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# METHODS FOR MEASURING INDICATORS OF INTRINSIC BIOREMEDIATION: GUIDANCE MANUAL

Health and Environmental Sciences Department Publication Number 4658 November 1997

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- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

# Methods for Measuring Indicators of Intrinsic Bioremediation: Guidance Manual

Health and Environmental Sciences Department

**API PUBLICATION NUMBER 4658** 

PREPARED UNDER CONTRACT BY:

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iii

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# ABSTRACT

Evaluating intrinsic bioremediation at a particular site typically includes a characterization of the site's groundwater for geochemical indicators of naturally occurring biodegradation. A number of protocols offer guidance on the suite of geochemical parameters that should be included in these site characterizations, for example, dissolved oxygen (DO), nitrate, sulfate, alkalinity, etc. However, there is less guidance available on the most appropriate sampling and analytical methods for these parameters. The American Petroleum Institute (API) implemented a project to evaluate and compare various sampling and analytical methods for these geochemical parameters. Performance data on various sampling methods were generated in both laboratory and field studies. The field studies also included an evaluation of field analytical methods for select parameters. The quality of the data obtained varied with the specific sampling and analytical methods used. No single sampling or analytical method was found to be the most appropriate method in every situation. Selecting the most appropriate method depends on project-specific and site-specific considerations. Factors to be considered in the selection of sampling and analytical methods include the intended data use (e.g., qualitative versus quantitative), and the associated factors of complexity, level of effort, and cost. In many cases, method selection involves a balance of data quality and cost control objectives. This document provides guidance on method selection, method implementation, and data interpretation for intrinsic bioremediation projects.

# TABLE OF CONTENTS

Section Page
1. INTRODUCTION1-1
BACKGROUND1-1
OBJECTIVES AND USE OF GUIDANCE MANUAL1-2
REPORT ORGANIZATION1-3
2. SAMPLING AND ANALYTICAL METHOD SELECTION OVERVIEW2-1
WHY BE CONCERNED WITH SAMPLING AND ANALYTICAL METHODOLOGY?2-1
Geochemical Considerations2-2
Sampling and Analytical Considerations
FACTORS TO BE CONSIDERED IN METHOD SELECTION
Data Use2-7
Data Quality Objectives2-9
Level of Effort, Complexity, and Cost2-10
3. SAMPLING METHODOLOGY
CONVENTIONAL PURGE/BAILER METHOD
Description3-1
Potential Effects of Sampling Method on Data Quality
Advantages and Disadvantages3-4
Recommendations
NO PURGING
Description3-6
Potential Effects of Sampling Method on Data Quality
Advantages and Disadvantages
Recommendations
MICROPURGING METHOD
Description3-10
Potential Effects of the Sampling Method on Data Quality
Advantages and Disadvantages
Recommendations

i

1

1

# TABLE OF CONTENTS (Continued)

<u>Section</u>	'age
3. SAMPLING METHODOLOGY (Continued)	
USE OF INERT GAS IN THE WELL BORE	3-14
Description	3-14
Potential Effects of Sampling Method on Data Quality	3-14
Advantages and Disadvantages	3-14
Recommendations	3-15
SUMMARY	3-16
4. MEASUREMENTS AND SAMPLE ANALYSES	.4-1
DISSOLVED OXYGEN (DO)	.4-8
Purpose of DO Measurement	.4-8
Methods of DO Measurement	.4-8
Discussion4	<b>1-11</b>
NITRATE (NO, )4	<b>I-11</b>
Purpose of Nitrate Measurement4	<b>i-11</b>
Methods of Nitrate Measurement4	<b>I-12</b>
Discussion4	<b>1-13</b>
FERROUS IRON (Fe <sup>2+</sup> )4	<b>1-</b> 13
Purpose of Ferrous Iron Measurement4	<b>1-13</b>
Methods of Ferrous Iron Measurement4	<b>i-13</b>
Discussion4	<b>-</b> 15
MANGANESE4	<b>1</b> -15
SULFATE (SQ <sup>2</sup> )4	<b>1-15</b>
Purpose of Sulfate Measurement	<b>1-15</b>
Methods of Sulfate Measurement4	<b>1</b> -16
Discussion	<b>1-16</b>
METHANE (CH.)	<b>1</b> -17
Purpose of Methane Measurement4	<del>1-</del> 17
Methods of Methane Measurement4	4-17
Discussion	4-17

ì

١

#### TABLE OF CONTENTS (Continued)

# Section Page 4. MEASUREMENTS AND SAMPLE ANALYSES (Continued) Methods of CO, Measurement ......4-19 Discussion......4-19 ALKALINITY......4-19 Methods of Alkalinity Measurement ......4-20 OXIDATION-REDUCTION POTENTIAL (ORP) ......4-20 Purpose of Oxidation-Reduction GLOSSARY ......G-1 APPENDIX A STANDARD OPERATING PROCEDURE

STD.API/PETRO PUBL 4658-ENGL 19	97 🔳	0732290	0603665	927	
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# LIST OF FIGURES

Figure	Page
2-1 Potential Effects of Artificial Aeration	2-4
2-2 Geochemical Consequences of Hydrocarbon Biodegradation	2-4

# LIST OF TABLES

l,

ì

<u>Tab</u>	<u>]</u>	<u>Page</u>
3-1	Dissolved Oxygen as a Function of Drawdown	3-3
3-2	Summary Comparison of Sampling Methods	.3-17
4-1	Comparison of Commercial Laboratory Versus Field Methods	4-2
4-2	Methods of Key Geochemical Parameters	4-4
<b>4-</b> 3	Gas Analysis by Headspace Equilibrium	.4-18
4-4	Additional Geochemical Parameters of Interest and Data Use	.4-24

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# Section 1 INTRODUCTION

This manual, sponsored by the American Petroleum Institute (API), provides guidance on the selection and use of field sampling and analytical methods for measuring geochemical indicators of intrinsic bioremediation.

#### BACKGROUND

Intrinsic bioremediation is a risk management strategy that relies on naturally occurring biodegradation for mitigation of the potential risks posed by subsurface contaminants. This strategy is being considered at sites contaminated with petroleum hydrocarbons because of the growing recognition that 1) aqueous phase (dissolved) petroleum hydrocarbons are biodegradable at significant rates by indigenous microorganisms without artificial enhancement; and 2) in many cases, the cost of conventional groundwater remediation approaches far outweighs the benefits in terms of protection of human health and the environment.

Various technical articles and protocols offer guidance on the groundwater parameters and properties that should be measured to characterize intrinsic bioremediation of petroleum hydrocarbons. These include dissolved oxygen (DO), nitrate, sulfate, ferrous iron, methane, carbon dioxide, alkalinity, oxidation/reduction potential (ORP), pH, conductance, and temperature.

These parameters are being measured at an increasing number of petroleum hydrocarbon contaminated sites. However, there is generally a lack of specific guidance on appropriate sampling and analytical procedures to ensure that these intrinsic bioremediation measurements generate quality data. This lack of guidance is

1-1

of concern because the extent to which intrinsic bioremediation is ultimately embraced will depend, to a large degree, on the valid characterization of site conditions. Therefore, API initiated a study to evaluate and compare the methods used to characterize intrinsic bioremediation, with the ultimate objective of providing this guidance document on sampling methods and analytical procedures. The laboratory and field studies conducted to support the guidance are described in a companion document (CH2M HILL, 1997).

# **OBJECTIVES AND USE OF THIS MANUAL**

This guidance manual is intended to be a resource for practitioners of intrinsic bioremediation in the following areas:

- <u>Scoping field investigations</u>: Allowing selection of sampling and analytical methods that meet project-specific and site-specific needs.
- <u>Performing field investigations</u>: Allowing field staff implementing field investigations to understand how sampling and field analytical techniques can affect the data collected. Provides procedures that will improve the representative quality of the collected data.
- <u>Evaluation of field investigation data</u>: Allowing those responsible for evaluation of geochemical indicators of intrinsic bioremediation to consider potential biases introduced into data through the sampling and analytical techniques employed in the site investigation.

This document is not intended to serve as guidance on the broader issues of how to assess intrinsic bioremediation and what parameters to measure. These issues are addressed in other documents, including the Air Force's *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Weidemeier *et al.*, 1995), an upcoming ASTM guide for remediation by natural attenuation at petroleum release sites (in preparation), Mobil Oil Corporation's A Practical Approach to Evaluating Intrinsic

1-2

Bioremediation of Petroleum Hydrocarbons in Ground Water (Mobil Oil Corporation, 1995), and Chevron's Protocol for Monitoring Intrinsic Bioremediation in Groundwater (Buscheck and O'Reilly, 1995), among others.

Site data on geochemical indicators of intrinsic bioremediation can be used in a variety of ways, ranging from very qualitative uses (e.g., comparison to background data) to very quantitative uses (e.g., input parameters to numerical fate and transport models). The ultimate data use dictates the data quality objectives. The data quality that can be expected from the various sampling and analytical methods and impacts on data use, are discussed in this report. This report should not be interpreted as providing endorsement of any particular data use.

This guidance document focuses on collection of representative intrinsic bioremediation data at petroleum hydrocarbon sites. However, the observations and findings presented here will generally be applicable to any site where biodegradable organic constituents occur.

#### **REPORT ORGANIZATION**

This report is organized in four sections:

- 1. Introduction to report purpose and organization.
- 2. Overview of sampling and method selection. Information is presented on how sampling and analytical methodology can affect intrinsic bioremediation data. The general factors that should be considered in selecting sampling and analytical methods are reviewed.
- 3. Discussion of sampling methodology. Four different groundwater sampling methods are described. The manner in which the sampling method may affect data quality is discussed, advantages and disadvantages of the methods are presented, and

1-3

recommendations to improve the representative quality of geochemical data collected using the method are offered.

4. Comparison of measurement methods. The merits of using field methods versus commercial laboratory services are evaluated. Methods for determination of individual geochemical indicators are presented. For each of these parameters, the purpose of measuring the geochemical parameter is discussed, available test methods are summarized, and important considerations in test method selection and use are presented.

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#### Section 2

#### SAMPLING AND ANALYTICAL METHOD SELECTION OVERVIEW

This section presents an overview of the key considerations in sampling and analytical methodology. Information is presented on how sampling and analytical methodology can alter data on geochemical indicators of intrinsic remediation. The general factors that should be considered in selecting sampling and analytical methods are reviewed.

#### WHY BE CONCERNED WITH SAMPLING AND ANALYTICAL METHODOLOGY?

The characterization of key geochemical parameters of groundwater is a tool that has emerged in recent years for evaluating intrinsic bioremediation. Microbial metabolism of petroleum hydrocarbons has predictable geochemical consequences (Wilson *et al.*, 1994). For example, respiration of hydrocarbons may result in the loss of oxygen, nitrate, and sulfate, and the conversion of iron from the ferric to ferrous oxidation state. Petroleum hydrocarbons may also be biodegraded by an anaerobic process that results in the production of methane (i.e., methanogenesis). Measuring the trends in the distribution and concentration of these and other parameters can help to qualitatively establish hydrocarbon biodegradation activity. Data on the spatial distribution of these parameters, together with hydrogeologic and stoichiometric data, are also sometimes used to support the quantitative estimation of contaminant biodegradation rates and the prediction of plume migration.

Why be concerned with sampling and analytical methodology? The uses of geochemical data previously described will be valid only to the extent that measurements of these parameters are representative of geochemical conditions in the groundwater system sampled. Sampling and analytical methodology can significantly affect measurements of key geochemical indicators of intrinsic bioremediation, as described below.

2-1

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#### **Geochemical Considerations**

To understand how sampling and analytical methods may impact results, one must first have a basic understanding of the geochemistry of the groundwater being sampled, and recognize that the geochemical condition of groundwater from biologically active zones is typically not stable during and after extraction from the subsurface.

In recent years, it has become widely recognized that microorganisms can have profound effects on groundwater quality. This is particularly true where large masses of biodegradable organic compounds, such as petroleum hydrocarbons, are present in the vadose and groundwater zones. Hydrocarbon biodegradation involves microbiologically mediated oxidation coupled with reduction of an electron acceptor through the biological process of respiration. The reduction of highly oxidized electron acceptors (e.g., DO) results in an overall decrease in the oxidizing potential of the groundwater. As species with the highest oxidizing potential are exhausted, the oxidizing potential of the groundwater system is progressively reduced, and the next most highly oxidized electron acceptor is used. Thus, a general sequence of electron acceptor utilization and lowering of the oxidizing potential of the groundwater is as follows:

- 1. Consumption of DO through aerobic respiration;
- 2. Nitrate reduction;
- 3. Reduction of ferric iron and corresponding production of ferrous iron;

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- 4. Sulfate reduction; and
- 5. Methanogenesis, in which carbon dioxide is used as an electron acceptor and produces methane, and/or acetate is cleaved to carbon dioxide and methane.

The above is a generalized and simplistic presentation of the progressive lowering of the oxidizing potential of a groundwater system through biodegradation of petroleum hydrocarbons. More complete descriptions of this process may be found in a variety of technical references (e.g., Wiedemeier *et al.*, 1995; Atlas, 1984; Chapelle, 1993). Water in equilibrium with the atmosphere will contain approximately 8 mg/L DO. This is the upper bound of oxidizing conditions within natural groundwater systems. As described earlier, biodegradation of petroleum hydrocarbons results in the consumption of this DO. At many petroleum hydrocarbon sites, the oxidizing potential of the groundwater is lowered to the extent that sulfate is reduced and ferrous iron and methane are produced (Admire *et al.*, 1995; Borden *et al.*, 1995). When the oxidizing potential has been reduced to this point, the groundwater is in considerable nonequilibrium with the atmosphere.

When groundwater from subsurface zones of low oxidizing potential is brought to the surface and exposed to the atmosphere, fairly rapid changes in the oxidizing potential and concentrations of certain geochemical parameters can occur as the water begins to equilibrate with the atmosphere (See Figure 2-1). A common example of this phenomenon is the formation of rust colored solids in water samples containing nonaqueous phase petroleum hydrocarbons. This is a visible manifestation of the transfer of oxygen from the atmosphere into the aqueous phase, subsequent oxidation of soluble ferrous iron to ferric iron, and the ultimate precipitation of the relatively insoluble ferric oxyhydroxide.

