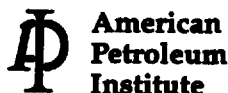


EFFECTS OF SAMPLING AND ANALYTICAL PROCEDURES ON THE MEASUREMENT OF GEOCHEMICAL INDICATORS OF INTRINSIC BIOREMEDIATION: LABORATORY AND FIELD STUDIES

Health and Environmental Sciences Department
Publication Number 4657
November 1997



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Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies

Health and Environmental Sciences Department

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ABSTRACT

In recent years, recognition that natural attenuation processes often play an important role in lessening risks posed by inadvertent releases of petroleum hydrocarbons to the subsurface has increased. General consensus is growing concerning the groundwater geochemical parameters (dissolved oxygen, nitrate, sulfate, alkalinity, etc.) that should be measured to assess the presence of naturally occurring petroleum hydrocarbon biodegradation. There is less consensus on the appropriate sampling and analytical protocols for measurement of these parameters. This report presents a study to evaluate the effects of various sampling and analytical methods of collecting groundwater geochemical data for intrinsic bioremediation studies. Sampling and analytical methods were tested in the laboratory and in the field. The field sites consisted of a gas plant site in Colorado and an underground storage tank site in Missouri. The results indicate that several groundwater sampling and analytical methods may be appropriate for measuring geochemical indicators of intrinsic bioremediation. The methods vary in accuracy, level of effort, and cost. The choice of the best method for a given application should be based on project-specific and site-specific considerations, particularly the specific manner in which the data are to be used.

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EXECUTIVE SUMMARY

In recent years, recognition that natural attenuation processes, particularly biodegradation, often play an important role in mitigating risks posed by inadvertent releases of petroleum hydrocarbons to the subsurface has increased. General consensus is growing concerning the groundwater geochemical parameters that should be measured to assess the presence of naturally occurring petroleum hydrocarbon biodegradation. These include dissolved oxygen (DO), nitrate, iron, methane, etc. There is less consensus on the appropriate sampling and analytical protocols for measurement of these parameters. The American Petroleum Institute sponsored this laboratory and field study to compare the effects of various sampling and analytical methods used for the collection of groundwater geochemical data in support of intrinsic bioremediation studies.

Groundwater collected from zones of active petroleum hydrocarbon biodegradation is commonly characterized by 1) electron acceptor depletion; 2) elevated levels of bicarbonate, methane, and ferrous iron; and 3) geochemical conditions that are in dramatic disequilibrium with the atmosphere. Based on theoretical considerations, one would anticipate that the geochemistry of a groundwater sample from a geochemically reduced zone would be altered by sampling techniques that involve contact between the groundwater and the atmosphere. Such alterations in concentrations of dissolved oxygen, ferrous iron, and methane were confirmed in the project through both the laboratory and field studies.

COMPARISON OF SAMPLING METHODS

In the laboratory study, samples of known geochemical composition were collected from a sealed tank by three sampling methods: 1) a micropurging sampling method with a low flow submersible pump, 2) a variation of the micropurging sampling techniques with a peristaltic pump, and 3) a bailer. All sampling techniques resulted in some introduction of DO, and some loss of methane and ferrous iron. The micropurging method with the submersible pump consistently introduced the least bias. The most bias was introduced with the bailer.

To further compare the effects of sampling methods, groundwater samples were collected from multiple wells at two different field sites. Wells were sampled using the micropurging method

ES-1

with a low flow submersible pump, and were then sampled with bailers. Results generally were consistent with the laboratory studies, particularly with respect to the greater loss of ferrous iron and methane with the bailer method.

A limited amount of field work was done to evaluate data collection methods involving no purging of monitoring wells. For wells in zones geochemically affected by hydrocarbon releases, downhole DO probe measurements on unpurged monitoring wells often yield DO readings that are higher than the DO of formation groundwater. Of the sampling methods examined, the no purging method resulted in the greatest loss of iron and methane from groundwater in geochemically reduced zones.

