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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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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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PREPARED UNDER CONTRACT BY:
CH2M-HILL
10 SOUTH BROADWAY
ST. LOUIS, MO 63102

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API STAFF CONTACTS

Bruce Bauman, Health and Environmental Sciences Department
Roger Claff, Health and Environmental Sciences Department

MEMBERS OF THE API BIODEGRADATION PROCESSES RESEARCH GROUP

Tim E. Buscheck, Chevron Research and Technology Company

Chris Neaville, Shell Development Company

Norm Novick, Mobil Oil Corporation

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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

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 CO_2:

$$2\ HCO_3^- \rightarrow CO_2\uparrow + CO_3^{2-} + H_2O$$

$$CO_3^{2-} + H_2O \rightarrow OH- + HCO_3^-$$

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.

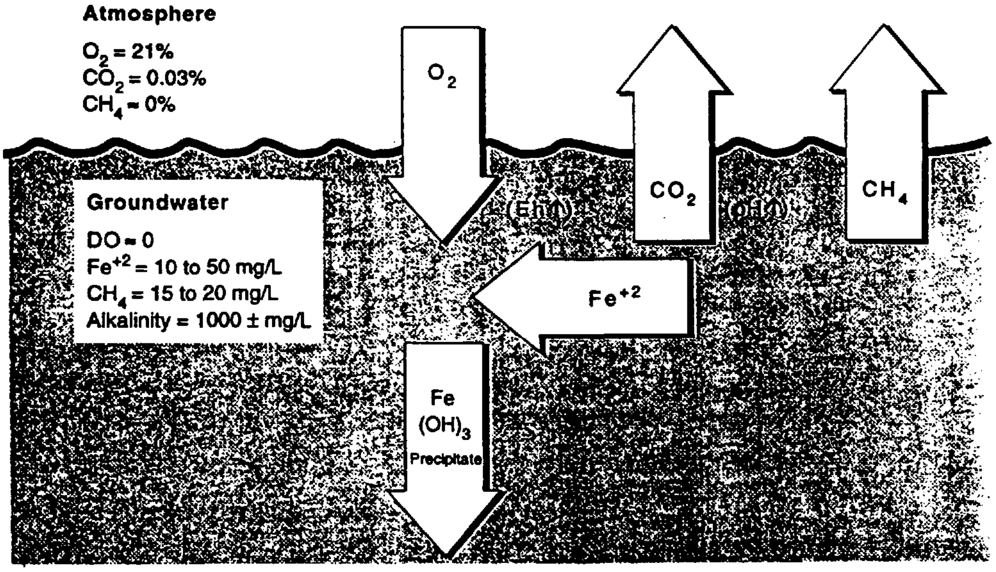


Figure 2-1. Potential Impact of Artificial Aeration

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.

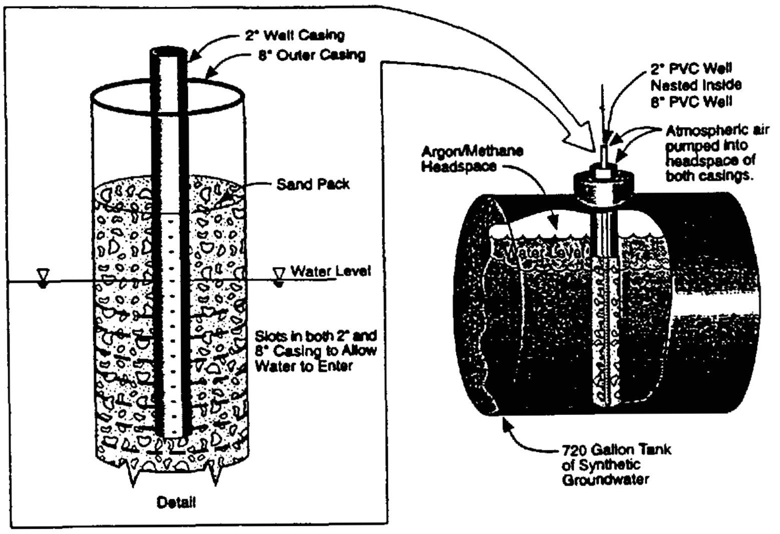


Figure 3-1. Simulated Monitoring Well System

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.

