 to 25mg/L for the titrimetric procedure, and from 0.05 to 1400mg/L for the electrode method.	Preservation by addition of conc. H_2SO_4 to pH < 2 and refrigeration at 4˚C.	Colorimetric Titration, Potentiometric Distillation Procedure. This method covers the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen (Ammonia)	350.3	Range from 0.03 to 1400 mg NH_3 -N/L. In a single laboratory, using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13mg NH_3 -N/L, standard deviations were 0.038, 0.017, 0.007, and 0.003, respectively.	Preservation by addition of conc. H_2SO_4 to pH < 2 and refrigeration at 4˚C.	Potentiometric, Ion Selective Electrode. This method covers the determination of ammonia in drinking, surface and saline waters, domestic and industrial wastes.

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen (Ammonium)	350.6	MDL = 0.05 mg/ L Range: 0.05 - 2.00mg/L N as NH_4^+	Collect in HDPE containers that have been thoroughly rinsed with ASTM type II water. Filtration through pre-rinsed 0.45 μm filters, followed by refrigeration at 4˚C. Holding time one week or less.	Electrometric detection of ammonia using a gas-sensing ion-selective electrode. This method is applicable to the measurement of ammonium in wet deposition samples: rain, snow, dew, sleet, and hail.
Nitrogen (Ammonium)	350.7	MDL = 0.03 mg/ L Range: 0.03 - 2.00mg/L N as NH_4^+	See 350.6	This colorimetric method (phenate) is applicable to the measurement of ammonium in wet deposition samples: rain, snow, dew, sleet, and hail.
Nitrogen (Ammonia)	1689	Method detection limits and minimum levels for ammonia-N have not been formally established for this draft method. These values will be determined during the validation of the method.	See 1685	Ion selective electrode potentiometry. This method describes procedures for the determination of ammonia as N in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Distillation of the ammonia from the sludge is followed by analysis using an ion-selective probe. This method is based on U.S. Environmental Protection Agency (EPA) Methods 350.2.
Nitrogen (Ammonia)	1690	Method detection limits and minimum levels for ammonia-N have not been formally established for this draft method. These values will be determined during the validation of the method.	See 1685	This automated colorimetric method describes procedures for the determination of ammonia-N in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Distillation of ammonia from the sample is followed by analysis using an automated colorimetric analyzer. This method is based on 350.1 and 350.2.
Nitrogen (Nitrate, Nitrite), Sulfate	300.0	MDLs (mg/L): Nitrite-N 0.004 Nitrate-N 0.002 Sulfate 0.02 Ranges (mg/L) Nitrate-N 0.42 - 14.0 Nitrite-N 0.36 - 12.0 Sulfate 2.85 - 95.0	Samples should be collected in scrupulously clean glass or polyethylene bottles. Sample preservation and holding times for the anions that can be determined by this method are as follows: Nitrate-N, cool to 4˚C, 28 days Nitrite-N, cool to 4˚C, 48 hours Sulfate, cool to 4˚C, 28 days	Determination of Inorganic Anions in Water by Ion Chromatography