2-3



Figure 2-1. Potential Effects of Artificial Aeration

Parameter	Concentration in Plume Relative to Background
Dissolved Oxygen	Û
Nitrate	Û
Ferrous Iron	Û
Sulfate	Û
Methane	Û

Figure 2-2. Geochemical Consequences of Hydrocarbon Biodegradation

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The evolution of dissolved gases from samples is another concern. Hydrocarbon oxidation results in the production of water and carbon dioxide. Increases in bicarbonate (the dominant total carbonate species at neutral pH) from a typical range of 5 to 500 mg/L (Kemmer, 1988) to as high as 1,800 milligrams per liter (mg/L) have been observed in a biologically active petroleum hydrocarbon plume (Admire *et al.*, 1995). Methane may also be produced under geochemically reduced conditions. Dissolved methane concentrations as high as approximately 50 mg/L have been observed down-gradient of petroleum release sites (Wiedemeier *et al.*, 1995), while methane concentrations in potable water are typically not detectable.

When groundwater samples with elevated methane and carbon dioxide are brought to the surface and exposed to atmospheric conditions, gases dissolved in the groundwater will reach equilibrium with gases in the atmosphere, as described by Henry's law. Agitation of the water sample or lengthy exposure to the atmosphere results in loss of carbon dioxide and methane. The loss of carbon dioxide will result in both a higher pH and probable precipitation of calcium carbonate. This loss of dissolved carbon dioxide from a groundwater sample prior to analysis is one of the reasons the field pH measurement is often lower than the subsequent laboratory pH measurement.

#### Sampling and Analytical Considerations

Groundwater samples from zones in which petroleum hydrocarbons are being biodegraded are often in dramatic nonequilibrium with normal atmospheric conditions. Furthermore, contact of these samples with the atmosphere can cause significant shifts in aqueous geochemistry.

The key to minimizing potential shifts in the geochemistry of reduced samples is minimizing contact with atmospheric air. Associated sampling considerations include the following:

2-5

- Purging wells at a high rate may lower the water level in the well. During recharge of the well under these conditions, there is significant contact between the groundwater and the atmosphere as the groundwater trickles, or cascades, into the well.
- Use of a bailer for sample collection surges the well contents and introduces air contact with groundwater. Furthermore, air/groundwater contact occurs as the sample is poured from the bailer into the sample bottle.
- Other than samples for volatile organic analysis, water samples are often collected in such a way that there is headspace in the sample bottle. Agitation of the sample bottle during handling and shipping may result in thorough mixing of the groundwater and gases of atmospheric composition in the headspace.

Other sampling and analytical considerations include the following:

- Bailing a well and/or purging a well at high rates can result in increased sample turbidity. Turbidity in the sample can result in nonrepresentative sample geochemistry. Solids that accumulate in the bottom of a well may be at a different oxidation-reduction state than formation groundwater and serve as either a source or sink of electron acceptors. For example, DO in formation groundwater may be consumed through contact with geochemically reduced solids that accumulate in the well. Solids that accumulate in the well, or aquifer solids brought into the well through vigorous sampling techniques (e.g. high well entrance velocity), may also be comprised of compounds that will contribute to detected concentrations of analytes of interest.
- Changes in water geochemistry, resulting from both the presence of headspace in the sample and ongoing microbiologically mediated processes within the sample, can occur during the sample holding time typical with off-site laboratories.
- Dissolved gases can be partially removed from solution when a vacuum is used to lift samples from a well.

2-6

#### FACTORS TO BE CONSIDERED IN METHOD SELECTION

Generally, there is no single sampling or monitoring method that will be the most appropriate method in every situation. Selecting the most appropriate method will depend on project-specific and site-specific considerations. Factors to be considered in selection of sampling and analytical methods for measuring geochemical indicators of intrinsic remediation are discussed in this section.

#### Data Use

Commonly employed sampling techniques may change the geochemistry of a groundwater sample. The significance of these potential changes is a function of how the data are used. The data may be used qualitatively or quantitatively.

A general strategy recommended by the National Research Council (NRC) for demonstrating that *in situ* bioremediation is active (NRC, 1993) relies on the convergence of three lines of evidence:

- 1. Documented loss of constituents of concern from the site;
- 2. Laboratory assays showing that microorganisms have the *potential* to transform the constituents of concern under the expected site conditions; and
- 3. One or more pieces of evidence showing that the biodegradation potential is *actually realized* in the field.

Within this strategy, geochemical indicators of intrinsic bioremediation are most often used to support the third line of evidence. Microbial metabolism of petroleum hydrocarbons has predictable geochemical consequences (Wilson *et al.*, 1994), as illustrated in Figure 2-2. When the geochemical trends illustrated in Figure 2-2 are exhibited at a petroleum hydrocarbon site, there is strong evidence that hydrocarbon biodegradation is occurring. In this manner, trends in concentrations of key parameters across the site are more important than the specific concentration at a single location.

2-7

Not for Resale

Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS Geochemical data may also be used quantitatively. These uses of geochemical data will often not be required or be appropriate at small petroleum hydrocarbon release sites where the plume has reached or is receding from its steady-state limit.

Calculating the expressed assimilative capacity is one method used for interpreting geochemical data at a given site. The expressed assimilative capacity is an estimate of the hydrocarbon mass per unit volume of groundwater potentially mineralized through aerobic and anaerobic biodegradation under existing site conditions (see the glossary for additional information). This method is sometimes used semi-quantitatively to judge which contaminant biodegradation mechanisms are most significant at a given site (Wiedemeier *et al.*, 1995), although considerable debate still exists regarding the methods and merits of quantifying the contributions of aerobic versus anaerobic processes.

For example, the expressed assimilative capacity can be converted to an equivalent DO concentration and used in the BIOPLUME II model. BIOPLUME II is a fate and transport model that incorporates an oxygen-limited biodegradation component (Rifai *et al.*, 1988). The geochemical data may also be used in the newer BIOPLUME III and BIOSCREEN models. The BIOPLUME III Model is a revision of the BIOPLUME II Model in which the biodegradation component of the model will be expanded to simulate the transport and uptake of anaerobic electron acceptors (Newell *et al.*, 1995). BIOSCREEN is a model based on the Domenico analytical solute transport model which has the ability to simulate both aerobic and anaerobic decay of petroleum hydrocarbons in groundwater (Newell *et. al.*, 1996). With these models, data on DO, nitrate, iron, sulfate, ferrous/ferric iron and methane can be used as input for numerical simulations of the various contaminant biodegradation mechanisms and quantitative predictions of biodegradation-controlled migration.

2-8

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The specific concentrations of key parameters measured at specific locations becomes more important as the use of site geochemical data becomes more quantitative. Changes in sample geochemistry resulting from sampling and/or analytical methodology will be most significant with the most quantitative uses of the resulting data. The impact of specific sampling and analytical methods on intrinsic bioremediation geochemical indicator data is discussed in Sections 3 and 4 of this document.

Development of a plan for the specific manner (e.g., qualitative versus quantitative) in which intrinsic bioremediation is to be evaluated should be an early step in planning a field investigation. Once this has been defined, decisions can then be made on data quality objectives (e.g., data quality and accuracy) and the appropriate level of effort in field measurements, sample collection, and sample analysis.

#### **Data Quality Objectives**

In characterizing intrinsic bioremediation, one would like to minimize the cost by eliminating the collection of unnecessary, duplicative, or overly precise data. At the same time, one must collect data of sufficient quality and quantity to support defensible decision making. The most efficient way to accomplish both goals is to begin by ascertaining the type, quality, and quantity of data necessary to address the problem before the study begins. EPA guidance (USEPA, 1993) describes a Data Quality Objective (DQO) Process that can be used to accomplish these goals. The DQO Process is a series of planning steps designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application.

Information presented in this document will assist in the development of appropriate data quality objectives. This information includes the discussion of data

2-9

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use, as well as the effects of different sampling and analytical methods on the accuracy and precision of the resulting data.

#### Level of Effort, Complexity, and Cost

There are a number of options for obtaining a measurement of a specific geochemical indicator of intrinsic bioremediation. Generally, these options will vary with respect to how accurately the results generated reflect *in situ* geochemical conditions. However, these options (briefly described below) will also vary with respect to the related factors of level of effort, complexity, and cost.

- <u>Level of effort</u>: The options may vary in the level of effort needed in planning and mobilization for the field effort (e.g., equipment procurement), time required to implement the option, and the number and type of staff needed in the field. Each of these factors will influence the cost of the field effort.
- <u>Complexity</u>: Use of conventional sampling and analytical techniques can generally be accomplished with little or no additional training of field sampling crews or added expertise. Other techniques are more complex and may require that sampling crews receive additional training or be supplemented with staff having the required expertise (e.g., an experienced analytical chemist). In addition, it is generally true that the more complex the field investigation effort, the more likely something may go awry, and the more likely that contingencies with increased costs will be incurred.
- <u>Costs</u>: In all sectors of the environmental remediation community there are increasing pressures to manage costs. As described above, options for measuring geochemical indicators of intrinsic bioremediation vary in level of effort and complexity, and, therefore, will also vary in cost.

In Sections 3 and 4 of this document, information on the relative level of effort, complexity, and cost of various options for measuring geochemical indicators of intrinsic bioremediation are presented. Information on the impact of these

2-10

techniques on data quality is also discussed. In many cases, selection of methods will involve a balancing of data quality and cost control objectives.

#### Section 3

#### SAMPLING METHODOLOGY

In this section, four different groundwater sampling methods are discussed in terms of the advantages/disadvantages of each method and the method's impact on data quality. Recommendations for improving the representative quality of the geochemical data are also provided. The methods considered are:

- Conventional purge/bailer method;
- No purge method;
- Micropurging method; and
- Inert gas sampling method.

A summary comparison of these sampling methods is also presented.

#### CONVENTIONAL PURGE/BAILER METHOD

#### **Description**

The conventional purge/bailer method consists of purging the well of three-to-five well volumes, and then collecting groundwater samples through use of a bailer. An EPA guidance document (USEPA, 1986) contributed to the establishment of this method as the generally practiced sampling method.

Minimizing the time and cost of the monitoring effort is typically the primary consideration in selecting the purging method. For small wells, particularly those in low permeability formations, a bailer is often used to purge the well. For larger wells, purging is more typically accomplished through use of pumps (e.g., electric submersible pump, peristaltic pump, or bladder pump). When the formation permeability is great enough to allow multiple purge volumes, field groundwater

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parameters (e.g., temperature, conductivity, pH) are checked periodically to determine when the groundwater quality has stabilized (i.e., the purging endpoint).

Once the required amount of groundwater is purged, samples are collected with a bailer. Sample bottles are filled directly from the bailer. If filtered samples are collected, they are obtained by various methods, such as using a bailer equipped with a bottom-fitting filter and applying pressure to the top of the bailer; or, by pouring groundwater from a bailer into a bucket, after which samples are pumped from a bucket through an in-line filter into sample bottles using a peristaltic pump.

# Potential Effects of Sampling Method on Data Quality

Purging is usually done as quickly as possible in order to minimize labor hours and the overall costs of the monitoring effort. However, purging at high rates typically lowers the water level in the well, particularly in formations of medium to low permeability. During recharge of the well, there is significant contact between the groundwater and the atmosphere as the groundwater trickles or cascades into the well. This artificial aeration can change the geochemistry of the groundwater. In the interest of quickly purging wells, field technicians may lower the bailer in the well so quickly that it splashes upon hitting water, further increasing the potential for artificial aeration of the sample.

The parameters most vulnerable to significant changes in concentration brought about by artificial aeration are DO, oxidation-reduction potential (ORP), ferrous iron, and methane. The assumption that excessive drawdown may alter the geochemistry of extracted groundwater was tested in the API field study by varying the drawdown during purging and observing the effect on DO readings. Results showed a clear relationship of increasing DO with increasing drawdown, providing evidence that

drawdown does result in groundwater aeration and alteration of sample geochemistry, as shown in Table 3-1 (CH2M HILL, 1997).

The bias introduced by artificial aeration will generally be a conservative bias, in that the loss of iron and methane would result in an underestimation of microbial activity (e.g, as determined from calculation of the expressed assimilative capacity). In the study of sampling methods, expressed assimilative capacities were calculated using field data generated using the purge/bailer and micropurging methods. The expressed assimilative capacity for iron reduction and methanogenesis calculated with data generated with the conventional purge/bailer method was lower by a factor of two for one site, and similar at the other site (CH2M HILL, 1997).

Table 3-1. Dissolved Oxygen as a Function of Drawdown			
Steady-State DO Measurements Micropurging Sampling at MW-B1 (Missouri UST Site)			
	Dra	awdown	
Step	(Ft)	(% Wetted Screen)	DO (mg/L)
1	1.9	15	0.75
2	1.4	11	0.52
3	0.5	5	0.28
4	1.7	14	0.66

Table 3-1. Dissolved Oxygen as a Function of Drawdown

Purging at high rates and use of a bailer can increase sample turbidity, which can result in a non-representative sample of geochemistry. Solids that accumulate in the bottom of a well may be at a different oxidation-reduction state than formation groundwater and may serve as either a source or sink of electron acceptors. For example, DO in formation groundwater may be consumed through contact with geochemically reduced solids that accumulate in the well. Aquifer solids or solids that accumulate in the well may be comprised of compounds that will contribute to detected concentrations of analytes of interest.

The introduction of turbidity into the sample can also impact contaminant concentration data. Bailers and high-speed pumps cause increased disturbance or stress on the well formation. This increased stress may cause normally immobile particles with adsorbed contaminants to become part of the groundwater sample. Large concentrations of these particles contained in samples may cause erroneous analytical results, since we are usually only concerned with the mobile contaminants (Puls and Paul, 1995).

#### Advantages and Disadvantages

Advantages of the conventional purge/bailer method are:

- The conventional purge/bailer method is a widely employed groundwater sampling technique. Due to its widespread use, the method generally requires no additional training of field staff.
- This method is widely known and accepted by regulatory agencies.
- If geochemical indicator data are collected for qualitative purposes (e.g., spatial trend analysis), the method will generally produce samples that are adequately representative of formation groundwater. (However, caution should be exercised in interpretation of ORP, DO, iron, and methane data.)
- The conventional purge/bailer method may have been previously used to generate a large database of time series monitoring data. If this is the case, it may be advantageous to continue using the purge/bailer method.

Disadvantages of the conventional purge/bailer method are:

- If the data on geochemical indicators of intrinsic bioremediation are to be used quantitatively, the impact of sampling method on data quality can be significant, particularly for the parameters of ORP, DO, iron, and methane.
- The combination of purging the well at a fast rate and using a bailer to generate a sample for DO measurement or analysis is the least favored

method for obtaining DO data. The method will result in DO measurements that are highly biased.