Sampling Methods

As part of this project, three sampling methods were investigated: (1) a micropurging method, (2) a variation of the micropurging method using a different pump type, and (3) a method employing high well purge rates and bailers for sample collection. In addition, a glove box arrangement was used to obtain samples of the water for characterization of the standard solution.

Glove Box Arrangement. Nine feed samples were collected from the tank at a depth corresponding to the sampling pump intake. The samples were collected in a glove box arrangement which was purged with argon gas to maintain an oxygen-free environment. Five samples were collected prior to, and four samples were collected after, the monitoring well sampling. The average of the pre- and post-test samples was used as the baseline for comparing possible geochemical changes produced by the sampling methods.

Micropurging Method. Based on many of the considerations discussed in Section 2, there has been a movement toward using well sampling methods involving low purge rates to minimize drawdown and turbidity (USEPA, 1993). A micropurging method was adapted from protocols specified by EPA in its most recent groundwater monitoring guide (USEPA, 1992). The method has been demonstrated to provide consistent monitoring results for volatile constituents and/or geochemical parameters (Barcelona, 1994; Puls and Paul, 1995). The method, illustrated in Figure 3-2, consists of the following:

- A small diameter, submersible Grundfos® pump with an electric controller and a valve on the effluent tubing to regulate and reduce the flow rate;
- Use of the pump to purge the well at a low rate to minimize the drawdown within the well and therefore minimize aeration of water entering the well; and
- Use of a flow cell for probe readings and a bottle filling procedure to minimize aeration of the sample.

Using this method, nine samples were collected with the pump, which was located at an elevation corresponding to 15 feet of lift.

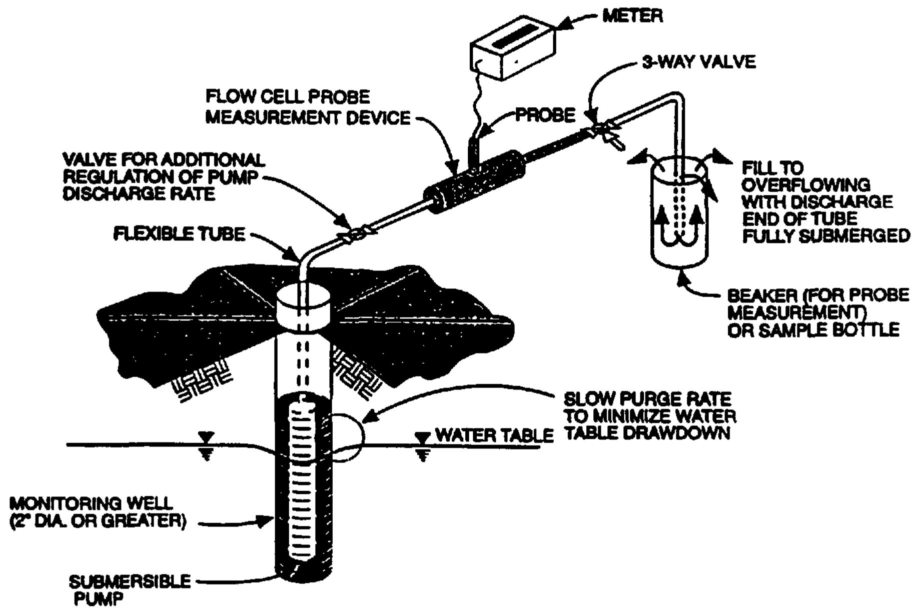


Figure 3-2. Schematic of Minimal Aeration Sample Collection Method

Micropurging with Peristaltic Pump. This sampling method was the same as that described above, with the exception that a peristaltic pump was used instead of the submersible Grundfos® pump.

