
METHODS FOR MEASURING INDICATORS OF INTRINSIC BIOREMEDIATION: GUIDANCE MANUAL

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Methods for Measuring Indicators of Intrinsic Bioremediation: Guidance Manual

Health and Environmental Sciences Department

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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.



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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

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:

- Scoping field investigations: Allowing selection of sampling and analytical methods that meet project-specific and site-specific needs.
- Performing field investigations: 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.
- Evaluation of field investigation data: 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*

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

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.

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.

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;
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.

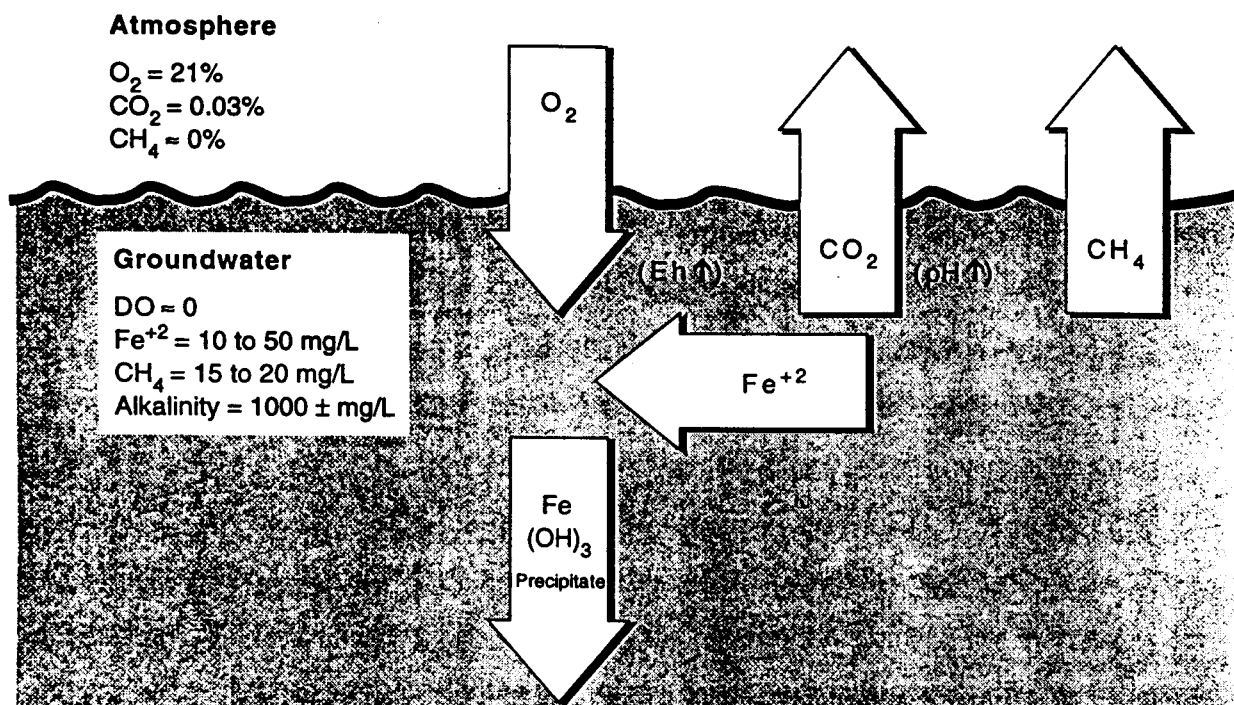


Figure 2-1. Potential Effects of Artificial Aeration

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

Figure 2-2. Geochemical Consequences of Hydrocarbon Biodegradation

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:

- 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 non-representative 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.

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.

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.

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

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.

- Level of effort: 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.
- Complexity: 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.
- Costs: 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

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

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