COMPARISON OF ANALYTICAL METHODS

During the field studies, a comparison of field and commercial laboratory analytical methods for nitrate, sulfate, iron, and alkalinity was made. Field methods are of interest because the rapid sample analyses reduce the potential for changes in composition during shipment and storage, and allow for "real time" data evaluation in the field. Generally, there was fairly good correlation among data produced using the two methods, suggesting that field methods are generally viable alternatives to use of a commercial laboratory.

CONCLUSIONS

While certain groundwater sampling techniques can alter the samples' geochemistry, these changes may or may not significantly affect data interpretation. Groundwater in hydrocarbon bearing zones often has a geochemistry radically different than background groundwater as a result of naturally occurring hydrocarbon biodegradation. These general shifts in geochemistry can be readily detected using conventional groundwater monitoring and sampling techniques. If the objective is simply to provide geochemical evidence of hydrocarbon biodegradation activity, then any of the groundwater monitoring and sampling techniques examined in this study generally will suffice, as long as they are consistently applied across a particular site. It is typically the differences among multiple measurements at a site that are important. If, on the other hand, the geochemical data are used in quantitative projections of plume migration (e.g., input parameters in BIOPLUME III modeling), the potential biases in geochemical data

introduced through sample collection should be considered in scoping data collection activities. The potential for sampling methodology to significantly affect a quantitative intrinsic bioremediation evaluation will be highest on sites where the dominant biodegradation mechanisms are aerobic respiration, iron reduction, and/or methanogenesis.

In summary, there are several groundwater sampling and analytical methods that may be appropriate for measuring geochemical indicators of intrinsic bioremediation. The methods vary in accuracy, level of effort, and cost. The choice of the best method for a given application should be based on project-specific and site-specific considerations, particularly the specific manner in which the data are to be used.

A companion document (CH2M HILL, 1997) provides guidance on the selection and use of field sampling and analytical methods for measuring geochemical indicators of intrinsic bioremediation.

Section 1

INTRODUCTION

This report, sponsored by the American Petroleum Institute (API), presents the results of laboratory and field studies on field methods for the measurement of geochemical indicators of intrinsic bioremediation.

Intrinsic bioremediation is a risk management strategy that relies on naturally occurring biodegradation for mitigation of the potential risks posed by subsurface contaminants. 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, conductivity, and temperature. Measurement of these parameters is being performed at an increasing number of petroleum hydrocarbon sites. However, there is a lack of guidance on appropriate sampling and analytical procedures to ensure that these measurements generate quality data. This lack of guidance is cause for concern because the extent to which intrinsic bioremediation is ultimately embraced will depend, to a large degree, on the valid characterization of site conditions.

The project consisted of a laboratory study, which allowed comparison of sampling methods under controlled conditions, as well as field studies, which allowed verification of laboratory results on sampling methods under actual field conditions. The field studies also incorporated a comparison of commercial laboratory and field analytical methods. Field analytical methods are of interest because their use makes possible rapid sample analyses, thus reducing the potential for changes in the composition of the sample during sample shipment and storage, and allowing for "real time" data evaluation in the field.

Based on these studies, a companion document (CH2M HILL, 1997) was prepared to provide guidance on the selection and use of field sampling and analytical methods for measuring geochemical indicators of intrinsic bioremediation.

The primary objective of this report is to document and discuss the findings of the laboratory and field studies. This report should not be interpreted as providing endorsement of a particular sampling or analytical method. Guidance on the selection and use of sampling and analytical methods used to support intrinsic bioremediation site characterizations is presented in the companion document (CH2M HILL, 1997).

Site data on 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 obtained through the various sampling and analytical methods, and effects on data use, are discussed in this report. This report should not be interpreted as providing endorsement of any particular data use.

The field studies described in this report were conducted at petroleum hydrocarbon sites, and the report focuses on applications of intrinsic bioremediation at petroleum hydrocarbon sites. However, the observations and findings presented will generally be applicable to any site where biodegradable organic constituents exist.