Nine samples were collected with the pump, which was located at an elevation corresponding to 15 feet of lift. This resulted in a vacuum of approximately 0.56 atmosphere plus vacuum sufficient to overcome pipe or tube friction. The samples were collected concurrent with the collection of samples using the Grundfos® pump.

The peristaltic pump created a noticeable hydraulic pulse, and a significant amount of gas bubbles was observed in the sample line. The gas bubbles were observed in the peristaltic pump line at the beginning of the sampling and were not observed in the Grundfos® pump sample line. The peristaltic sample line was disconnected and purged using the Grundfos® pump to ensure the gas bubbles were not caused by insufficient purging of the sample line. After purging with the Grundfos® pump, the peristaltic pump was reconnected and when sampling was restarted, the bubbles formed immediately. This degassing was most likely caused by the vacuum drawn and/or the hydraulic pulse caused by the pump. Similar degassing has also been observed when sampling groundwater at petroleum hydrocarbon sites.

Fast Purge/Bailer Method. For this method, the Grundfos® pump was used to quickly purge the well, resulting in a drawdown of the water level in the well and an associated cascading of water along the well screen. The bailer was rapidly lowered into the well, resulting in splashing of water within the well bore. This was done to simulate bailing in the field, which is often performed in this manner consistent with an objective of reducing the labor cost of the sampling effort to the maximum extent possible. The synthetic groundwater collected with the bailer was placed in a container to produce a composite sample, resulting in additional exposure of the sample to the atmosphere.

Number of Samples Collected and Analyzed.

The purpose of this effort was to quantify the geochemical changes, if any, resulting from the sampling methods used in a laboratory setting. To determine a possible geochemical change, the test results from the synthetic groundwater feed were compared to test results from the various sample collection methods. To determine confidence in this comparison, the reproducibility (precision) of sample collection and analysis was required.

To determine precision, nine samples were collected from the synthetic groundwater (feed) using each of the sample collection methods. Collecting nine data points for each sample provided the statistical basis to estimate precision and quantify the changes, if any, resulting from the sampling methods.

SAMPLE ANALYSES

Table 3-2 presents the analytical methods, type of sample container and preservative required, and the recommended holding time between sample collection and analysis.

Table 3-2. Analytical Methods

Parameter	Test Method	Sample Container	Preservative	Recommended Holding Time
Temperature	SM 2550B	NA	NA	Field Test
pH	SM 4500-H-B	NA	NA	Field Test
Dissolved Oxygen	SM 4500-O-B	NA	HA	Field Test
Ferrous Iron	SM 3500-Fe-C	250 mL; pp	filter, acidify	6 months
Methane	CH2M HILL modification of RS Kerr Lab SOP-175	40 mL; VOA	None	Immediately, otherwise ASAP

NA = Not Applicable

During collection of samples using the micropurging methods, the discharge from the Grundfos® and peristaltic pumps were monitored for temperature, pH, and DO using a flow-through cell. These measurements were made before and after the laboratory samples were collected. The temperature, pH, and DO measurements for the samples collected with the bailer were performed on the composite sample and without the flow-through cell. The DO measurements were made using a membrane-covered Clark-type polarographic sensor with built-in thermistors for temperature measurement and compensation.

The soluble iron samples were collected using an in-line 0.45 micron filter located on the aboveground pump discharge tubing. The samples were then analyzed in the laboratory for total iron. When this method is applied to all the wells at a site, it is assumed that a change in soluble iron concentration between wells is equivalent to the change in ferrous iron concentration.
The methane samples were collected in volatile organic analysis (VOA) vials, and analyzed using a modified CG Headspace Equilibration Technique method (Kampbell *et al.*, 1989) for the measurement of DO and methane in water. This method was modified by using a capillary column to improve chromatography and a flame ionization detector (FID) to improve sensitivity.

Quality Assurance/Quality Control (QA/QC) samples analyzed as part of the experiment are summarized in Table 3-3.