The practice for groundwater sampling has been evolving away from the conventional "three well volume purge" method, based partly on data quality considerations and partly on the desire to reduce purge water volumes and associated groundwater monitoring costs (Shanklin *et al.*, 1995).

# **Recommendations**

In summary, there are aspects of the conventional purge/bailer method that offer potential for artificial aeration of the sample and changes in the concentrations of geochemical parameters of interest, particularly for the parameters of ORP, DO, ferrous iron, and methane. However, the conventional purge/bailer method will, in many cases, produce geochemical data of adequate representative quality if the data are used for qualitative purposes only.

If the conventional purge/bailer method is used, this method's effectiveness can be improved by:

- DO data collected with the conventional purge/bailer method will be particularly suspect, and so should be supplemented with downhole DO probe measurements. Downhole measurements with a DO probe are generally preferable to DO measurements made on a sample obtained with a bailer.
- DO measurements should be made both before and after purging except in a very permeable formation where drawdown during purging will be minimal. The lowest DO readings obtained will in most cases be the most representative of formation groundwater.
- Measure and mark the line of the bailer at a length a few inches shorter than the bottom of the well. Avoid lowering the bailer below this mark to avoid hitting the bottom of the well and re-suspending accumulated sediments.

- Lower and raise the bailer <u>slowly</u> in and out of the water column in the well to reduce the piston effect of the bailer, which can cause formation solids adjacent to the well screen to be suspended. Likewise, if using a pump to purge the well prior to sampling, slow down the rate of purging to minimize drawdown.
- Collect samples from the bailer carefully. Avoid splashing groundwater into sample bottles. If possible, fill sample bottles from the bottom of the bailer using a sampling adapter, instead of pouring from the top of the bailer.

# NO PURGING

# Description

The no purging sampling method involves no purging of the well or downhole probe measurement prior to sample collection. The method is based on the following assumptions:

- 1. Groundwater continuously flows through the screened portion of the well;
- 2. Water within the screened portion of the well is representative of formation groundwater; and
- 3. Only the well water above the screened interval is stagnant and not representative of formation groundwater.

Based on the assumptions, the objective in no purge sampling is to collect water from the screened portion of the well. If the water level in the well rises above the screened interval, the sample should be extracted from the screened interval at a rate that does not exceed the rate of groundwater flow into the well. In such a case, it is also preferable to extract the sample with a pump. Use of a bailer will cause mixing between the stagnant water above the well screen and the water within the screened interval. It is generally acknowledged that water in the well casing above the screened interval is not representative of the formation groundwater. The presence of stagnant water above the screened interval is not a concern for wells screened across the water table.

If the above procedures are followed, the no purging method is very similar to the micropurging method, with the only differences being the purge volume (which with micropurging typically involves only a fraction of a pore volume), the monitoring to ensure steady-state conditions in the extracted water, and monitoring/minimizing of drawdown within the well bore during sample collection.

#### Potential Effects of Sampling Method on Data Quality

If the pump intake is located in the screened interval and the rate of water extraction from the well is equal to or lower than the rate of groundwater flow through the well, the method should generally generate samples that are representative of formation groundwater.

However, there is some uncertainty as to whether the water initially present in the well is of the same geochemical composition as formation groundwater. In field studies at two different sites, evidence that water initially present in the wells (prior to purging) had higher DO than formation groundwater was consistently observed for wells located in geochemically reduced zones (CH2M HILL, 1997). This appears to be evidence of exchange between the headspace air and the water in the well bore. The impact of such exchange will be greatest in wells with the lowest rate of natural groundwater flow through the well (i.e., in low permeability formations), where the contact time between air and water in the well bore is longest. The impact of such exchange will be greatest for the parameters of ORP, DO, iron, and methane. Based on comparisons of sampling methods at a single well, iron and methane concentrations in water initially present in the well were approximately 60% and 70% lower, respectively, than concentrations determined through use of the micropurging sampling method.

The impact of this sampling method on geochemical indicator data may be exacerbated in wells with completely submerged screened intervals. Pumping rates greater than the

3-7

rate of natural groundwater flow through the well will result in blending of water from the screened portion of the well (where the pump intake is set) with stagnant water from upper portions of the well bore.

The no purging method, particularly if consistently applied across a site, will in many cases produce geochemical data of adequate representative quality if the data are to be used for qualitative purposes only. Based on comparisons of various methods for determining DO at two sites, downhole DO probe measurements in unpurged wells appear valid for DO trend analysis, as long as the measurements are made at a consistent depth (CH2M HILL, 1997).

A study is being conducted to compare TPH and BTEX results obtained using various sampling methods at petroleum hydrocarbon sites in California. A preliminary data review and statistical analysis indicate no systemic significant differences in the results when comparing pre-purged versus post-purged concentrations, regardless of purging method (WSPA, 1996).

The impact of sampling method on data quality will be most significant when the data are used in a quantitative manner (e.g., input parameters for numerical modeling). The bias introduced by the factors described here will generally be a conservative bias, in that the loss of iron and methane would result in an underestimation of the rate and/or magnitude of microbial activity (e.g., as determined from calculation of the expressed assimilative capacity). Based on comparison of sampling methods at a single well, iron and methane concentrations in water initially present in the well were approximately 50 percent lower than concentrations determined through use of the micropurging sampling method (CH2M HILL, 1997).

3-8

#### Advantages and Disadvantages

The advantages of the no purge sampling method are:

- This method requires less time than other sampling methods.
- This method produces a minimal amount of waste water requiring special handling and/or disposal.
- This method will typically be less expensive than other sampling methods.
- Based on limited available data, the method will, in many cases, produce geochemical data of adequate representative quality, particularly when 1) the data are to be used for qualitative purposes only (e.g., spatial trend analyses), and 2) the method is consistently applied across a site.
- This method may be the most practical method at very low permeability sites, where even very low rates of purging cause excessive drawdown and artificial aeration of the groundwater entering the well.

The disadvantages of the no purge sampling method are:

- There is some evidence that water initially present in a well is at a different geochemical condition than formation groundwater due to exchange between the headspace and water in the well.
- Impact on data quality will be more significant at sites with wells having completely submerged well screens and on low permeability sites where even low pumping rates will exceed the rate of natural groundwater flow through the well.
- The no purge sampling method goes against the conventional wisdom that purging is necessary to remove stagnant water in a well and ensure that the groundwater sample is representative of formation water. Regulatory agency acceptance of this sampling method may be an issue in some circumstances.

3-9

#### **Recommendations**

There is evidence that the no purge sampling method may generate samples with a different geochemistry than formation groundwater. However, based on limited available data, the method will, in many cases, produce geochemical data of adequate representative quality, particularly when 1) the data are to be used for qualitative purposes only (e.g., spatial trend analyses), and 2) the method is consistently applied across a site. To maximize the representative quality of samples collected using the no purge method, some field recommendations include:

- Measure drawdown during sampling to ensure that the rate of water extraction does not significantly exceed the rate of natural groundwater flow through the well.
- If dedicated pumps and tubing are used, the water in this equipment should be purged before groundwater samples are collected.
- It is important that all sample bottles are prepared ahead of time so that very little water is lost after sampling begins.
- It is important to place the intake of the sampling pump at consistent depths throughout the monitoring well network in order to obtain data usable for trend analysis. Evidence from the API study (CH2M HILL, 1997) indicates that a DO gradient exists in monitoring wells, based on downhole DO surveys.

# MICROPURGING METHOD

# Description

The micropurging method described in this section has been adapted from the protocols specified by EPA in its most recent draft groundwater sampling guidance (USEPA, 1992), and as described in a more recent EPA technical support document (Puls and Barcelona, 1996). The key components of the micropurging sampling method are intended to reduce the potential for artificial aeration and entrainment of particulates in the groundwater sample. This is accomplished by purging and sampling at a flow rate that matches the natural groundwater flow velocity, thereby avoiding excessive drawdown in the well. Micropurging sampling has also been called low-flow

purging, minimal drawdown sampling, micropurging, or millipurging. A detailed explanation of the micropurging sampling procedure is presented in Appendix A.

The main sampling equipment required for micropurging sampling includes:

- submersible pump and discharge tubing;
- field meters that measure DO, pH, ORP, specific conductance, etc.;
- a flow cell that will allow in-line measurements of the above parameters; and
- a water level indicator to monitor drawdown in the well during purging.

With this method, use of submersible pumps such as variable flow centrifugal pumps and bladder pumps may be advantageous. There is evidence of loss of volatile organics such as methane from the groundwater during extraction with peristaltic pumps. In a laboratory study of different sampling methods, use of a peristaltic pump resulted in the loss of approximately 40 percent of the methane present in solution, while only 13 percent of the methane was lost from solution with use of the variable flow centrifugal pump (CH2M HILL, 1997).

With the micropurging method, purging continues until the extracted groundwater exhibits steady-state measurements of key groundwater quality parameters (DO, pH, temperature, and ORP). When the extracted groundwater exhibits steady-state conditions for these parameters, it is assumed that the groundwater is representative of formation groundwater, and groundwater samples are then collected. Use of this method significantly reduces the purge volume compared to the traditional "three well volume" purge method. Using the micropurging method, steady-state conditions are typically achieved, and sample collection is then initiated, after purging only a fraction of a pore volume.

3-11
# Potential Effects of the Sampling Method on Data Quality

Artificial aeration of a groundwater sample can alter its geochemistry and affect measurements of geochemical indicators of intrinsic bioremediation, most notably ORP, DO, iron, and methane. The micropurging sampling method incorporates procedures that reduce the potential for artificial aeration of the sample. A laboratory and field comparison of sampling methods found that, relative to the conventional purge/bailer and no purging methods, the micropurging method generally provides groundwater samples having geochemical composition more representative of formation groundwater. Others have also concluded that micropurging sampling achieves more representative samples (Puls and McCarthy, 1993; USEPA, 1993; Puls and Paul, 1995).

A field study compared a minimal purging method similar to the micropurging method described here with a more conventional sampling method comprised of purging with a peristaltic pump and collecting the sample with a bailer (Payne *et al.*, 1995). The minimal purging method involved a slow purge rate (100 ml/min or less) to minimize drawdown, and a total purge volume typically in the 1 to 2 liter range. No significant variance was observed between the methods for most of the geochemical parameters of interest. However, the more conventional sampling method tended to increase DO in monitoring wells that had a DO of less than 1 mg/L as determined by the minimal purging method.

Even the micropurging method can cause some introduction of DO and loss of iron and methane, particularly when the permeability of the formation is so low that even very low rates of purging cause excessive drawdown. The bias introduced by the factors described here will generally be a conservative bias, since the loss of iron and methane would result in an underestimation of the rate and/or magnitude of microbial activity (e.g., as determined from calculation of the expressed assimilative capacity).

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## Advantages and Disadvantages

Advantages of the micropurging method are:

- This method has the ability to obtain a groundwater sample more representative of formation groundwater than other commonly employed sampling methods.
- This method reduces the cost of handling water generated during sampling by decreasing the purge volume (USEPA, 1993).

Disadvantages of the micropurging sampling method are:

- Some additional training may be necessary for field staff.
- This method requires some additional equipment.
- At sites with very low permeability, the slowest practical purge rates will still cause excessive lowering of the water table, resulting in artificial aeration of the sample.

A common perception is that the micropurging sampling method requires more time, and therefore the method is more expensive. Micropurging sampling is not necessarily more time-consuming, particularly at high permeability sites. Some regulations require purging of three-to-five well volumes of water. The well is considered purged (with micropurging sampling) when geochemical parameters stabilize (pH, conductivity, temperature, DO, etc.). At flow rates of approximately 1 L/min or less, stabilization of the critical parameters is typically achieved after pumping less than one-half of a well volume (Barcelona *et al.*, 1994). However, well purging will typically take longer at low permeability sites, where very low purge rates are required to prevent excessive drawdown.

# **Recommendations**

Recommendations that will facilitate implementation of the micropurging method and improve the representative quality of data collected with this method are included in the standard operating procedure presented in Appendix A.

3-13

### USE OF INERT GAS IN THE WELL BORE

#### Description

This method is a variant of other sampling methods in which an inert gas atmosphere is maintained in the headspace of the well during well purging and sampling. This method is based on the recognition that the formation groundwater is often in a state of dramatic nonequilibrium with the atmosphere, and that the presence of oxygen in the well headspace can result in artificial aeration of the groundwater both prior to and during well purging and sampling. Argon is used because it is heavier than air and will "sit" in the well at the air/water interface. This method has been used to minimize potential changes in sample geochemistry induced by artificial aeration.

As described by Borden *et al.* (1995), the inert gas method involves filling monitoring wells with argon gas before purging at least 5 well volumes of water using a submersible pump. Groundwater is then pumped through tubing to the surface and collected directly into sample bottles.

### Potential Effects of Sampling Method on Data Quality

The inert gas method should permit the least artificial aeration of the groundwater and will generally introduce the least bias into the geochemical data collected to support evaluation of intrinsic bioremediation.

#### Advantages and Disadvantages

The advantages of the inert gas method are:

- The inert gas method should produce the most representative data of the methods evaluated.
- With the inert gas in the well bore, limiting purge rates to minimize well drawdown is not as critical. This method may be more efficient than the micropurging method at low permeability sites, because higher purge rates can be employed.

3-14

The inert gas method may be the only method that eliminates significant artificial aeration of groundwater samples in very low permeability formations, where even the lowest practical well purging rates will result in excessive drawdown.

The disadvantages of the inert gas method are:

- This method is generally the most complex of the methods described herein.
- This method requires additional equipment (bottled gas, gauges, tubing, etc.)
- This method will often be the most expensive of the methods (with the possible exception of low permeability sites) discussed here, considering both time and equipment required.

# **Recommendations**

The inert gas method may be most appropriate in instances when the goal is to obtain the highest quality geochemical data, particularly on low permeability sites.

The following practices will facilitate use of this method:

- Use a high grade argon or other inert gas. Some grades have a significant amount of oxygen mixed with the inert gas. The oxygen contained in lower grade inert gases have the potential of aerating the groundwater sample.
- Before purging, lower the feed tube of inert gas below the water level in the well so the inert gas displaces all the oxygen in the well bore. If the feed tube is placed above the water surface, mixing with oxygen in the atmosphere may occur.
- After the air initially in the well has been displaced, raise the feed tube to just above the water level in the well. Do not keep the argon feed tube below the water level. Bubbling argon through the groundwater will strip other dissolved gases (e.g., DO, methane, etc.) from the groundwater.

3-15

• To ensure that inert gas is filling the well properly, lower a dissolved oxygen probe to one foot above the water level in the well. When the probe reads zero, inert gas has replaced the oxygen in the well.