Section 2

BACKGROUND

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 production of ferrous iron. Petroleum hydrocarbons may also be biodegraded through 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 be used qualitatively to establish hydrocarbon biodegradation activity. Data on the spatial distribution of these parameters, together with hydrogeologic and stoichiometric data, are also sometimes used to support quantitative estimation of contaminant biodegradation rates and projection of plume migration.

These uses of geochemical data will be valid only to the extent that these parameters are representative of geochemical conditions in the groundwater system sampled. Key considerations in the collection of representative geochemical data are outlined below.

GEOCHEMICAL CONSIDERATIONS

In recent years, it has become widely recognized that microorganisms can have profound effects on groundwater quality (Chapelle, 1993). This is particularly true where large masses of biodegradable organic compounds (e.g., 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. Once species with the highest oxidizing potential are exhausted, the next most highly oxidized electron acceptor is reduced. This process continues and the oxidizing potential of the groundwater system is progressively reduced. 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.

This 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).

Water in equilibrium with the atmosphere will contain approximately 8 mg/L DO. The presence of DO at this concentration is the upper bound of oxidizing conditions within natural groundwater. Biodegradation of petroleum hydrocarbons results in the consumption of this dissolved groundwater. 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, 1995). When the oxidizing potential of the groundwater reduces to this point, the groundwater is then in dramatic disequilibrium with the atmosphere.

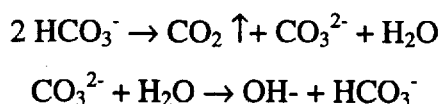
When groundwater from subsurface zones of low oxidizing potential is brought to the surface and is exposed to the atmosphere, fairly rapid changes in the oxidizing potential and concentrations of certain geochemical parameters can occur as the water begins to equilibrate with the atmosphere (see Figure 2-1). A common example of this phenomenon is the formation of rust colored solids in water samples drawn from water bearing zones 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.

Another concern is the evolution of dissolved gases from samples. Hydrocarbon oxidation results in the production of water, carbon dioxide, and methane, which are produced under

moderately reducing conditions. 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 mg/L have been observed in a biologically active petroleum hydrocarbon plume (Admire *et al.*, 1995).

Methane levels as high as 31 mg/L have been observed downgradient of petroleum release sites (Admire *et al.*, 1995) although in potable water, methane is typically not detected.

When groundwater samples with elevated methane and carbon dioxide are brought to surficial 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 the methane and carbon dioxide. The loss of carbon dioxide will raise the pH, as the carbonate system shifts to compensate for the loss of CO₂:



Loss of dissolved carbon dioxide from a groundwater sample prior to analysis is one of the reasons the field pH is often lower than the laboratory pH.