Table 3-3. QA/QC Samples

Test Parameter	Method Blank	SRM	Matrix Spike	Matrix Spike Duplicate
Ferrous Iron	Yes	Yes	Yes	Yes
Methane (CG)	Yes	Yes	NA	NA
NA = Not Applicable				

RESULTS

Analytical data for individual samples are presented in Table 3-4 and summarized in Table 3-5. Obtaining a representative baseline sample of the synthetic groundwater was critical for an accurate evaluation of the sampling methods. Care was taken to ensure collection of representative baseline samples, including the use of an argon gas-filled glove box.

Table 3-4. Laboratory Test Results (mg/L)

Sample No.	**Synthetic Groundwater**		**Grundfos® Pump**		**Peristaltic Pump**		**High-Purge Bailer**	
	Methane	**Iron**	**Methane**	**Iron**	**Methane**	**Iron**	**Methane**	**Iron**
1	17.2	10.8	15.1	8.0	9.7	7.3	10.0	8.0
2	17.3	10.0	13.9	7.9	10.1	7.2	11.6	7.7
3	16.7	10.7	1.4	7.8	10.2	7.6	11.9	7.7
4	17.0	10.6	14.9	7.8	9.7	7.6	12.1	7.9
5	16.9	10.0	14.8	8.0	9.1	7.4	11.7	7.7
6	17.1	10.0	13.7	8.0	9.6	7.1	12.1	7.6
7	15.8	10.8	14.8	8.0	9.2	7.6	12.0	7.7
8	16.6	10.0	15.0	7.8	9.0	7.6	10.5	7.9
9	16.7	9.9	14.6	7.9	8.6	7.0	12.0	7.8
Average	**16.8**	**10.3**	**14.6**	**7.9**	**9.5**	**7.4**	**11.5**	**7.8**
Standard Deviation	**0.4**	**0.4**	**0.5**	**0.1**	**0.5**	**0.2**	**0.7**	**0.1**

The first five synthetic groundwater test results shown in Table 3-4 represent samples collected prior to the collection of samples from the simulated monitoring well; the remaining four test results represent samples collected after sampling the simulated monitoring well. These results demonstrate that the synthetic groundwater parameters did not significantly change during the time of the sampling process. Further analysis of Table 3-4 and 3-5 data is presented in Section 6.

Table 3-5. Sample Analysis Summary

Test Parameter	**Synthetic Groundwater**	**Micropurging Grundfos® Pump Sample**	**Micropurging Peristaltic Pump Sample**	**High-Purge Bailer Sample**
Methane mg/L	16.8	14.6	9.5	11.5
% difference		-13%	-43%	-32%
Soluble Iron, mg/L	10.3	7.9	7.4	7.8
% difference		-24%	-29%	-25%
pH, units	6.2	6.3	6.2	6.3
Dissolved Oxygen, mg/L	0.3	0.4	0.5	2.5
% difference		+25%	+67%	+733%
Temperature, C	17.8	17.7	17.5	18.9
% difference		< 1%	-2%	+6%

Notes: Results for methane and iron are the average of nine replicate samples. Percent difference is relative to the results for the synthetic groundwater.

Section 4

FIELD STUDIES

Field studies were performed at two petroleum hydrocarbon sites. Intrinsic bioremediation characterizations were performed at both sites using the micropurging sampling method and a commercial laboratory for analyses of most of the geochemical parameters of interest. These tasks were supplemented with the following actions:

- While sampling the wells with the micropurging sampling method, additional sample volume was generated for analyses of samples with in-field techniques.
- Selected wells were resampled using the conventional fast purge/bailer sampling method to allow comparison of sampling methods.
- A variety of DO measurement methods were used.

The specific activities performed at the two sites are described in subsequent sections. Further description of the methods used in the field studies is provided in the subsection entitled METHODS.