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen (Nitrate)	352.1	The applicable range of concentrations is 0.1 to 2 mg NO_3 -N/liter. ± std. dev., mg N/L 0.16 ± 0.92 0.19 ± 0.083 1.08 ± 0.245 1.24 ± 0.214	Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4˚C. When samples must be stored for more than 24 hours, they should be preserved by acidification to pH < 2 with sulfuric acid and refrigeration.	This colorimetric method (brucine) is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes. Modification can be made to remove or correct for turbidity, color, salinity, or dissolved organic compounds in the sample.
Nitrogen (Nitrate, Nitrite)	353.1	The applicable range of this method is 0.01-10mg/L nitrate-nitrite nitrogen. In a single laboratory using drinking water, surface water and industrial waste at concentrations of 0.39, 1.15, 1.76 and 4.75ug NO_3 -N/L, the standard deviations were 0.02, 0.01, 0.02 and 0.03, respectively.	Analysis should be made as soon as possible. If analysis can be made within 24 hours, samples should be preserved by refrigeration at 4˚C. When samples must be stored for more than 24 hours, they should be preserved by acidification to pH < 2 with sulfuric acid (H_2SO_4) and refrigerated at 4˚C.	This colorimetric (hydrazine) method is applicable to drinking and surface water, and domestic and industrial wastes.
Nitrogen (Nitrate, Nitrite)	353.2	The applicable range of this method is 0.05 to 10.0 mg/L nitrate-nitrite nitrogen. The range may be extended with sample dilution.	Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4˚C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid to pH < 2 and refrigeration at 4˚C. CAUTION: Samples for reduction column must not be preserved w/ mercuric chloride.	This automated colorimetric method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes.
Nitrogen (Nitrate, Nitrite)	353.3	The applicable range of this method is 0.01 to 1.0 mg/L nitrate-nitrite nitrogen. The range may be extended with sample dilution.	Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4˚C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid to pH < 2 and refrigeration to 4˚C. CAUTION: Samples for reduction column must not be preserved w/ mercuric chloride.	Manual, copper-coated cadmium reduction column. This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen (Nitrate, Nitrite)	353.4	A statistically deter-mined method detection limit (MDL) of 0.075µg N/L has been determined by one laboratory in seawaters of five different salinities. The method is linear to 5.0 mg N/L using a Flow Solution System (Alpkem, Wilsonville, Oregon) with respect to analyte concentration.	Turbid samples should be filtered as soon as possible after collection. After collection and filtration, samples should be analyzed as soon as possible. If samples will be analyzed within 3 hours then keep refrigerated in tightly sealed, high density polyethylene bottles in the dark at 4˚C until analysis can be performed.	Automated gas segmented continuous flow colorimetric method for the analysis of nitrate. Copper-coated cadmium reduction column.

Table A1. continued

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen, Nitrate	353.6	MDL = 0.02 mg/L Range: 0.02 - 5.00mg/L N as NH_4^+	Collect in HDPE containers that have been thoroughly rinsed with ASTM type II water. Filtration through pre-rinsed 0.45 µm filters, followed by refrigeration at 4˚C. Holding time one week or less.	This colorimetric method is applicable to the measurement of nitrate in wet deposition samples: rain, snow, dew, sleet, and hail.
Nitrogen (Nitrite)	354.1	The method is applicable in the range from 0.01 to 1.0 mg NO_2-N/L. MDL not available	Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4˚C.	This spectrophotometric method is applicable to the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen (Nitrate, Nitrite)	1685	Method detection limits and minimum levels for nitrate/nitrite-N have not been formally established for this draft method. These values will be determined during the validation of the method.	Samples should be collected in wide mouth glass jars with a minimum of air space above the sample. Minimize exposure of samples to air and intense light as much as possible. Nitrate can be formed or lost during storage due to biological activity or lost by oxidation. If the sample contains free water or is aqueous: samples should be checked for residual chlorine and treated with sodium thiosulfate, if necessary, during collection. Samples should be preserved by acidification to pH < 2 with concentrated H_2SO_4 and cooled to 4˚C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling. If the sample contains no free water or is solid, the sample should be cooled to 4˚C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling.	This method describes procedures for the determination of nitrate/nitrite-nitrogen, or oxidized nitrogen, in drinking, ground, and surface water; domestic and industrial waste; and biosolids (treated municipal sewage sludge). Automated photometry is used to determine the nitrate/nitrite concentration of the sample. This method is based on U.S. Environmental Protection Agency (EPA) Method 353.2.
Nitrogen (Nitrate, Nitrite)	1686	This is a draft method, and is currently undergoing validation. Method performance criteria will be set following the validation of the method.	See 1685	This method describes procedures for the determination of nitrate/nitrite-nitrogen, or oxidized nitrogen, in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Manual colorimetry is used to determine the nitrate/nitrite-N concentration. This method is based on U.S. Environmental Protection Agency (EPA) Method 353.3.
Nitrogen (Nitrate, Nitrite), Sulfate	5050	The method detection limit (MDL) varies for anions as a function of sample size and the conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05mg/L for F^- and 0.1mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{-3}, and SO_4^{-2}.	Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4˚C. Samples may be collected in teflon, polyethylene, or glass containers.	Sequential determination by ion chromatography of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen (Nitrate, Nitrite), Sulfate	6500	Nitrate, Nitrite and, Sulfate in the concentration range of 0.1 to 50mg/L. Creek water, mg/L nitrite <0.072 nitrate 3.00 ± 0.30 sulfate 0.37 ± 0.19	Analyze samples as soon as possible after collection. For nitrite, nitrate, and phosphate refrigerate the sample at 4°C after collection and warm to room temperature before dilution and analysis. Determine nitrite and nitrate within 48 hours.	Capillary ion electrophoresis with indirect UV detection. This test method is applicable for determination of the dissolved inorganic anions; fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in aqueous matrices.
Nitrogen (Nitrate, Nitrite), Sulfate	9056	Generally, minimum detectable concentrations are in the range of 0.05mg/L for F^- and 0.1mg/L for Br^-, Cl^-, NO_3^- NO_2^-, PO_4^{-3}, and SO_4^{-2}-	Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4°C. Collect samples in teflon, polyethylene, or glass containers.	Sequential determination by ion chromatography of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.
Nitrogen (Nitrate)	9210 9210A	The method detection limit is 2.0mg/L. Nitrate concentrations from 0.2 to 1,000mg/L may be measured. However, using a linear calibration, results less than 2mg/L may be biased up to approximately 420 percent high; results greater than 400 mg/L may be biased up to approximately 50 percent low.	In the presence of a reducing agent *(e.g.,* organic matter), bacteria can utilize nitrate as an oxidant, causing a slow decrease in the nitrate concentration. This potential interference can be obviated by using a preservative. Therefore, samples must be preserved by adding 1mL of 1M boric acid solution per 100mL of sample. Samples should be stored at 4°C and contained in teflon, polyethylene, or glass bottles.	Total solubilized nitrate is determined potentiometrically using a nitrate ion-selective electrode (ISE).
Nitrogen, Total Kjeldahl (TKN)	351.1	Range is 0.05 to 2.0 mg N/L. Std. Dev. Kjeldahl-N mg N/L 1.89 ± 0.54 2.18 ± 0.61 5.09 ± 1.25 5.81 ± 1.85	Samples may be preserved by acidification to pH < 2 with H_2SO_4 and refrigeration at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Therefore, samples should be analyzed as soon as possible.	Colorimetric, Automated Phenate Surface and saline waters
Nitrogen, Total Kjeldahl	351.2	The applicable range of this method is 0.1 to 20mg/L TKN. The range may be extended with sample dilution. In a single laboratory, using sewage samples of concentrations of 1.2, 2.6, and 1.7 mg N/L, the precision was ±0.07, ±0.03 and ±0.15, respectively.	See Method 351.1.	Semi-automated colorimetric determination of total Kjeldahl nitrogen in drinking and surface waters, domestic and industrial wastes.