# SUMMARY

In this section, four groundwater sampling methods were discussed. A comparison of these sampling methods is summarized in Table 3-2. The methods vary in terms of data quality, complexity, level of effort, and cost. Any of the methods will generally produce geochemical data of adequate representative quality, particularly when both of the following contitions apply:

- 1. The data are used for qualitative purposes only (e.g., spatial trend analyses); and
- 2. The method is consistently applied across a site.

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Method	Data Quality	Level of Effort	Complexity	Cost
Micropurging	Generally yields more representative and consistent data than conventional purge/bailer method, particularly in lower permeability formations where fast purging results in excessive drawdown.	Increased level of effort compared to fast purge/bailer method. May be offset by smaller purge volumes required. Dedicated pumps also decrease the level of effort. On very low permeability sites, the level of effort increases significantly.	More complex than conventional purge/bailer method. More equipment is required (e.g. a flow cell, a DO meter, a submersible pump, etc.) May also require some additional training of technicians.	Generally requires more equipment and time than conventional purge/bailer approach. These factors can be offset by decreased purging and purge water disposal requirements. Approximate cost <sup>a</sup> = \$200.00 per well.
Conventional Purge/Bailer	Data generated will generally be adequate for trend analyses. However, increased aeration and turbidity of groundwater sample may significantly affect DO, iron, and methane data.	Generally a minimal level of effort. Time required to purge the required 3-to-5 well volumes and purge water disposal requirements are important considerations.	Generally requires the least amount of equipment and training of technicians.	Less expensive than other methods given minimal equipment and training requirements. Approximate cost <sup>*</sup> = \$100.00 per well.
No Purge	Generally yield data adequate for qualitative (trend) analysis. DO, iron, and methane data may not be representative of formation groundwater.	Equipment requirements similar to the micropurging method. Does not require purging wells before sampling.	Slightly less complex than the micropurging method because it eliminates the monitoring required to determine completion of well purging.	Least costly because of reduced well purging and purge water disposal requirements. Approximate cost <sup>*</sup> = \$60.00 per well.
Inert Gas in the Well Bore	Will yield the most representative geochemcial data, particularly at low permeability sites.	This method requires the most equipment. May be faster than micropurging method on low permeability sites (excessive drawdown not a concern).	Requires the most equipment and additional training for technicians.	Most costly due to increased equipment costs and the required additional training of technicians. Approximate cost <sup>*</sup> = \$300.00 per well.
Cost is an estimat	e prepared solely for purpose	es of judging relative sampling costs.	Actual costs will depend on many fac	tors including number of wells,

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3-17

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depth to water, purge water disposal costs, etc.

Great care should be exercised in selecting a sampling method when one or more of the following conditions apply:

- 1. The data are to be used quantitatively (e.g., input parameters for numerical fate and transport modeling); or
- 2. Aerobic respiration, iron reduction, and methanogenesis are the critical biodegradation processes (these are the parameters most susceptible to changes induced by aeration); or
- 3. The site has a low permeability.

The micropurging sampling method generally provides more representative data than the conventional purge/bailer and no purge methods, and under any one of the conditions listed above, may be a more appropriate sampling method. At sites with very low permeability, where even the lowest practical purge rates may cause excessive drawdown, the inert gas method will produce the highest quality data. However, the micropurging and inert gas methods are generally more complex and expensive than the conventional purge/bailer and no purge methods, depending largely on purge water disposal issues.

# Section 4

## MEASUREMENTS AND SAMPLE ANALYSES

Analysis of groundwater samples for intrinsic remediation parameters is often accomplished with a combination of field and laboratory test methods. Dependable and easy field tests exist and are typically used for some parameters such as DO and pH. For other parameters (nitrate, sulfate, etc.), commercial laboratory analysis is generally preferred because it reduces the scope of the field effort, is relatively inexpensive, allows for a higher level of QA/QC, and therefore, generates data of a known quality.

On the other hand, greater use of field methods offers a number of potential benefits. Some parameters of interest are not stable, and holding times associated with sample shipment and storage could potentially alter results. With reliable field methods or test kits this potential problem can be minimized. Another possible advantage of field tests is that overall project QA/QC can actually be increased by having an experienced analytical chemist in the field performing tests and contributing to the sampling effort. However, the true value of field tests lies in the ability of the investigators to exercise judgment and make decisions in a very timely manner. Field results can be compared to expected site geochemical patterns, allowing for identification of probable data outliers and the potential need for re-sampling and/or re-analysis to provide a complete and representative data set.

The advantages and disadvantages of field methods and analytical laboratory services are summarized in Table 4-1. More detailed information on field methods versus commercial laboratory methods is presented in subsequent parts of this section, dealing with individual geochemical indicator parameters. Selection of a field or analytical laboratory should be based on individual project needs and constraints. Table 4-1. Comparison of Commerical Laboratory Versus Field Methods

Option	Advantages	Disadvantages
Commercial L'aboratory	• Ability to select a certified, high quality lab	<ul> <li>Normal data turn around is 3-5 weeks</li> </ul>
Laborator	• Lab has established QA/QC methods and experienced staff to produce data of a consistent and known quality	<ul> <li>Requires careful field sampling and laboratory planning to meet the short holding time on some samples</li> </ul>
	• If prearranged, a potential to negotiate fast turn-around data and cost-effective pricing	
	<ul> <li>Reduces complexity of field effort</li> </ul>	
Field Methods	• Can be cost-effective for a large number of samples	• Most field methods, based on color development procedures,
	<ul> <li>Fast turn-around reduces potential constituent loss during sample storage</li> </ul>	can be attected by intertering substances commonly tound at petroleum hydrocarbon sites. (e.g. dissolved iron can bias nitrate results)
	<ul> <li>Allows "real-time" data evaluation</li> </ul>	<ul> <li>Adds to complexity of the field effort</li> </ul>
	• Improves prospects of obtaining complete and representative data set	<ul> <li>Quality of data is dependent on the skill of the analyst</li> <li>Difficult to generate a defined quality of data</li> </ul>
		<ul> <li>Field analysis of methane and carbon dioxide is usually not practical since those measurements are conducted by a technique using gas chromatography (GC), and field GC is usually not cost-effective</li> </ul>

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4-2

The remainder of this section provides information on several key geochemical parameters for evaluating intrinsic bioremediation. The geochemical indicators covered are:

- Dissolved oxygen;
- Nitrate;
- Iron;
- Manganese;
- Sulfate;
- Methane;
- Carbon Dioxide;
- Oxidation-Reduction Potential (ORP); and
- Others of potential interest.

For each of these parameters, the purpose of measurement is discussed with a brief description of available test methods, important considerations in method selection, and use of the results. This information is summarized in Table 4-2.

Test procedures used to measure geochemical parameters should be selected to meet specific project needs and generate data of an appropriate quality to match project data use (e.g., field screening, regulatory reports).

The test method recommendations presented here were developed based on *typical* project site conditions and the objective of generating data of superior quality. In any given situation, project budgets and specific use of the data may warrant the selection of alternate methods. The referenced methods are from *Standard Methods for the Examination of Water and Wastewater* (Greenberg *et al.*, 1992). Equivalent methods are available from other sources such as ASTM and various EPA publications.

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				Sample A	\nalysis			
Parameter	Container	Preservation	Holding Time	Field or Lab*	Method Reference	Method Description	Typical Reporting Limits	Discussion
Dissolved Oxygen	Use flow cell or as down hole measurements	not applicable	not applicable	Field	SM4500-O-G EP A360.1	Membrane Electrode Method	0.6 mg/L	Most interfering substances experienced with other methods have little or no effect. Polarographic probe requires constant flow or movement of probe.
				Field	SM4500-O-C EPA 360.2	Winkler Azide Modification	0.2 mg/L	Many interferences, including ferrous iron above 1 mg/L and atmospheric oxygen. Requires field titration.
				Field	HACH, EM Science or Equivalent	Winkler Azide HRDO Indigo Carmine	Varies	Various interferences, including reduced compounds. Requires field spectrophotomer or colorimeter.
	VOA Vial	4°C	14 days**	Lab	RS Kerr-175	Headspace equilibration; GC- TCD	0.5 mg/L	Very difficult to prevent or limit atmospheric contamination of sample (sampling, storage, and analysis).
Vitrate	Plastic/Glass	Field Filter 4°C	48 hours	Lab	SM 4110 EPA 300	Ion Chromotography	0.2 mg/L	Very high concentrations of other ions can increase reporting limit. Lab pretreatment for organics removal may be required.
	Plastic/Glass	Field Filter 4°C	48 hours	Lab or Field	SM 4500-NO3, EPA 353.1, 353.3	Cadmium, titanous chloride, Hydrazine reduction. Field Kits available from HACH, EM Science, or equivalent.	0.2 mg/L	Requires nitrite compensation. Multiple interferences including ferric iron, chloride, oil and grease, chlorine. Field studies have demonstrated significant matrix interferences at hydrocarbon sites. Requires spectrophotometer.
	Plastic/Glass	Field Filter 4°C	48 hours	Lab or Field	SM 4500-NO3-D. HACH or equivalent.	Nitrate ion specific electrode.	Varies	Several interferences at varying concentrations, including: chloride, carbonate, bicarbonate, nitrite, sulfide, and organic acids. Sensitive to pH, use of buffer required.

Table 4-2. Methods for Key Geochemical Parameters

		Discussion	al iron analysis of filtered sample resents soluble ferrous iron.	al iron analysis of filtered sample resents soluble ferrous iron. Typically re expensive than ICP. Susceptible to rix interferences.	al iron analysis of filtered sample resents soluble ferrous iron. Requires estion by boiling sample. Color or anic matter requires drying, ashing, and dissolving steps. Color development is dependent. uires spectrophotometer or colorimeter.	l iron analysis of filtered sample esents soluble ferrous iron. Digestion gested if precipitate present. Color elopment is pH dependent. Requires trophotometer or colorimeter.	l iron analysis of filtered sample esents soluble ferrous iron. Iron oxides ure digestion. Excess iron will inhibit r development. Extreme pH requires strment. Requires spectrophotometer or rimeter.
		Typical Reporting Limits	0.04 mg/L Tot rep	0.12 mg/L Tot rep mon	0.01 mg/L Tot repuise orgi PH PH	data not Tot available repr sugg dev	data not Tota available repr requ colo adju adju
		Method Description	Inductively Coupled Plasma (ICP) with acid digestion	Hame Atomic Absorption Spectrometry (AA) with acid digestion	Phenanthroline Method; Color Development	Ferrozine Method; Color Development	Ferrover Method; Color Development
ochemical Parameters	nalysis	Method Reference	SM 3120 B EPA 200.7	SM 3111 B BPA 236.1	SM 3500 Fe-D	HACH Ferrozine	HACH Ferrover
	Sample A	Field or Lab*	Lab	Lab	Lab or Field	Lab or Field	Lab or Field
		Holding Time	6 months	6 months	48 hours**	6 months	6 months
r Key Geo		Preservation	Field Filter HNO <sub>3</sub> pH<2	Field Filter HNO <sub>s</sub> pH⊲2	Field Filter 4°C	Field Filter HNO₃pH⊄	Field Filter HNO, pH⊲2
Methods fo		Container	Plastic/Glass	Plastic/Glass	Plastic/Glass	Plastic/Glass	Plastic/Glass
Table 4-2.		Parameter	Ferrous Iron				

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		Discussion	Total iron analysis of filtered sample represents soluble ferrous iron. Color development is pH dependent. Several metal elements interfere at low ppm levels to inhibit color development or create precipitate.	Requires dilution of sample to below 3 mg/l. Ferrous iron converts to ferric iron (not measured by test) within minutes. Requires spectrophotometer or colorimeter tubes.	Total manganese analysis of filtered sample represents soluble manganese.	Total manganese analysis of filtered sample represents soluble Mn <sup>4+</sup> Typically more expensive than ICP. Susceptible to matrix interferences.	Total manganese analysis of filtered sample represents soluble Mn <sup>4</sup> . Digestion required. Requires spectrophotometer or nessler tubes.	Very high concentrations of other ions can increase reporting limit. Lab pretreatment for organics removal may be required.	Large quantities of organic or solids material may interfere.	Also provides oxygen and methane data.
		Typical Reporting Limits	data not available	data not available	0.04 mg/L	0.12 mg/L	data not available	0.2 mg/L	1 mg/L	0.5 mg/L
		Method Description	TPTZ Method; Color Development	Ferrous Iron	Inductively Coupled Plasma (ICP with acid digestion)	Hame Atomic Absorption Spectometry (AA) with acid digestion	PAN Method; Color Development	ion Chromotography	Turbidimetric Method	Headspace equilibrium; GC- ICD
ters	nalysis	Method Reference	HACH TPTZ	HACH Phenanthroline	SM 3500-MnC EPA 200.7	SM 3500-MnB EPA 243.1	НАСН	SM 4110 EPA 300	SM 4500-SO <sub>4</sub> -E. HACH Sulfaver EPA 375.4	RS Kerr-175
r Key Geochemical Parame Samule A	Sample A	Field or Lab*	Lab or Field	Field	Lab	Lab	Lab or Field	Lab	Lab or Field	Lab
		Holding Time	6 months	mmediate i minutes**)	6 months	6 months	6 months	28 days	28 days	ASAP
		Preservation	Field Filter HNO, pH⊲2	Requires i analysis (<5	Field Filter HNO <sub>3</sub> PH<2	Field Filter HNO <sub>3</sub> PH 2	Field Filter HNO,pHC	Field Filter 4°C	Field Filter 4°C	4°C
Methods for		Container	Plastic/Glass	Plastic/Glass	Plastic/Glass	Plastic/Glass	Plastic/Glass	Plastic/ Glass	Plastic/Glass	VOA
Table 4-2. 1		Parameter	Ferrous Iron (Continued)	· · · · · ·	Manganese	<b>a</b> . <del></del>	к ?	Sulfate		Carbon Dioxide

4-6

. Methods for Key Geochemical Parameters	Sample Analysis	Container     Preservation     Holding     Field or     Method Reference     Method Description     Typical     Discussion       Time     Lab*     Reporting     Reporting     Limits	VOA 4°C ASAP Lab RS Kerr-175 Headspace equilibrium; GC- 0.125 mg/L Also provides oxygen and carbon dioxide TCD TCD data. Detection limit generally acceptable.	Headspace equilibrium; GC-FID     0.0005 mg/L     Superior sensitivity. Sensitive to all carbon       containing compounds, creating possible	Plastic/Glass       4°C       14 days       Lab or       SM 2320-B       Titration Method       1 mg/L       Use PH probe or indicator. Phenolphtalein         Field       EPA310.1       alkalinity end point is 8.3, total alkalinity       alkalinity end point is 8.3, total alkalinity         end point is 4.5. Oily matter may coat pH       end point is 4.5. Oily matter may coat pH       electrode, creating interference to test.	Ial Use flow cell or     Field     SM 2580-B     Electrometric probe     data not     ORP reading is converted to Eh. Use       as down hole     as down hole     available     standard redox solutions to calibrate       measurement     available     electrode system at the expected       measurement     electrode system at the expected	alytical labs can be set up in the field, this note is based on the budget constraints of a "typical" project.
4-2. Methods		neter Container	VOA		ty Plastic/Glass	otential Use flow cell as down hole measurement	gh analytical labs can

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## DISSOLVED OXYGEN (DO)

## Purpose of DO Measurement

Dissolved oxygen is a critical parameter for evaluating intrinsic remediation. During aerobic biodegradation, dissolved oxygen is consumed. Oxygen is the most thermodynamically favored electron acceptor in the biodegradation of organic compounds. Therefore, it is one of the first parameters to be affected by enhanced biological activity.