COLORADO GAS PLANT SITE

The first field site used for this project was a natural gas processing site in northeastern Colorado. A plan view of the site is presented in Figure 4-1. Groundwater occurs approximately 30 feet below grade in eolian sand and silt deposits. A network of wells were sampled using the micropurging sampling method. Figure 4-1 also shows the wells that were resampled using the fast purge/bailer method. The wells that were sampled using both sampling methods included one well upgradient of the NAPL zone (Well 04-WCGP), wells in the interior of the NAPL zone (Wells BH-02 and BH-03), and wells downgradient of the NAPL zone (Wells 05-WCGP, 06-WCGP, and 08-WCGP). These wells were selected to allow comparison of sampling/analytical methods under the range of geochemical conditions found at the site. The commercial laboratory and in-field analyses performed on samples from these wells are summarized in Table 4-1.

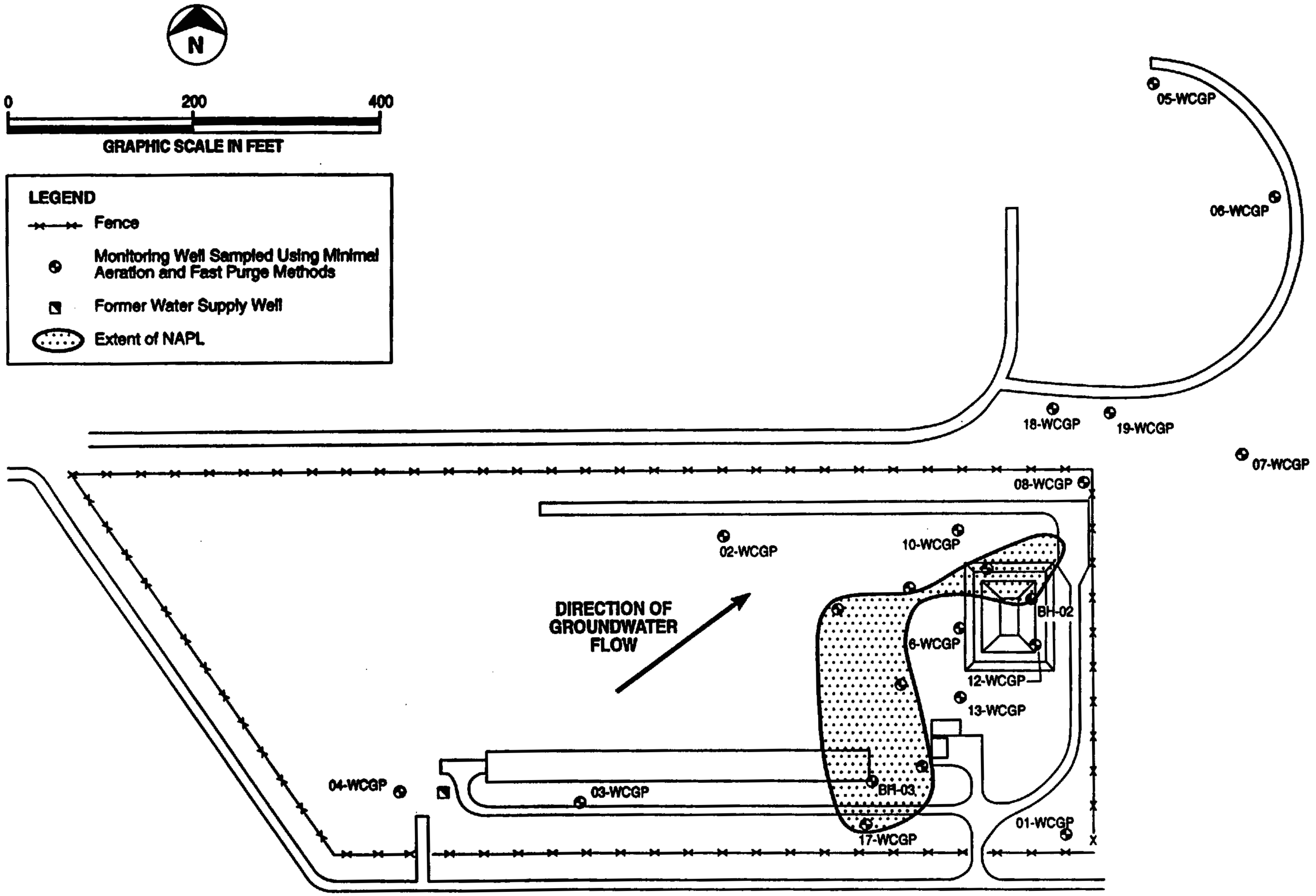


Figure 4-1. Colorado Gas Plant Site

Table 4-1. Analyses Performed on Samples from the Colorado Gas Plant Site

Well Number	No Purge	Minimal Aeration	Fast Purge	Argon Head-Space	Dissolved Oxygen (Winkler)	Nitrate		Sulfate		Alkalinity		Chloride	Iron		Methane		BTEX	TMB[1]
					Field	Field	Lab	Field	Lab	Field	Lab	Lab	Field	Lab	with HCl	no HCl	Lab	Lab
04-WCGP		X			1	1	1	1	1	1	1	1	1	1		1	1	
			X		1								1	1		1		
05-WCGP		X			1	1	1	1	1	1	1	1	1	1		1	1	
			X		1								1	1		1		
06-WCGP		X			1	1	1	1	1	1	1	1	1	1		1	1	
			X		1								1	1		1		
08-WCGP		X			1	3	2	3	2	3	2	2	3	2		3	2	
			X		1								1	2		3		
BH-02		X			1	1	1	1	1	1	1	1	1	1		1	1	
			X											1		1		
BH-03		X			3	3	2	3	2	3	2	2	3	2		3	2	
			X		3	3	1	3	1	3	1	1	3	1		3		

[1]-Trimethyl Benzene

MISSOURI UST SITE