Analyte	Method	Detection Limits	Preservation	Description
Nitrogen, Total Kjeldahl	351.3	Method applicable to the range 0.05 to 1400mg/L. ± std. dev. 0.20 ± 0.197 0.31 ± 0.247 4.10 ± 1.056 4.61 ± 1.191	See Method 351.1.	This colorimetric method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen, Total Kjeldahl	351.4	This method covers the range from 0.03 to 25 mg TKN/L.	See Method 351.1.	This potentiometric method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes.
Nitrogen, Total Kjeldahl	1687	Method detection limits and minimum levels for TKN have not been formally established for this draft method. These values will be determined during the validation of the method.	Ammonia can be formed or lost during storage due to biological activity or lost by volatilization or oxidation. The following preservation procedures will help prevent significant changes in the analyte concentration. Samples should be collected in wide mouth jars with a minimum of air space. If the sample contains free water or is aqueous: samples should be checked for residual chlorine and treated with sodium thiosulfate, if necessary, during collection. Samples should be preserved by acidification to pH < 2 with concentrated H_2SO_4 and cooled to 4˚C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling. If the sample contains no free water or is solid, the sample should be cooled to 4˚C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling.	This method describes procedures for the determination of total kjeldahl nitrogen (TKN) and/or organic nitrogen in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Digestion/distillation of the TKN from the sample is followed by analysis using automated colorimetry. This method is based on U.S. Environmental Protection Agency (EPA) Method 351.1.
Nitrogen, Total Kjeldahl	1688	Method detection limits and minimum levels for TKN have not been formally established for this draft method. These values will be determined during the validation of the method.	See 1687.	This method describes procedures for the determination of total kjeldahl nitrogen (TKN) and/or organic nitrogen in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Automatic digestion of the sample is followed by analysis using automated colorimetry. This method is based on U.S. Environmental Protection Agency (EPA) Method 351.2.