If DO is present in groundwater at a concentration above approximately 1 to 2 mg/L, aerobic biodegradation can occur (McAllister and Chiang, 1994). At DO concentrations below 0.5 to 1 mg/L, biodegradation of subsurface petroleum hydrocarbons is likely to be dominated by anaerobic processes. In anaerobic zones of petroleum hydrocarbon plumes, DO will also often be reduced to near-zero concentrations through abiotic processes (e.g., oxidation of ferrous iron generated in microbially mediated reduction of ferric iron). However, accurate DO measurements become increasingly difficult at  $O_2$  concentrations below 1 mg/L.

Evaluation of trends in DO concentrations across a site can be used as evidence that aerobic biodegradation of petroleum hydrocarbons is occurring. In more quantitative evaluations, the distribution of DO concentrations across a site can be stoichiometrically used to estimate the rate and/or mass of petroleum hydrocarbon biodegraded through aerobic respiration.

# Methods of DO Measurement

The three most commonly used techniques for DO measurements for intrinsic bioremediation investigations are the DO probe, the Winkler (iodometric) method, and the GC headspace method.

4-8

<u>Electrometric Method-Membrane Electrode (DO Probe</u>). The membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane and generally provides an excellent method for DO analysis in a variety of waters.

Oxygen-sensitive membrane electrodes are available as a polarographic or galvanic type. Each is composed of two solid metal electrodes in contact with a supporting electrolyte separated from the test sample by a selective membrane. The basic difference between the galvanic and polarographic systems is that the polarographic probe consumes oxygen during the measurement process and requires a constant flow of sample across the membrane surface. The polarographic probe is the most commonly used field DO probe, and is available from a number of manufacturers. The advantage of the galvanic probe is that it does not consume oxygen. The galvanic probes are more expensive and are not specifically designed for field use.

The use of the membrane electrode is recommended by Greenberg, *et al.* (1992) when conditions do not favor the use of the Winkler method, and/or when modification of the basic Winkler method is required to overcome a serious interference.

<u>Winkler Method</u>. The Winkler method is a titrimetric procedure based on the oxidizing property of DO. This method is also referred to as the Iodometric method. Variants of this method, including field kits, are often referred to as modified Winkler methods. The Winkler method is a precise and reliable method for evaluating clean water samples. However, the iodometric method is affected by several interferences that may be present at petroleum hydrocarbon sites. These interferences include the following (Greenberg *et al.*, 1992):

- ferrous iron >1 ppm;
- ferric iron >5 ppm;
- organic matter;
- biological solids; and
- highly colored waters.

4-9

There are several modifications to the iodometric method to compensate for these interferences. Unfortunately, no single modification will compensate for adverse affects of multiple interferences, a condition commonly found at petroleum hydrocarbon sites.

Because the DO concentration in water samples is unstable, rapid analysis in the field is required. Field analysis involves collecting the sample in a stoppered bottle, such as a biochemical oxygen demand (BOD) bottle, and immediate addition of reagents that chemically "fix" any oxygen present, followed by a titration step.

<u>GC Headspace Method.</u> This is a method that was established by the EPA R.S. Kerr Environmental Research Laboratory (Kampbell et al., 1989). Few analytical laboratories routinely perform the method. The analysis is performed using a headspace equilibrium technique and subsequent analysis using gas chromatography with a thermal conductivity detection (TCD) system. This method will also provide data on other geochemical parameters of interest, most notably methane and carbon dioxide. Atmospheric oxygen can contaminate the sample during sample collection, storage, and analysis. Because the maximum concentration of oxygen in natural water samples reflects equilibrium with the atmosphere, and groundwater samples are at or below this maximum concentration, atmospheric contamination causes dissolved oxygen results to be biased higher than the actual concentrations. Methods have been developed to reduce the potential for sample contamination, such as the use of a butyl-rubber lined septum for the sample vial. However, eliminating all of the potential method interferences requires great care, superior technique, and well trained samplers and lab analysts. Given the challenges with this test method, the developers recommend the use of other DO methods that are more cost-effective. The GC headspace method may be most appropriate when data for other method analytes (carbon dioxide, methane) are desired.

## **Discussion**

The membrane electrode is generally the preferred technique for measuring DO concentrations at the time of collection. To produce data of an optimum quality, several precautions must be observed when using the standard polarographic DO probe. These procedures, and limitations for the use of data, include the following:

- Due to background current and method sensitivity, the DO probe does not generally give accurate DO readings at concentrations below 1 mg/L.
- Because the probe consumes oxygen, the membrane electrode method requires a steady flow across the membrane surface for an accurate measurement. A flow-through cell should be used when possible. When performing downhole measurements, the probe should be moved about in a very slow up-and-down motion, to provide flow across the membrane while minimizing disturbance of the water column in the well.
- The probe response should be frequently checked using the manufacturer's recommended procedure. Frequent response checks are needed due to the potential for hydrocarbon contaminant coating of the membrane surface. Reducing agents (such as H<sub>2</sub>S) tend to lower cell sensitivity and responsiveness. A probe that allows for two point calibration (air saturated and zero oxygen), will provide or give more accurate readings of the low DO conditions at hydrocarbon sites. Sodium sulfite, an oxygen scavenger, can be used to perform the zero oxygen calibration.
- Periodic cross-check of the membrane probe using iodometric method field kits is often useful.

# NITRATE (NO<sub>3</sub>)

# Purpose of Nitrate Measurement

Once DO has been depleted in a zone of microbiological activity, nitrate (if present) is used as an electron acceptor in the anaerobic biodegradation process of denitrification. After DO, nitrate is the most thermodynamically favored electron acceptor. Evaluating the trends in nitrate concentrations across a site is a means to determine if anaerobic biodegradation of petroleum hydrocarbons is occurring. In quantitative evaluations of

4-11

biodegradation, a decrease of nitrate across a site can be stoichiometrically used to estimate the rate and/or mass of petroleum hydrocarbon degraded through denitrification.

# Methods of Nitrate Measurement

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Common analytical techniques for nitrate analysis are ion chromatography, colorimetry, and the nitrate ion-specific electrode.

<u>Ion Chromatography</u>. Ion chromatography is a laboratory method based on ion separation and detection. This is the most accurate and precise of the commonly employed analytical methods for nitrate. It is not susceptible to the matrix interference problems that plague colorimetric techniques. Ion chromatography has the added advantage of providing data on other anions, such as nitrite, sulfate, and phosphate, in a single analysis.

<u>Colorimetry</u>. There are several color development methods (cadmium reduction, titanous chloride reduction, hydrazine reduction) for nitrate analysis that can be used in either a laboratory or field setting. Field test kits for nitrate analysis are based on these colorimetric methods. There are several sample matrix conditions typical to petroleum hydrocarbon sites (oily material, ferric iron, color) that can interfere with the colorimetric test.

<u>Electrode</u>. The nitrate  $(NO_3^-)$  electrode is susceptible to several interferences. Because the electrode responds to  $NO_3^-$  activity rather than concentration, the ionic strength of the test solution must be held constant to obtain accurate results. The technique is not generally applicable to field use.

## **Discussion**

Commercial laboratory analysis by ion chromatography is generally the preferred method. Considerable variations between nitrate field kits and laboratory analysis with ion chromatography were noted (Payne *et al.*, 1995). In addition, QA/QC testing performed during a field study of colorimetry-based nitrate test kits indicated matrix interferences to the colorimetric nitrate measurement, and field chemists have noted interferences that caused rejection of some field data (CH2M HILL, 1997).

The holding time requirement for nitrate is 48 hours, which necessitates careful coordination with the laboratory and scheduling shipment of the samples. With rapid analysis of nitrate samples and proper sample preservation during shipment (ice to at least 4°C), potential loss of nitrate before analysis due to ongoing microbial activity should be minimal.

# FERROUS IRON (Fe<sup>2+</sup>)

# Purpose of Ferrous Iron Measurement

Under anaerobic conditions, ferric iron may be used as an electron acceptor in petroleum hydrocarbon biodegradation. In this process, ferric iron  $(Fe^{3+})$  is reduced to the ferrous  $(Fe^{2+})$  form. Evaluating the trends of increasing ferrous iron concentrations across a site can be used as evidence that anaerobic biodegradation is occurring. Owing to its insoluble nature, the use of ferric iron as an indicator of biodegradation is problematic and is not recommended. In quantitative evaluations of biodegradation, the distribution of ferrous iron across a site can be stoichiometrically used to estimate the degredation rate and/or degraded mass of petroleum hydrocarbon.

## Methods of Ferrous Iron Measurement

There are two general approaches available for determining differences in ferrous iron concentration across a site. These two approaches are: 1) immediate field filtering of samples to remove insoluble ferric iron and subsequent laboratory analysis for total iron, and 2) field methods for ferrous iron analysis.

4-13

Total Iron in Field-Filtered Samples. This protocol is based on the assumption that concentrations of aqueous phase ferric iron are very low across the site. In the pH range of 6 to 8, ferric iron concentrations are typically less than  $1 \mu g/L$  (Snoeyink and Jenkins, 1980). Given the insolubility of ferric iron, it is assumed that the differences across the site in the concentration of soluble iron (determined by total iron analyses of field-filtered samples) are essentially due to differences in ferrous iron concentration. For turbid groundwater, field filtering is essential to eliminate ferric iron precipitates that would contribute to total iron concentrations determined after sample digestion. Given the potential for rapid conversion of ferrous iron to insoluble ferric iron, the filtering is best accomplished with an in-line filter during sample collection.

The techniques most commonly employed by analytical laboratories for iron analysis are:

- Inductively coupled plasma (ICP). ICP analysis is generally the preferred method for total iron because of its low cost and lack of potential matrix interferences in petroleum hydrocarbon site samples.
- Atomic absorption by flame atomization (AA-F). AA-F analysis for total iron is more susceptible to matrix interferences and provides no advantage in data quality over the ICP technique. If the AA-F technique is used because of instrument availability or other considerations, the *Method of Additions* quality control evaluation should be performed to evaluate matrix interference.

<u>Field Analysis for Ferrous Iron</u>. Field test kits for ferrous iron typically employ colorimetry methods that measure only soluble ferrous iron. Hence, a potentially significant limitation of field analysis with ferrous iron test kits is the conversion of ferrous iron to insoluble ferric iron. This conversion has been shown to occur within minutes. Sunlight also causes instability of ferrous iron. Therefore, for samples exposed to the atmosphere, ferrous iron analysis must be conducted immediately after sample collection. There are also field kits that use colorimetry methods for total iron. As previously discussed, analysis for total iron will address the problems associated with conversion of iron from the ferrous to ferric oxidation states. The use of test kits to measure total iron is a viable alternative in cases where immediate in-field measurement of ferrous iron is impractical.

4-14

### **Discussion**

Filtering a sample in the field and analyzing the sample for total iron at an analytical laboratory using ICP is relatively simple and cost-effective. It may be the most convenient and cost-effective method for generating quality data on the distribution of ferrous iron. This method largely eliminates concerns regarding the instability of ferrous iron in samples exposed to sunlight and the atmosphere. Nonetheless, studies comparing methods for determining geochemical indicators of intrinsic bioremediation indicate a fairly good correlation between iron concentrations determined by field kits and laboratory analysis (Payne *et al.*, 1995; CH2M HILL, 1997). These studies suggest that the iron field kits are a viable alternative to analytical laboratory analysis. However, field sampling technique may affect the accuracy of the iron data.

## MANGANESE

The role of manganese in intrinsic bioremediation is very similar to that of iron. Relatively insoluble, more highly oxidized forms of manganese (commonly present as manganese dioxide, Mn<sup>4+</sup>) are transformed through anaerobic biodegradation of petroleum hydrocarbons into a more reduced, soluble form (Mn<sup>+2</sup>). The analytical options available for manganese are essentially the same as those for iron. The appropriate method for manganese analysis is the determination of total manganese of field-filtered samples at a commercial laboratory or with a field test kit. Field test kits are available for total manganese only; there is no field kit for Mn<sup>+2</sup>.

## SULFATE $(SO_4^2)$

### Purpose of Sulfate Measurement

Under highly reduced conditions, typically after available DO, nitrate, and ferric iron have been microbially depleted, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process transforms sulfate to sulfide and is termed sulfidogenesis. Evaluating the decrease in sulfate concentrations across a site can be used as evidence that anaerobic biodegradation of petroleum hydrocarbons is occurring. In quantitative

4-15

evaluations of biodegradation, a decrease of of sulfate across a site can be stoichiometrically used to estimate the rate and/or mass of petroleum hydrocarbon degraded through sulfidogenesis.

# Methods of Sulfate Measurement

Ion chromatography and colorimetry are common analytical techniques for the analysis of sulfate.

<u>Ion Chromatography</u>. Ion chromatography, the most accurate and precise of the commonly employed analytical methods for sulfate, is a laboratory method based on ion separation and detection. It is not susceptible to the matrix interference problems that plague colorimetry or turbidimetric techniques. Ion chromatography has the added advantage of providing data on other anions such as nitrite, nitrate, and phosphate in a single analysis.

<u>Colorimetry</u>. The colorimetric test for sulfate analysis can be used in either a laboratory or field setting. There are several sample matrix conditions typical to petroleum hydrocarbon sites (oily material, ferric iron, color) that can interfere with the colorimetric test.