The second field site used for this project was in eastern Missouri, where releases from underground storage tanks (USTs) at a vehicle fueling facility had occurred. A plan view of the site is presented in Figure 4-2. Groundwater occurs approximately 15 to 20 feet below grade in low permeability soil with occasional silty sand lenses. A network of wells was sampled using the micropurging sampling method. Figure 4-2 also shows the wells that were resampled using the fast purge/bailer method. The wells that were sampled using both sampling methods included wells upgradient of the NAPL zone (Wells GMW-12 and GMW-8), wells in the heart of the NAPL zone (Wells GMW-3 and GMW-4), and wells downgradient of the NAPL zone (Wells GMW-5 and GMW-14). These wells were selected to allow comparison of sampling/analytical methods under the range of geochemical conditions found at the site.

The subsurface at the Missouri UST site is composed primarily of low permeability silts and clays. Discontinuous, sandy strata also exist. The rate of groundwater production from a given well, which is a function of the number and thickness of more permeable strata that are intercepted, is generally quite low. Prior to the groundwater monitoring activities performed on this project, it was suspected that rates of groundwater production could potentially be too low for the micropurging sampling method to be practical (i.e., even very low purging rates would exceed well yield and result in significant drawdown).

Additional sampling tasks were planned to gain insight into the representative quality of geochemical data obtained using different sampling methods on low yield wells. These additional tasks included no purge sampling (collection of samples that comprised water initially present in the monitoring well), and purging the well and placing an argon headspace in the well bore while the well recharged. Methods used for these tasks are described in more detail in the next section, METHODS. During the field study, it was found that wells at this site recharged fast enough to allow micropurging sampling. Therefore, these additional sampling methods were used only on Well GMW-4. The commercial laboratory and in-field analyses performed on samples from the Missouri UST site are summarized in Table 4-2.