Analyte	Method	Detection Limits	Preservation	Description
Oxygen, Dissolved	360.1	Manufacturer's spec-ification claim 0.1mg/L repeatability with 1% accuracy.	Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen. Care must be taken to prevent turbulence and the formation of bubbles when filling bottle. At time of sampling, the sample temperature should be recorded as precisely as required. If samples must be preserved the method below may be employed. Add 2mL of manganous sulfate solution and then 2mL of alkaline iodide-azide solution to the sample contained in the BOD bottle. Both reagents must be added well below the surface of the liquid. Stopper the bottle immediately and mix the contents thoroughly. The sample should be stored at the temperature of the collection water, or water sealed and kept at a temperature of 10 to 20˚C, in the dark. Complete the procedure by adding 2mL H_2SO_4 at time of analysis.	The membrane electrode method for dissolved oxygen is recommended for those samples containing materials which interfere with the modified Winkler procedure such as sulfite, thiosulfate, polythionate, mercaptans, free chlorine or hypochlorite, organic substances readily hydrolyzed in alkaline solutions, free iodine, intense color or turbidity and biological flocs. The probe method is recommended as a substitute for the modified Winkler procedure in monitoring of streams, lakes, outfalls, etc., where it is desired to obtain a continuous record of the dissolved oxygen content of the water under observation.
Oxygen, Dissolved	360.2	Exact data are unavail-able on the precision and accuracy of this technique; however, reproducibility is approximately 0.2mg/L of DO at the 7.5mg/L level due to equipment tolerances and uncom-pensated displacement errors.	See 360.1 above.	Modified Winkler This method is applicable for use with most wastewaters and streams that contain nitrate nitrogen and not more than 1 mg/L of ferrous iron. Other reducing or oxidizing materials should be absent.
Sulfate	375.1	Range of 10 to 400 mg SO_4/L. In a single laboratory, using surface water samples at concentrations of 39, 111, 188 and 294mg SO_4/L, the standard deviations were 0.6, 1.0, 2.2, 4, and 0.8, respectively.	Refrigeration at 4˚C.	This automated colorimetric (chloranilate) method is applicable to drinking and surface waters, domestic and industrial wastes.
Sulfate	375.2	Samples in the range of 3 to 300mg SO_4/L can be analyzed. The sensitivity of the method can be increased by a minor modification to analyze samples in the range of 0.5 to 30mg SO_4/L.	Refrigeration at 4˚C.	Automated colorimetric, methyl thymol. This automated colorimetric method (methyl thymol) is applicable to drinking and surface waters domestic and industrial wastes.

Analyte	Method	Detection Limits	Preservation	Description
Sulfate	375.3	This method is the most accurate method for sulfate concentrations above 10mg/L. Therefore, it should be used whenever results of the greatest accuracy are required. A synthetic unknown sample containing 259mg/L sulfate, 108mg/L Ca, 82mg/L Mg, 3.1mg/L K, 19.9mg/L Na, 241mg/L chloride, 250 Fg/L nitrite N, 1.1mg/L nitrate N and 42.5mg/L alkalinity (contributed by $NaHCO_3$), was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.	Refrigeration at 4˚C.	This gravimetric method is applicable to drinking, surface and saline water, domestic and industrial wastes.
Sulfate	375.4	The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40mg SO_4/L. The minimum detectable limit is approximately 1mg/L sulfate.	Refrigeration at 4˚C.	This turbidimetric method is applicable to drinking and surface waters, domestic and industrial wastes.
Sulfate	5050			Bomb preparation
Sulfate	6500			Inorganic anions in aqueous matrices, capillary ion electrophoresis
Sulfate	9035	Applicable to ground water, drinking and surface waters, and domestic and industrial wastes containing 10 to 400mg SO_4^{-2} /liter.	Refrigerate at 4˚C. Samples should be centrifuged or filtered before analysis. Teflon, polyethylene, or glass bottles may be used.	Automated colorimetric (acid chloranilate ion)
Sulfate	9036		Refrigerate at 4˚C. Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion-exchange resin. Turbid samples should be filtered or centrifuged.	This automated colorimetric method using methylthymol blue is applicable to ground water, drinking and surface waters, and domestic and industrial wastes.