# **Discussion**

Commercial laboratory analysis by ion chromatography is generally the preferred method. However, in studies comparing sulfate analytical methods, good correlation has generally been observed between spectrophotometric field methods and laboratory analysis by ion chromatography (Payne *et al.*, 1995; CH2M HILL, 1997). These studies suggest that the field spectrophotometric method will generally be a viable alternative to commercial laboratory analysis.

# METHANE (CH<sub>4</sub>)

### Purpose of Methane Measurement

Methanogens are one of the most common classes of naturally-occurring microorganisms. Methanogens are anaerobic organisms that utilize simple organic compounds or hydrogen (produced as byproducts of other anaerobic processes) and nicotinamide adenine dinucleotide phosphate (NADP) to produce methane and carbon dioxide (Cookson, 1995). NADP is an electron (and hydrogen) carrier that reacts with cellular enzymes in anabolic (cell growth) reactions of all kinds. As a result of this reaction and the prevalent nature of methanogens, anaerobic respiration almost always produces methane as a reaction product. Methane is usually not a significant naturally-occurring constituent of groundwater. Therefore, elevated methane concentrations in the contaminated plume compared to upgradient monitoring points can be used as an indicator of anaerobic respiration. In quantitative evaluations, the increase in methane across a site can be stoichiometrically used to estimate the rate and/or mass of petroleum hydrocarbon (or byproduct) biodegraded through methanogenesis.

### Methods of Methane Measurement

Methane analyses in water are not routine for most commercial laboratories. There is basically only one approach for methane analysis, the GC headspace technique. This method offers two options for final detection of methane.

<u>Thermal Conductivity Detector (TCD)</u>. The TCD is advantageous due to its ability to detect methane and other gases, including carbon dioxide and oxygen. Unfortunately, the TCD method does not have as low a detection limit as the FID method (see Table 4-3). However, the typical TCD detection limit for methane is low enough to detect concentrations of methane that will be significant in terms of intrinsic bioremediation. For example, if methane concentrations are below the typical 0.125 mg/L detection limit for TCD, then methanogenesis will not usually be a significant biodegradation process relative to other biodegradation pathways.

4-17

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Copyright American Petroleum Institute Provided by IHS under license with API No reproduction or networking permitted without license from IHS <u>Flame Ionization Detector (FID)</u>. The FID is advantageous due to its lower limits of detection. Its disadvantage is a universal sensitivity to all carbon-containing compounds which can lead to a *forest* of chromatographic peaks with matrix interference, the need for special GC run programs, and care in the reporting of GC results. A summary of the compounds each detector can evaluate, along with typical detection limits for a GC-FID and GC with TCD operated in the high sensitivity mode, are presented in Table 4-3.

	Dete	Detector				
Compound	FID	TCD				
Methane	0.0005	0.125				
Carbon Dioxide		0.5				
Oxygen		0.5				

Table 4-3. Gas Analysis by Headspace Equilibrium, mg/L

### **Discussion**

Samples should be collected in 40-ml VOA vials and iced or refrigerated at 4 degrees Celsius to limit biological activity before analysis. Samples should be analyzed as soon as possible. An alternate preservation method is to preserve with sulfuric acid to pH 2, although concerns have been expressed about potential gas formation upon acidification and subsequent gas loss. If this method is used, samples should be examined for gas formation, and samples should be capped as soon as possible following acidification. A laboratory experienced with the headspace equilibrium procedure should be selected. Sampling technique may affect methane data (see Section 3).

# CARBON DIOXIDE $(CO_2)$

## Purpose of CO, Measurement

Biodegradation of petroleum hydrocarbons, as a result of both aerobic and anaerobic respiration processes, yields carbon dioxide. An accurate determination of the  $CO_2$  produced through intrinsic bioremediation of petroleum hydrocarbons is complicated by the carbonate-buffering system in groundwater (as measured by alkalinity), which can serve as both a source and sink of  $CO_2$ . In addition,  $CO_2$  can also be consumed during hydrocarbon biodegradation through the process of methanogenesis. Nonetheless, in many cases, spatial distribution of  $CO_2$  across a site can be used as a geochemical indicator of intrinsic bioremediation.

#### Methods of CO, Measurement

The only practical method for CO<sub>2</sub> measurement is analysis in a commercial laboratory using the GC headspace technique with the TCD detector previously discussed under Methods of Methane Measurements.

#### **Discussion**

Like methane,  $CO_2$  samples should be collected in 40-ml VOA vials iced or refrigerated at 4 degrees Celsius to retard biological activity until analysis, and analyzed as soon as possible. Selecting a laboratory experienced with micropurging sampling is suggested with the headspace equilbrium procedure.

#### ALKALINITY

### Purpose of Alkalinity Measurement

The total alkalinity of a groundwater system is indicative of water's capacity to neutralize acid. Alkalinity in natural waters results primarily from the presence of hydroxides, carbonates, and constituents such as organic acids and ammonia. In groundwater, these compounds result from the dissolution of rock (especially carbonate rocks), the transfer of  $CO_2$  from the atmosphere, and respiration of microorganisms. An increase in alkalinity across a contaminant plume is potentially an indicator of

4-19

bioactivity. This is due to the conversion of organic carbon into carbon dioxide and the possible increased dissolution of carbonate compounds due to reactions between soil minerals and the carbonic acid ( $CO_2$ ) generated during hydrocarbon biodegradation. Additionally, alkalinity is important for the maintenance of groundwater pH because it buffers the groundwater system against acids generated through both aerobic and anaerobic biodegradation processes.

# Methods of Alkalinity Measurement

Alkalinity is determined by a titration to specified end points. The titration can be performed in the field or laboratory using a burette or automatic pipette to add a standardized acid solution. The pH end points are 8.3 for phenolphthalein alkalinity and 4.3 for total alkalinity. Alkalinity relationships (hydroxide, carbonate, and bicarbonate) can be calculated nomographically.

# OXIDATION-REDUCTION POTENTIAL (ORP)

Purpose of Oxidation-Reduction Potential (ORP) Measurement

The oxidation-reduction (redox) potential of a sample is a measure of electron activity and is an indicator of the relative tendency of a solute or species to accept (gain) or transfer (lose) electrons. Oxidation is defined as the loss of an electron(s), while reduction is the gain of an electron(s). Redox reactions in groundwater are usually biologically mediated and therefore the redox potential is affected by and influences the rates of biodegradation. Knowledge of the redox potential of groundwater is also important because some biological processes operate within a prescribed range of redox conditions. The redox potential of groundwater can be used as an indicator of certain geochemical processes such as sulfate reduction (anaerobic processes).

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The redox potential of groundwater generally ranges from -400 millivolts (mV) to + 800 mV on an ORP scale. Under oxidizing conditions, which are typical of aerobic respiration, the redox potential of groundwater produces a positive ORP reading.

4-20

Reducing conditions are characterized by negative ORP readings. More specifically, ORP readings ranging from 150-400 mV indicate oxic, 0-15 mV indicates suboxic, and 50 mV indicates reducing. Under either aerobic or anaerobic conditions, the redox potential of groundwater within a contaminant plume should be somewhat less than that measured outside a plume. Thus, ORP measurements may be used to provide insight into the occurrence of petroleum hydrocarbon biodegradation activity, and the potential for specific biodegradation processes to occur. In addition, ORP readings can be used to help validate other measurements.

## Limitations of ORP Measurements

Oxidation-reduction potential measurements in natural waters and wastewaters can be difficult to interpret. The only potentials that will register in the ORP cell are those associated with electroactive species that can react at the indicator electrode. In natural waters, only a few reactions proceed at the electrode surface, for example:

 $Fe^{2+} = Fe^{3+} + e^{-}$  and  $Mn^{2+} = Mn^{4+} + 2e^{-}$ .

All the important redox reactions involved in the nitrogen cycle, the sulfur cycle, and the carbon cycle are not completed at the indicator electrode in an ORP cell. The voltage reading produced by an ORP cell is a reflection of many reactions — it is a *mixed potential* and its value is difficult if not impossible to interpret in any fundamental chemical terms. Moreover, when an ORP electrode combination is immersed in water the voltage reading will vary with time, usually falling from the initial reading obtained. This behavior is due to the general process of polarization or *poisoning* of the indicator electrode surface by the accumulation of oxidation products on the surface of the electrode (Snoeyink and Jenkins, 1980).

Perhaps the largest problem with using ORP is the observed lack of thermodynamic equilibrium in most water samples (Chapelle, 1993). For example, ORP measurements, as determined by platinum electrode, and numerous other redox pairs, including the

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 $O_2/H_2O$ , Fe<sup>2+</sup>, SO<sub>4</sub><sup>-</sup>/H<sub>2</sub>S, and CO<sub>2</sub>/CH<sub>4</sub> couples, showed little agreement with each other. Lindberg and Runnels (1984) interpreted this lack of agreement as a reflection of the substantial lack of thermodynamic equilibrium in groundwater systems.

Despite the limitations of ORP measurements, ORP data can be of qualitative use. However, the results of redox measurements are relative to a given situation and care is needed in interpreting the data.

# Methods of ORP Measurement

The ORP is measured in a galvanic cell consisting of a reference electrode (e.g., calomel) and an indicating electrode of a highly noble metal (e.g., platinum or gold). The calomel electrode is the cathode and the inert platinum or gold electrode is the anode. The anode is made of a highly noble metal so that the potential for its oxidation is less than that of any oxidizable solution components. The anode thus is a site of the oxidation of solution constituents but, ideally, is not itself affected. A platinum indicator electrode and calomel reference electrode are commonly used for ORP measurements. Combination redox electrodes are available that incorporate the indicator and reference electrodes.

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It is not possible to calibrate ORP electrodes over a range of redox potentials (as with pH electrodes). Instead, standard solutions that exhibit both chemical stability and known redox potentials for specific indicator electrodes are used to check electrode response at the temperature of sample measurement (Greenberg *et al.*, 1992). The use of a high quality millivolt (mV) meter, which allows calibration of the probe system by adjusting the intercept value, is recommended.

Sorption and poisoning effects on electrodes can be a problem. Contamination of the electrode surface, salt bridge, or internal electrolyte in the case of reference electrodes, can lead to excessive drift, poor electrode response, and artifact potentials. Organic

4-22

matter, sulfide, and bromide may cause these problems, particularly in long-term electrode use. If, after appropriate cleaning, refilling, or regeneration procedures, excessive drift occurs or erratic performance of paired electrodes is observed in redox standard solutions, discard the faulty electrode and use a new one (Greenberg *et al.*, 1992).

## Discussion

Despite the limitations of ORP measurements, they are a valuable geochemical indicator and can be used to check other geochemical measurements. Incorporation of ORP measurements into the characterization of the geochemistry of a site is neither expensive nor time consuming. When the micropurging method is used (which incorporates flow cell measurements), the ORP measurement is simple to obtain. Sampling technique can affect ORP data (see Section 3).

## ADDITIONAL GEOCHEMICAL PARAMETERS OF INTEREST

Information on additional groundwater geochemical parameters of potential interest is presented in Table 4-4.

## REFERENCES

Admire, J.D., J.S. de Albuquerque, J.A. Cruze, K.R. Piontek, and T.S. Sale. 1995. Case Study: Natural Attenuation of Dissolved Hydrocarbons at a Former Natural Gas Plant. *Proceedings*, SPE/EPA Exploration and Production Environmental Conference, Houston, Texas, March, 1995. pp. 619-630.

Barcelona, M.J., H.A. Wehrmann, and M.D. Varljen. 1994. Reproducible Well-Purging Procedures and VOC Stabilization Criteria for Groundwater Sampling. *Ground Water*. 32(1):12-22.

Borden, R.C., C.A. Gomez, and M.T. Becker. 1995. Geochemical Indications of Intrinsic Remediation. *Ground Water*. 33(2):180-189.

Buscheck, T.E. and K.T. O'Reilly. 1995. *Protocol for Monitoring Intrinsic Bioremediation in Groundwater*. Chevron Research and Technology Company. March 1995.

Chapelle, F.H. 1993. *Ground-Water Microbiology & Geochemistry*. John Wiley and Sons, Inc., New York, New York.

Cookson, J., 1995. *Bioremediation Engineering: Design and Application*. McGraw-Hill Pess. New York, New York

CH2M HILL, 1997. Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies. API Publication Number 4657. American Petroleum Institute, Washington, D.C.

Greenberg, A.E., L.S. Clesceri, and A.D. Eaton. 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th edition, American Public Health Association.

Kampbell, D.H., J.T. Wilson, and S.A. Vandegrift. 1989. Dissolved Oxygen and Methane in Water by a G.C. Headspace Equilibrium Technique. *International Journal of Environmental Analytical Chemistry*. 36:249-257.

Kemmer, F.N. Editor. 1988. *The NALCO Water Handbook, Second Edition*. McGraw-Hill, Inc. New York, New York.

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

McAllister, P.M. and C.Y. Chiang. 1994. A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water. *Ground Water Monitoring and Remediation*. 14(2):161-173.

Mobil Oil Corporation. 1995. A Practical Approach to Evaluating Intrinsic Bioremediation of Petroleum Hydrocarbons in Ground Water. Environmental Health Risk Assessment Group, Stonybrook Laboratories, Princeton, NJ.

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Newell, C.J., R.K. McLeod, J.R. Gonzales. <u>Bioscreen</u>: Natural Attenuation Decision Support System. EPA/600/R-96/087. U.S. Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. EPA/600/R-96/087. August, 1996.

Payne, R.E., N.J. Novick, T.L. Douthit, J.A. Brown, and D.N. Anderson. 1995. An Evaluation of Field Methods For Measuring Indicators of Intrinsic Bioremediation of Petroleum Hydrocarbons In Groundwater. *Proceedings*, 1995 Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Remediation Conference and Exposition, Houston, Texas, November 29 - December 1, 1995.

Puls, R. W., and M.J. Barcelona. 1989. Ground Water Sampling for Metals Analyses. *EPA Superfund Ground Water Issue*. EPA/540/4-89/001.

Puls, R.W., and J.F. McCarthy. 1993. Well Purging and Sampling. *Proceedings*, Ground Water Sampling --- A Workshop Summary, Dallas, Texas, November 30 - December 2, 1993. pp. 17-25.

Puls, R.W. and C.J. Paul. 1995. Low-Flow Purging and Sampling of Ground Water Monitoring Wells with Dedicated System. *Ground Water Monitoring and Remediation*. 15(1):116-123.

Puls, R.W. and M.J. Barcelona. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. *EPA Superfund Ground Water Issue*. EPA/540/S-95/5. April, 1996.