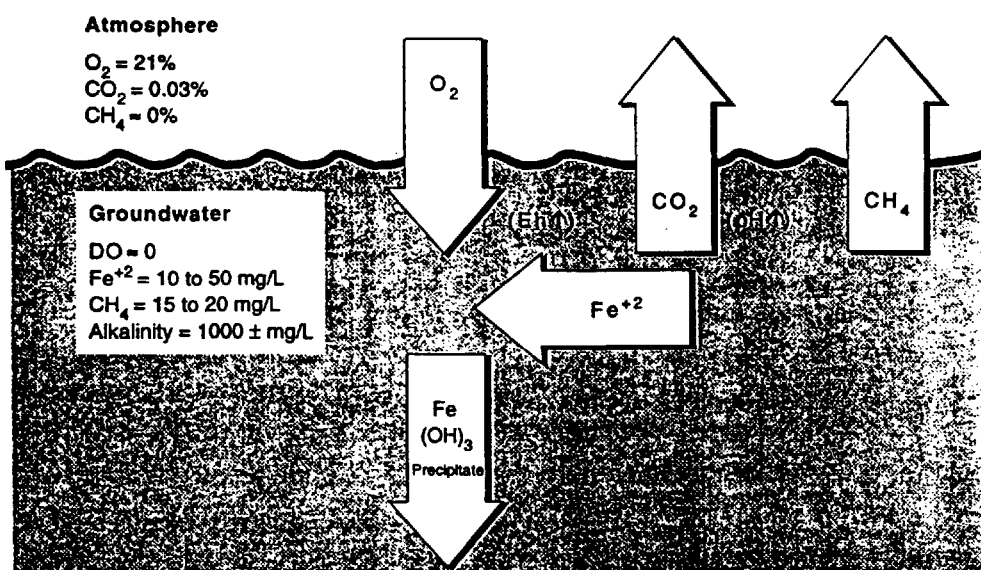


Figure 2-1. Potential Impact of Artificial Aeration

SAMPLING AND ANALYTICAL CONSIDERATIONS

Based on the preceding discussion, it is concluded that groundwater samples collected from zones in which petroleum hydrocarbons are being biodegraded are often in dramatic disequilibrium with normal atmospheric conditions. Furthermore, significant shifts in aqueous geochemistry can result when these samples come in contact with the atmosphere.

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 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:

- 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 allowable sample holding time typical with off-site laboratories; and
- Dissolved gases can be stripped from the sample when a vacuum is used to lift samples from a well.

In addition, bailing a well and/or purging a well at high rates can cause an increase in 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 potential 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. Aquifer solids or solids that accumulate in the well may also be comprised of compounds that will contribute to detected concentrations of analytes of interest.

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.

The National Research Council (NRC) has recommended a general strategy for demonstrating that *in situ* bioremediation is effectively working (NRC, 1993). The strategy relies on the convergence of three lines of evidence:

- Documented loss of constituents of concern from the site;
- Laboratory assays showing that microorganisms have the potential to transform the constituents of concern under the expected site conditions; and
- 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). 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. When geochemical data are used 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 more quantitatively. Note that these more quantitative uses of geochemical data will often not be required or appropriate at small petroleum hydrocarbon release sites where the plume has reached, or is receding from, its steady-state limit.

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

Figure 2-2. Geochemical Consequences of Hydrocarbon Biodegradation

One method used to interpret geochemical data at a given site is calculating the expressed assimilative capacity. The expressed assimilative capacity is a semi-quantitative estimate of the hydrocarbon mass per unit volume of groundwater that can potentially be mineralized through aerobic and anaerobic biodegradation under existing site conditions. Knowledge of contaminant biodegradation stoichiometry allows calculation of a utilization factor, which is defined as the mass of electron acceptor required (or byproduct produced) in the biodegradation of a given mass of hydrocarbon.

The difference in concentrations of electron acceptors and byproducts between background and locations, within or downgradient of the anaerobic core of the plume, can be divided by the corresponding utilization factor to estimate the equivalent concentration of hydrocarbon biodegraded through specific biodegradation mechanisms. Summation of the equivalent concentration of hydrocarbon biodegraded through the various mechanisms yields the total expressed assimilative capacity.

Calculation of the expressed assimilative capacity is more fully described in the Air Force *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for*

Natural Attenuation of Fuel Contamination Dissolved in Groundwater (Wiedemeier *et al.*, 1995). The expressed assimilative capacity is sometimes used semi-quantitatively to judge which contaminant biodegradation mechanisms are most significant at a given site (Wiedemeier *et al.*, 1995). However, there is still considerable debate regarding the methods and merits of quantifying the contributions of aerobic versus anaerobic processes.

Geochemical data are sometimes also used in quantitative projections of future plume migration. 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). In the newer BIOPLUME III model, the biodegradation component of the model will be expanded to simulate the transport and uptake of anaerobic electron acceptors (Newell *et al.*, 1995). With the BIOPLUME III model, data on DO, nitrate, sulfate, ferrous 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 more quantitative the use of site geochemical data, the more important the specific concentrations of key parameters measured at specific locations becomes. Changes in sample geochemistry, as a result of sampling and analytical methodology, will be most significant with the most quantitative uses of the resulting data.