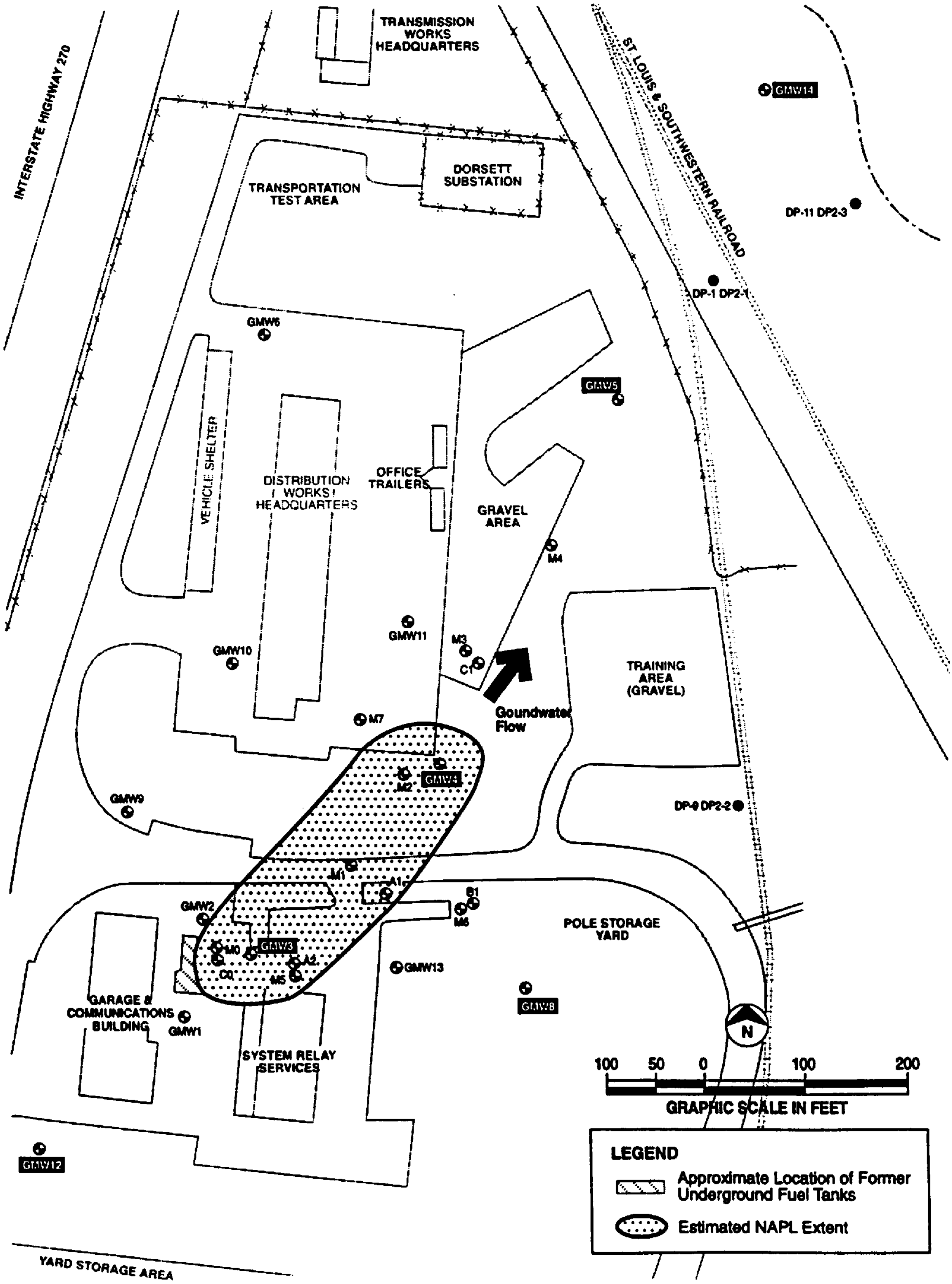


Figure 4-2. Missouri UST Site

Table 4-2. Analyses Performed on Samples from the Missouri UST Site

Well Number	No Purge	Minimal Aeration	Fast Purge	Argon Head-space	Dissolved Oxygen		Nitrate		Sulfate		Alkalinity		Chloride	Iron		Methane		BTEX	TMB[1]
					Field	Lab	Field	Lab	Field	Lab	Field	Lab	Lab	Field	Lab	with HCl	no HCl	Lab	Lab
GMW12		X			2		4	4	4	4	4	4	1	1	1		1	1	1
			X		1										1		1		
GMW8		X			1		1	1	1	1	1	1	1	1	1		1	1	1
			X		1										1		1		
GWM14		X			1		1	1	1	1	1	1	1	1	1		1	1	1
			X		1										1		1		
GMW5		X			1		1	1	1	1	1	1	1	1	1		1	1	1
			X		1										1		1		
GMW4	X				3										3		3		
		X			3		3	3	3	3	3	3	1	3	3	3	3	1	1
			X		3			3		3		3			3		3		
				X	3			3		3		3			3		3		
GMW3		X			3										3		3		
			X		3		3	2	3	2	3	2		3	3	3	3	1	1
				X	3			3		3		3					3		

[1]-Trimethyl Benzene

METHODS

Sampling Methods

Micropurging Sampling Method. The micropurging sampling method used in the field studies is detailed in the companion document (CH2M HILL, 1997). Key elements of this sampling method, all intended to reduce the potential for artificial aeration of the groundwater, include the following:

- Well purging at a slow rate to minimize well drawdown;
- Pumping groundwater to the surface through tubing that minimizes gaseous exchange with the atmosphere;
- An in-line flow cell for measurement of DO and ORP (redox potential); and
- A sample bottle filling procedure involving minimal exposure to the atmosphere.

Fast Purge/Bailer Sampling Method. The fast purge/bailer sampling method consisted of purging a minimum of three casing volumes of groundwater from the well at a rate sufficient to produce drawdown in the well. At the Colorado site, this was accomplished by using a submersible pump and purging at a flow rate sufficient to produce drawdown in the well. At the Missouri site, this was accomplished by using a stainless steel bailer. At both sites, samples were then collected using a clean bailer.

The bailer was rapidly lowered into the water column, which resulted in splashing and agitation of the water column within the well. This was intended to simulate common field practices, in which minimizing labor level of effort (LOE) and overall project costs is often a primary consideration.