Rifai, H.S., P.B. Bedient, J. T. Wilson, K. M. Miller, and J.M. Armstrong. 1988 "Biodegradation Modeling at an Aviation Fuel Spill Site." ASCE Journal of Environmental Engineering 114 (5):1007-1029.

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Shanklin, D.E., Sidle, W.C., and M.E. Fergusen. 1995. Micro-Purge Low-Flow Sampling of Uranium-Contaminated Groundwater at the Environmental Management Project. *Groundwater Monitoring and Remediation;* Summer 1995, pp 168-176.

Snoeyink, V. L., and D. Jenkins. 1980. *Water Chemistry*. John Wiley and Sons, Inc. New York, New York.

United States Environmental Protection Agency. 1992. *RCRA Ground-Water Monitoring*. Draft Technical Guidance. EPA/530-R-93-001. U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C.

United States Environmental Protection Agency. 1993. *Data Quality Objectives Process* for Superfund. Interim Final Guidance. EPA 540-R-93-071. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, D.C.

United States Environmental Protection Agency. 1986. RCRA Technical Enforcement Guidance Document. OSWER-9950-1. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, D.C.

Western States Petroleum Association. 1996. California Purging Study Update. Vol. 1, No. 1.

Wiedemeier, T.H., D.C. Downey, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. Air Force Center for Environmental Excellence, Brooks Air Force Base, San Antonio, Texas (11/11/95).

Wiedemeier, T.H., R.N. Miller, J.T. Wilson, and D.H. Kampbell, 1995. "Significance of Anaerobic Processes for the Intrinsic Bioremediation of Fuel Hydrocarbons", 1995. National Ground Water Association, Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference, Houston, Texas, November 1995.

Wilson, J.T., F.M. Pfeffer, J.W. Weaver, D.H. Kampbell, T.H. Wiedemeier, J.E. Hansen, and R.N. Miller. 1994. Intrinsic Bioremediation of JP-4 Jet Fuel. *Proceedings*, Symposium on Intrinsic Bioremediation of Ground Water, Denver, Colorado, August 30- September 1, 1994, pp. 60-72. EPA/540/R-94/515. U.S. Environmental Office Protection Agency, Office of Research and Development, Washington, D.C.

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# GLOSSARY

- <u>Abiotic</u> Occurring without the involvement of microorganisms.
- <u>Aeration</u> The introduction of and mixing with air.
- <u>Aerobic Respiration</u> Process whereby microorganisms use oxygen as an electron acceptor to generate energy.
- <u>Aliphatic Hydrocarbon</u> A compound built from carbon and hydrogen atoms joined in a linear chain. Petroleum products are composed primarily of aliphatic hydrocarbons.
- <u>Alkalinity</u> A measure of the acid neutralizing capacity of a particular liquid.
- <u>Anaerobic Respiration</u> Process whereby microorganisms use a chemical other than oxygen as an electron acceptor. Common "substitutes" for oxygen are nitrate, sulfate, iron and carbon dioxide.
- <u>Aquifer</u> An underground geological formation that stores groundwater.
- <u>Aromatic Hydrocarbon</u> A compound built from carbon and hydrogen atoms joined in a ring (e.g., benzene ring).
- <u>Biodegradation</u> biologically mediated conversion of one compound to another.
- Biomass Total mass of microorganisms present in a given amount of water or soil.

<u>Bioremediation</u> - Use of microorganisms to control and destroy contaminants.

- <u>Biotransformation</u> Microbially catalyzed transformation of a chemical to some other product.
- <u>Chlorinated Solvent</u> A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compounds structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning, and other operations.
- <u>Colorimetric</u> An analytical neutral based on comparison of a liquid's color with standard colors.
- <u>Cometabolism</u> A reaction in which microbes transform a contaminant even though the contaminant cannot serve as an energy source for the organisms. To degrade the contaminant, the microbes require the presence of other compounds (primary substrates) that can support their growth.

<u>Dechlorination</u> - The removal of chlorine atoms from a compound.

<u>Desorption</u> - Opposite of sorption; the release of chemicals attached to solid surfaces.

<u>Dissolution</u> - The process of dissolving; separation into component parts.

G-1

- <u>Drawdown</u> Lowering of the water elevation in a well or aquifer due to groundwater extraction from the well.
- <u>Electron</u> A negatively charged subatomic particle that may be transferred between chemical species in chemical reactions. Every chemical molecule contains electrons and protons (positively charged particles).
- <u>Electron Acceptor</u> Compound that donates electrons ( and therefore is reduced) in energy-producing oxidation - reduction reactions that are essential for the growth of microorganisms. Common electron acceptors are oxygen, nitrate, sulfate, iron and carbon dioxide. Highly chlorinated solvents (e.g., TCE) can act as electron acceptors.
- <u>Electron Donor</u> Compound that donates electrons (and therefore is oxidized) in oxidation-reduction reactions that are essential for the growth of microorganisms. in bioremediation organic compounds serve as electron donors. Less chlorinated solvents (e.g., VC) can act as electron donors.
- <u>Expressed Assimilative Capacity</u> An estimate of the hydrocarbon mass per unit volume of groundwater that can potentially be mineralized through aerobic and anaerobic biodegradation under existing site conditions. Derived from site geochemical data and utilization factors (see definition) derived from contaminant biodegradation stoichiometry. (See also the example calculation of expressed assimilative capacity at the end of this glossary.)
- <u>Geochemistry</u> A science that deals with the inter-related chemical and geological properties of a substance (in this case, groundwater).
- <u>Hydraulic Conductivity</u> A measure of the rate at which water moves through a unit area of the subsurface under a unit hydraulic gradient.
- <u>Hydraulic Gradient</u> Change in head (i.e., water pressure) per unit distance in a given direction, typically in the principal flow direction.
- <u>Inorganic Compound</u> A chemical that is not based on covalent carbon bonds. Important examples are metals, nutrients such as nitrogen and phosphorus, minerals, and carbon dioxide.
- <u>Intrinsic Bioremediation</u> A type of in situ bioremediation that uses the innate capabilities of naturally occurring microbes to degrade contaminants without taking any engineering steps to enhance the process.
- <u>Metabolic Intermediate</u> A chemical produced by one step in a multistep biotransformation.
- <u>Metabolism</u> The chemical reactions in living cells that convert food sources to energy and new cell mass.

- <u>Methanogen</u> A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide as an electron acceptor.
- <u>Methanogenesis</u> The anaerobic metabolic process in which organics are oxidized and methane is produced.
- <u>Microcosm</u> A laboratory vessel set up to resemble as closely as possible the conditions of a natural environment.
- <u>Microorganism</u> An organism of microscopic or submicroscopic size. Bacteria are microorganisms.
- <u>Micropurge Sampling Method</u> A method for sampling groundwater which is intended to reduce artificial aeration and entrainment of particulates by purging and sampling at a flow rate that matches the natural groundwater flow velocity. Also called low-flow purging, minimal drawdown sampling, or millipurging.
- <u>Mineralization</u> The complete degradation of an organic chemical to carbon dioxide, water, and possibly other inorganic compounds.
- <u>Nonaqueous-phase liquid (NAPL)</u> A liquid solution that does not mix easily with water. Many common ground water contaminants, including chlorinated solvents and many petroleum products, enter the subsurface in nonaqueousphase solutions.
- <u>Oxidation Reduction Potential (ORP)</u> An oxidation-reduction reaction consists of two parts or half-reactions. These are the oxidation reaction in which a substance loses or donates electrons and the reduction reaction in which a substance gains or accepts electrons. The oxidation-reduction potential is measure of the electrical state or tendency to oxidize or reduce.

<u>Redox</u> - Common alternate term for oxidation reduction potential.

- <u>Stoichiometry</u> The quantitative relations between elements and compounds in chemical reactions.
- <u>Utilization Factor</u> the ratio of mass of contaminant biodegraded to the mass of electron acceptor utilized (or metabolic byproduct produced). The following utilization factors are commonly used for the BTEX constituents of petroleum hydrocarbons (Wiedemeier *et al.*, 1995):

Oxygen utilized	0.32
Nitrate utilized	0.21
Ferrous iron produced	0.05
Sulfate utilized	0.21
Methane produced	1.28

G-3

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Example Calculation of Expressed Assimilative Capacity					
		Concentration of Geochemical Parameter			
	Utilization		Geochemically		Equivalent BTEX
Parameter	Factor	Background	Reduced Zone	Difference	<b>Concentration</b>
Dissolved	0.32	7.0	<0.1	7.0	2.2
Oxygen					
Nitrate	0.21	21	<0.1	21	4.4
Iron	0.05	< 0.025	36	36	1.8
Sulfate	0.21	1575	42	1533	321.9
Methane	1.3	0.0005	11.0	11.0	14.3
Total Expressed Assimilative Capacity				344.6	

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#### NOTES:

All concentrations in mg/L.

Data from Colorado Gas Plant Site (CH2M HILL, 1996).

As groundwater passes through impacted zone, the concentrations of geochemical parameters change in response to contaminant biodegradation. Data from the background zone is compared to data from the impacted zone in which biodegradation is occurring.

The difference in the concentrations of individual geochemical parameters is multiplied by the corresponding utilization factor to determine the equivalent amount of BTEX biodegraded by the biodegradation process.

The total expressed assimilative capacity is the summation of the equivalent BTEX biodegraded through the individual biodegradation processes.

In this example, the total expressed assimilative capacity is approximately 340 mg/L BTEX. That is, the geochemical data indicates that a total of 340 mg of BTEX is biodegraded in each liter of water passing though the impacted zone.

Calculation of the expressed assimilative capacity is more fully described in the Air Force protocol for intrinsic remediation (Wiedemeier *et al.*, 1995).

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APPENDIX A

## STANDARD OPERATION PROCEDURE

### MICROPURGING

### GROUNDWATER SAMPLING METHOD

## FOR

## GEOCHEMICAL INDICATORS

### OF

### INTRINSIC BIOREMEDIATION

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#### INTRODUCTION

This document presents a protocol for measurements and groundwater sampling in support of intrinsic bioremediation characterizations. This protocol was developed because of the potential adverse effects of commonly employed groundwater sampling methodology on the quality of intrinsic bioremediation data.

Naturally occurring contaminant biodegradation can result in groundwater that is in dramatic non-equilibrium with the atmosphere. Commonly employed sampling collection techniques include use of bailers and excessive rates of groundwater purging. These practices may result in exposure of the groundwater to the atmosphere and will often produce groundwater samples with a geochemistry that is different than formation groundwater. Parameters for characterization of intrinsic bioremediation are listed in Table 1. The potential adverse effects of groundwater sampling technique on data quality for select intrinsic bioremediation parameters is summarized in Table 2. The specific mechanisms in which the geochemistry of groundwater samples can be altered through sample collection techniques include the following:

- Excessively lowering the water level in the well by purging at high flow rates. During recharge, water trickling into the well may be exposed to the atmosphere, resulting in artificial aeration of the groundwater sample, which can cause loss of volatiles, introduction of oxygen, and elevation of the sample ORP.
- Sample aeration caused by sample collection with a bailer and/or excessive exposure of the groundwater to the atmosphere during field measurements or filling of sample containers.
- Increased turbidity caused by bailing the well, or purging the well at high flow rates creating high entrance velocities through the well screen and mobilizing sediment in the well, sand pack, and formation.
- De-pressurization of samples of deep groundwater can result in supersaturation of the groundwater with certain constituents and de-gassing

of the constituents from the sample. (However, this should not be a significant problem at LNAPL sites, where the groundwater zone of interest is typically the uppermost saturated interval.)

The micropurging method described in this protocol will enable collection of representative groundwater samples for characterization of intrinsic bioremediation, except at sites of very low permeability. Considerations for very low permeability settings are discussed.

Parameter	Objective	Method
Dissolved oxygen	Preferred electron acceptor	<b>SM4500-O.G (Membrane</b> electrode) and/or Winkler Field test kit (Azide modified Winkler)
Nitrate	Electron acceptor	<b>SM4110/EPA 300</b> or SM 4500-NO <sub>3</sub> -C
Sulfate	Electron acceptor	<b>SM4110/EPA300</b> or SM 4500-SO4-E
Ferrous iron (Fe <sup>2+</sup> )	Produced when ferric iron is the electron acceptor	<b>SM 3120B/EPA 200.7</b> or SM 3500-Fe-D
Methane/Carbon Dioxide	Produced when carbon dioxide or acetate is the electron acceptor	<b>R.S. Kerr 175</b> (Kampbell <i>et al.,</i> 1989)
Alkalinity (Carbonate and bicarbonate)	Indicators of contaminant mineralization	SM 2320.B
Oxidation/reduction potential (ORP)	Confirmation of general redox state as determined from electron acceptor chemistry	Field measurement SM 2580-B
pH, electrical conductance	Standard water quality parameters. Determination of pH especially important	Field Instruments SM 4500-H-B
Temperature	Standard water quality parameter	Field measurement SM 2550.B

Table 1. Intrinsic Bioremediation Groundwater Characterization<sup>a</sup>

Preferred method is in bold type face.

<sup>a</sup> This list is the *typical minimum* for characterizing site groundwater geochemistry to support evaluations of intrinsic bioremediation. Refer to other protocols and guidance documents to determine the complete suite of parameters that best meets the project needs.

SM - Standard Methods for the Examination of Water and Wastewater, 18th Edition, Greenberg, et al., 1992.

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Table 2. Potential Effects of Sampling Protocol on Select Intrinsic Bioremediation Parameters

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Parameter	Artificial Aeration	Turbidity
Oxidation/reduction potential (Eh)	Introduction of oxygen raises Eh through oxidation of reduced species.	Solids in bottom of well may be at different geochemical state than formation; introduction of these solids into groundwater may alter Eh in resulting groundwater sample.
Dissolved oxygen	May increase D.O. of sample.	May lower D.O. of sample through oxygen demand exerted by geochemically reduced solids.
Nitrate		Nitrate may be lowered through electron acceptor demand exerted by geochemically reduced species associated with solids.
Sulfate		Analysis may yield sulfate concentration greater than in formation groundwater because of sulfate associated with solids.
Iron	Oxidation/precipitation of iron may decrease concentration of ferrous iron.	Analysis may yield iron concentration greater than in formation groundwater because of iron associated with solids.
Methane	May reduce concentration through loss to the atmosphere.	Turbidity not likely to affect methane concentration.
Note: Turbidity may also adversely	impact field measurements based on colorime	tric methods.