Section 3

LABORATORY STUDY

The objective of this laboratory study was to determine the effects, if any, of several commonly employed sampling techniques on the geochemistry of the associated groundwater samples. The laboratory study involved preparing a groundwater solution of known geochemical composition, using several commonly employed sampling methods to generate samples from a simulated well, and subsequently analyzing the groundwater samples to allow quantification of the changes, if any, resulting from the sampling methods.

MATERIALS AND METHODS

Construction of the Simulated Monitoring Well

Figure 3-1 illustrates the components of the simulated monitoring well. A 2-inch polyvinyl chloride (PVC) pipe with 0.010-inch slots and capped bottom was used as the inside casing. An 8-inch PVC pipe with 0.010-inch slots and capped bottom was used as the outer casing. The outer casing slots were below the water level, while the inner casing was slotted both above and below the water and sand level. The space between the casings was filled with a medium silica sand (particle diameter 0.85 mm x 0.425 mm). This setup was used to mimic a monitoring well in a porous matrix and to allow water drawdown in the inner casing.

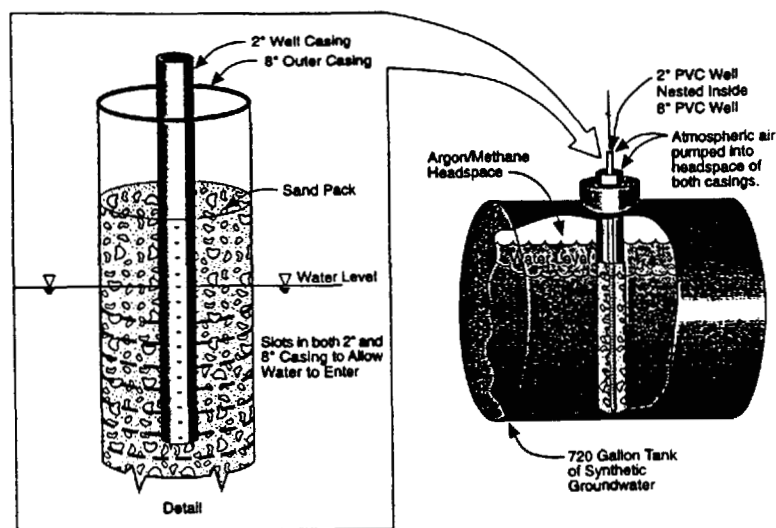


Figure 3-1. Simulated Monitoring Well System

The headspace in the tank above the water surface contained a methane/argon mixture. Air was contained in the headspace above the sand pack in the 8-inch casing and the headspace above the water in the 2-inch casing. The slots in the 8-inch casing were below the surface of the water, so the air in the casings did not contaminate the headspace in the tank.

Preparation of Synthetic Groundwater Feed

A synthetic groundwater solution was prepared to evaluate the sampling methods. The composition of the solution is presented in Table 3-1. DO, iron, and methane were selected as test parameters because their concentrations could be altered by sample aeration; thus, they would be good indicators of geochemical changes resulting from sampling methodology.

Table 3-1. Composition of Synthetic Groundwater Solution

Parameter	Target Concentration
Temperature	10°C
pH	7.0 units
Dissolved Oxygen	Minimum
Ferrous Sulfate	8 mg/L (as Fe)
Methane	15-20 ppm ^a
^a Parts per million	

The synthetic groundwater solution was prepared by filling two 720-gallon feed tanks connected in series with municipal tap water. The water was purged with argon gas to minimize the DO content and remove chlorine. The argon gas purging was conducted continuously for approximately 1 week to ensure a minimal DO content. To bring aqueous phase methane concentrations in the tanks to near saturation prior to sampling, the methane was then added by diffusing research grade gas into the water for 24 hours. The iron was added as a premixed ferrous sulfate solution approximately 3 hours prior to sample collection.