Analyte	Method	Detection Limits	Preservation	Description
Sulfate	9038	The minimum detectable limit is approximately 1mg/L of SO_4^{-2}. Use a sample aliquot containing not more than 40mg/L of SO_4^{-2}.	Preserve by refrigerating at 4˚C.	Turbidimetric method by nephelometer, filter photometer, or spectrophotometer applicable to ground water, drinking and surface waters, and domestic and industrial wastes.
Sulfate	9056			Ion chromatography
Sulfide	376.1	This method is suitable for the measurement of sulfide in concentrations above 1mg/L. Precision and accuracy for this method have not been determined.	If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.	This iodimetric method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes. Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).
Sulfide	376.2	The method is suitable for the measurement of sulfide in concentrations up to 20mg/L. The precision has not been determined. The accuracy is about 10%.	Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards. The analysis must be started immediately.	This colorimetric method (methylene blue) is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes. Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
Sulfide, Acid Volatilized	9030B	Detection Limit - The detection limit was determined by analyzing seven replicates at 0.45 and 4.5mg/L. The detection limit was calculated as the standard deviation times the student's t-value for a one-tailed test with n-1 degrees of freedom at 99% confidence level. The detection limit for a clean matrix (H_2O) was found to be between 0.2 and 0.4mg/L. Method 9030 is suitable for measuring sulfide concentrations in samples which contain between 0.2 and 50mg/kg of sulfide.	All aqueous samples and effluents must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100mL of sample. Adjust the pH to greater than 9 with 6N sodium hydroxide solution. Fill the sample bottle completely and stopper with a minimum of aeration. The treated sample is relatively stable and can be held for up to seven days. If high concentrations of sulfide are expected to be in the sample, continue adding zinc acetate until all the sulfide has precipitated. For solid samples, fill the surface of the solid with 2N zinc acetate until moistened. Samples must be cooled to 4˚C and stored head space free.	The distillation procedure described in this method is designed for the determination of sulfides in aqueous, solid waste materials, or effluents. For acid-soluble sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70˚C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles, where it is precipitated as zinc sulfide.

Analyte	Method	Detection Limits	Preservation	Description
Sulfide, Acid Volatilized (Extractable)	9031	Method 9031 is suitable for measuring sulfide in solid samples at concentrations above 1mg/kg.	All samples must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of aqueous or multiphasic sample. Adjust the pH to greater than 9.0 with 50% NaOH. Fill the sample bottle completely and stopper with a minimum of aeration. For solid samples, fill the surface of solid with 2N zinc acetate until moistened. Samples must be cooled to 4˚C during storage.	Separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70˚C and the hydrogen sulfide which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide. The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of excess iodine. Then the excess iodine is determined by titration with a standard solution of phenylarsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. The use of standard sulfide solutions is not possible because of their instability to oxidative degradation. Therefore quantitation is based on the PAO or sodium thiosulfate.
Sulfide, Acid Volatilized	9034	Method 9034 is suitable for measuring sulfide concentrations in samples which contain 0.2 mg/kg to 50 mg/kg of sulfide.	Distillates that are not analyzed immediately should be stored in a sealed flask at 4˚C.	This procedure may be used as a determinative step for acid-soluble and acid-insoluble sulfides following distillation of the sample by SW-846 Method 9030. Sulfide is extracted from the sample by a preliminary distillation procedure (see Method 9030) and precipitated in a zinc acetate scrubber as zinc sulfide. The sulfide is oxidized to sulfur by adding a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

Analyte	Method	Detection Limits	Preservation	Description
Sulfide	9215	The method detection limit is 1.0mg/L. Sulfide concentrations from 0.1 to 12,000mg/L may be measured. However, when a linear calibration is used, results less than 1mg/L may be biased up to approximately 90 percent low.	All original, undistilled samples should be handled as described in Section 6 of Methods 9030 and/or 9031. Samples should be stored at 4˚C prior to analysis. The distilled samples should be analyzed with the ISE immediately following distillation, distillates that are not analyzed immediately should be stored in a sealed flask at 4˚C.	This method can be used for measuring total sulfide in a distilled sample. The method is meant to be used as an alternate determinative step following the distillation in either SW-846 Methods 9030 or 9031. The distillations in Methods 9030 and/or 9031 are performed, except that the scrubber solution is sulfide anti-oxidant buffer (SAOB), with ascorbic and salicylic acids added as oxygen scavengers. The distillates are then analyzed potentiometrically using a sulfide ion-selective electrode (ISE) in conjunction with a double-junction reference electrode and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of sulfide concentration.

EPA

United States
Environmental Protection
Agency

National Risk Management
  Research Laboratory
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/R-02/002
January 2002

Please make all necessary changes on the below label,
detach or copy, and return to the address in the upper
left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐;
detach, or copy this cover, and return to the address in the
upper left-hand corner.