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#### STANDARD OPERATING PROCEDURE

The micropurging method described here has been adapted from the protocols specified by EPA in their most recent groundwater monitoring guidance (EPA, 1992), demonstrated by Barcelona for providing consistent monitoring results for volatile constituents (Barcelona *et al.*, 1994), and discussed in a recent EPA technical support document (Puls and Barcelona, 1996). The method is described below.

#### EQUIPMENT REQUIREMENTS

Equipment needed for sample collection are provided in the attached checklist (Attachment A).

#### GENERAL PRE-SAMPLING PROCEDURE

Prior to purging and groundwater sampling, the routine procedures listed in the attached check list (Attachment B) should be conducted.

#### MONITORING WELL PURGING

The objective of purging the monitoring well is to collect groundwater samples representative of the formation groundwater. At most petroleum hydrocarbon sites, the groundwater near the water table surface will have the highest constituent concentrations, and monitoring wells are therefore screened across the water table. In these wells, the pump intake should be placed approximately 1 foot below the water level. If the well has a discrete screen length that is entirely submerged, the pump intake should be placed within the screened interval.

To collect intrinsic bioremediation parameter samples, monitoring wells should be purged at a rate that does not lower the water level significantly (i.e., less than 10

A-7

percent of the screen length). The specific pumping rate that will not cause excessive drawdown is dependent on the size of the well, permeability of the formation, etc. Check previous purge records for insight into the proper rate. When this information is not available, start with a flow rate of approximately 0.5 L/min and check the water level response in the well, increasing or decreasing the rate accordingly. The purging rate should be controlled as needed using the pump's variable speed flow controller and/or the gate valve in the discharge line. Collect water level measurements frequently during purging to ensure that the water level has not dropped lower than desired (see the attached sampling form). Monitoring wells should be purged until the field parameters have stabilized to within the ranges presented in Table 3. If an electric submersible pump is used, temperature may slightly increase rather than stabilize during low flow rate purging.

Field Parameter	Stabilization Criterion	
Dissolved Oxygen	0.10 mg/L or 10% of value (whichever is greater)	
Electrical Conductivity	3% Full Scale Range, ±5-10 μmhos/cm	
рН	0.10 pH unit	
Temperature	0.2° C	

Table 3. Criteria for Stabilization of Indicator Parameters During Purging

The method described above is recommended as an alternative to the conventional "three well volume" purging protocol. Purging until the parameters in Table 3 have stabilized is a technically sound method for obtaining groundwater samples that are representative of formation groundwater. Most regulatory agencies accept this newer method based on its technical merits. However, some regulatory agencies may still require the older "three well volume" method. For wells completed in very transmissive zones, it may not be practical to purge at a slow rate with minimal water

table depression while still achieving the required purge volume. In these cases, a higher purge rate may be acceptable initially, but purging rates should be decreased as the required purge volume is approached, with the objective of producing groundwater samples that are not turbid and have not been artificially aerated.

As a cost control measure, it may be appropriate to terminate purging and collect the sample at pre-determined, arbitrary endpoints (e.g., after 3 well volumes, after one hour of purging, etc.), regardless of whether or not the criteria in Table 3 have been achieved.

#### FIELD INDICATOR PARAMETER MEASUREMENT

During purging, continuously measure dissolved oxygen, electrical conductance, pH, ORP, and temperature with the flow cell or equivalent arrangement (e.g., discharge line from pump to small beaker in which the probes are immersed). Flow cells are commercially available from a number of vendors. If using the beaker arrangement for measuring the field indicator parameters, direct the discharge into the bottom of the beaker and allow the beaker to continuously overflow during measurements to minimize aeration. Allowing the discharge to pour into the container will artificially aerate the water, thus altering the properties of the water with respect to key parameters such as dissolved oxygen and oxidation reduction potential.

Record indicator parameter and water level measurements in a field notebook or onto well development logs every three to five minutes or at a minimum frequency of approximately 1/4 well volume increments (see the attached sampling form). Purging is complete once the parameters have stabilized to within the ranges presented in Table 3 regardless of the number of well volumes purged.

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If using the electric submersible pump care must be taken to prevent flow interruption. If the flow is interrupted for any reason (e.g., loss of power), entry of air into the tubing usually occurs, with the potential result of artificially aerating the groundwater sample. In addition, restarting the pump may cause a surge in flow that will suspend particulate matter in the well.

### GROUNDWATER SAMPLE COLLECTION

When purging is complete, collect aliquots for the analytical parameters listed in Table 1. To ensure the most consistent, comparable results, individual samples and/or measurements from all wells should be collected in the same order. The order used in this protocol is based on the approximate order of susceptibility to artificial aeration: volatile organics, total organic carbon (TOC), methane, iron, alkalinity, and sulfate.

Reduce the pumping rate and/or use the 3-way valve to collect the methane, volatile organics and TOC samples. Direct the discharge toward the bottom, inside wall of the jar to minimize volatilization, and fill to overflowing. Filter the discharge prior to filling the ferrous iron sample jar using an in-line 0.45 micron filter. Filtration is recommended to eliminate bias introduced with particulates. In-line filtration is recommended to prevent artificial aeration of the sample.

If additional samples are collected for dissolved oxygen analysis using field kits (i.e., Winkler), submerge the sample jar into the bottom of the large container, continue to fill the container to overflowing, and allow the sample jar to fill without aeration.

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Preserve and analyze the samples as described in the sampling and analysis plan.

A-10

#### QUALITY CONTROL CHECK FOR FIELD MEASUREMENTS

Field checks should be performed to ensure that representative measurements are being made. At a minimum, ORP and DO readings should be in agreement. DO readings should be less than one when the ORP is negative. If this is not the case, one or the other measurement is in error. When additional geochemical parameters are measured in the field, additional checks can be made. For example, ferrous iron should be present in elevated concentrations only when DO is less than one and the ORP is negative. When all measurements are not in agreement, measurements should be repeated until agreement is reached. In this process of achieving consistent results, there may be merit in trying alternative measurement techniques; for example, use of a field kit for DO rather than a DO measurement probe.

Another check for representative results can be made by comparing the DO and ORP of well water before and after purging. In almost all cases, the DO/ORP measurements taken from the well water prior to purging should be equal to or higher than the DO/ORP of the formation groundwater. Increase in the DO and ORP as a result of purging is an indication of artificial aeration of the water.

In many cases, generation of valid field measurements for these parameters is not a trivial matter. Consideration should be given to including an analytical chemist on the field sampling crew. If this is not practical, the field crew should have familiarity with the problems that may arise in obtaining valid measurements and/or have access to an analytical chemist during the sampling effort to assist in resolution of measurement difficulties and apparent anomalies.

#### RECOMMENDATIONS

The following are recommendations that will facilitate implementation of the micropurging method and improve the representative quality of data collected.

- Dedicated pumps are recommended by many investigators (Kearl, *et al.*, 1994), (Barcelona, *et al.*, 1994), and (Kearl, *et al.* 1992) to reduce data quality variations due to inconsistent sampling technique, avoid cross contamination from sampling equipment, save time during sampling events, and reduce the overall cost of sampling.
- Wells should be thoroughly developed when installed at pumping rates greater than anticipated purging and sampling rates to eliminate or minimize production of sediment and colloidal particulates.
- Determine the depth of the well from well construction logs. Measuring the depth to the bottom of the well will cause suspension of settled solids and mixing of water within the well, thus requiring longer purge times. If well depth measurements are desired, perform the measurements after sampling is completed.
- Lower the pump slowly into the well to minimize surging the water column. Have the pump tubing measured and marked off before placing it down the well so you know where exactly to place the pump intake (i.e., one foot below water level or a minimum of one foot below the top of screen, whichever is lower).
- If using a submersible electric pump, use a generator that will allow the pump to run smoothly. Usually, a 2500-watt with automatic throttle, supplying 15 amps or greater, works well.
- Do not start the pump too quickly. This may create a surge of water flow and cause unwanted turbidity in the sample. On the same note, make sure that you have a check valve on the pump tubing. If the pump shuts off accidentally, the check valve will prevent water in the tubing from rushing back into the well causing the groundwater to be aerated.

- Select a pump setting low enough that it will not break suction and stop pumping. Check any previous records on the purge rates versus drawdown in the well. It is helpful to have some prior knowledge about the well's recharge rate and drawdown, so that stopping the pump, and/or lowering the pump are avoided. Periodically measure the water level in the well to prevent pump shutdown or drawdown that is too far down the well screen.
- Record data regarding the well's purge rate and drawdown for the next sampling event.
- Use tubing with as small a diameter as possible. If the submersible pump requires larger tubing, use a reducer to minimize the diameter of the tubing. Small diameter tubing will reduce the chance of aeration within the tubing and improve the responsiveness of flow cell measurements (see the following bullet).
- Minimize the volume of water within the tubing and flow cell or beaker in which probe measurements are made. A large volume of water up-stream of the monitoring point (i.e. probe location) increases the amount of time required for steady-state conditions in the well to manifest themselves at the monitoring point. Flow cells or measurement beakers with a large volume and residence time are particularly probelematic, due to the dilution effects and the longer time required to achieve a steady-state reading at the measurement point. Small diameter flow cells that most closely acheive plug flow are preferred. If using a beaker set-up, try to ensure flow from the discharge tubing directly across the probes.
- Be careful of air bubbles trapped in the pump tubing. To minimize bubbles, hold the end of the groundwater discharge tubing vertical and higher than any other point in the tubing. It is also helpful to tap the tubing lightly to force bubbles to rise to the end of the tubing. It is important to minimize air bubbles because they could potentially aerate the groundwater sample.
- A three-way valve or tee with valves on two legs is recommended so that the pump rate is not altered and a constant flow rate can be maintained while sampling. The valve is configured so that one leg is connected to the discharge tubing, one leg flows into the flow-cell, the third is turned on only when filling sample bottles.

A-13

#### CONSIDERATIONS FOR VERY LOW PERMEABILITY SETTINGS

Monitoring wells screened across very low permeability materials (silts, clays, etc.) typically purge dry and are then allowed to recharge prior to sampling. However, recharge into a dewatered well results in increased exposure of the water entering the well to the air present at the water table interface and in the well, potentially altering the groundwater geochemistry as summarized in Table 2. To attempt to minimize these effects, the pump intake should be placed 2-3 feet below the water level and operated at as low a rate as is achievable, ideally equal to the recovery rate. In this manner, water drawn into the pump would be primarily from the formation and sand pack pore spaces. Close monitoring of the indicator parameter measurements is necessary since stabilization should occur prior to one borehole volume.

In some cases, a well may recharge so slowly that it may be impractical or even impossible to collect a groundwater sample that is truly representative of formation groundwater with respect to key geochemical parameters. If there is a need to collect samples/measurements for intrinsic bioremediation parameters in such cases, slowly purge the well dry and collect the groundwater samples as soon as the necessary volume has recharged into the well. As previously described in Section 2.6, the DO and ORP should be measured prior to, during, and after purging. An increase in DO or ORP is an indication of artificial aeration of the water, and results should be qualified accordingly.

#### REFERENCES

Barcelona, M.J., H.A. Wehrmann, and M.D. Varljen. 1994. Reproducible Well-Purging Procedures and VOC Stabilization Criteria for Groundwater Sampling. *Ground Water*. 32(1):12-22.

Greenberg, A.E., L.S. Clesceri, and A.D. Eaton. 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th edition, American Public Health Association.

Kampbell, D.H., J.T. Wilson, and S.A. Vandegrift. 1989. Dissolved Oxygen and Methane in Water by a G.C. Headspace Equilibrium Technique. *International Journal of Environmental Analytical Chemistry*. 36:249-257.

Kearl, P.M., N.E. Korte, and T.A. Cronk. 1992. Suggested Modifications to Groundwater Sampling Procedures Based on Observations From the Colloidal Borescope. *Ground Water Monitoring and Remediation*. 12(2):155-61.

Kearl, P.M., N.E. Korte, M. Stites, and J. Baker. 1994. Field Comparison of Micropurging vs. Traditional Ground Water Sampling. *Ground Water Monitoring and Remediation*. 14(4): 183-190.

Puls, R.W. and M.J. Barcelona. 1996. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. *EPA Ground Water Issue*. EPA/540/S-95/504. US Environmental Protection Agency, office of Research and Development. Ada, Oklahoma.

United States Environmental Protection Agency. 1992. RCRA Ground-Water Monitoring: Draft Technical Guidance. EPA/530-R-93-001.

Walton-Day, K., *et al.*, 1990. Field Methods for Measurement of Ground Water Redox Chemical Parameters. *Groundwater Monitoring and Remediation*. 10(4):81-89.

A-15

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Attachment A: Equipment Checklist

_	Monitoring well construction details (geologic log, screened
	interval, well depth, borehole diameter, etc.).
	Water level indicator
	Submersible positive displacement pump and controller or bladder pump
	Fluoroethylene polymer (FEP) tubing in sufficient quantity to use new tubing for each well. Note: Teflon <sup>®</sup> is quite permeable to certain gases.
	Throttling valves and 3-way flow-tee sampling valve (See Figure 1)
	Field meters for pH, ORP, dissolved oxygen, temperature, electrical conductance (including instrument manuals and calibration materials)
	Calibrated bucket or beaker to measure flow rate
	Flow cell with ports for each of the field meter probes (optional).
	Field note book and/or well purging log forms
	Sample containers, preservatives, ice and cooler(s)
	Decontamination supplies
	Personal protective equipment

Attachment B: Pre-Purging Checklist

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	Decontaminate submersible pump (if not a dedicated
	pump).
	Decontaminate or replace discharge tubing (if not a
	dedicated pump).
	Calibrate field meters (pH, ORP, specific conductance,
	dissolved oxygen, HNu, etc.) If possible, perform two point
	calibration on DO meter.
	Decontaminate water level indicator probe and tape.
	Unlock the monitoring well and measure vapor
	concentrations in accordance with the site specific Health
	and Safety Plan.
	Measure depth to water.
	Evaluate whether water table surface is above or within the
	screened interval.
	Calculate the volume of water in the well and borehole filter
	sand pack pore space (borehole volume).
	Insert dissolved oxygen probe into the monitoring well and
	measure the dissolved oxygen in the water column. If
	practical, also measure ORP of water in well.
	Install submersible pump into the well slowly to minimize
	aeration, placing the pump intake within the screened
	interval or approximately 1 foot below the water level.
	It gasoline or diesel powered generators or compressors are
	used to operate the pump, take precautions to prevent the
	exnaust from contaminating the samples.
·	Configure the discharge tubing with a gate valve and 3-way
	valve, with discharge directed through the 3-way valve and
	how cell (optional), and into a calibrated decontaminated
	Ducker (See Figure 1).

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