At both sites, filtered iron samples were collected by pouring groundwater from the bailer into a clean bucket. This groundwater was then pumped through a 0.45 micron filter into a sample bottle.

No Purge Sampling Method. The no purge sampling method involved collecting groundwater from a well using a 2-inch submersible stainless steel pump and 1/2-inch tubing, which are the same pieces of equipment used for micropurging. The pump was placed 2 feet below the level of groundwater in the well. The groundwater that was initially pumped through the 1/2-inch tubing was collected directly into sample bottles.

Argon Headspace Sampling Method. The argon headspace sampling method involved bleeding laboratory grade argon into the well at a rate of 15 cubic feet per hour by placing tubing from an argon tank approximately 1 foot into the well. An MSA 261 Combustible Gas Indicator was used to determine when argon had completely filled the well. Argon was allowed to flow into the well for 15 more minutes. Then, a 2-inch submersible stainless steel pump and 1/2-inch tubing were lowered through the argon headspace and secured 2 feet below the level of groundwater in the well. Groundwater pumped through the 1/2-inch tubing was collected directly into sample bottles.

DO Measurements

Downhole Probe Survey. The downhole probe survey was the initial measurement taken at a well before the groundwater in the well was disturbed. Measurements were taken with a Yellow Springs Instrument Company, YSI58–DO meter at three intervals:

- just below the water surface,
- midway down the water column, and
- near the bottom of the well.

Flow Cell Probe Measurements. During purging, DO was continuously measured by placing the YSI58–DO probe in a flow cell. The probe was placed as close as possible to the discharge from the pump so that an accurate measurement of the newly discharged water was taken. The companion document (CH2M HILL, 1997) contains a more detailed explanation of this measurement.

Winkler Analyses. Groundwater samples for Winkler analyses were collected in glass biological oxygen demand (BOD) bottles. Winkler reagents were added in the field, and the samples were analyzed (via titration) in a field lab.

Analytical Methods

Field and laboratory analytical methods are given in Table 4-3.

Table 4-3. Comparison of Analytical Methods

	Method	
Parameter	**Commercial Laboratory**	**Field**
Nitrate	SM4500-NO_3^-C (Ion Chromatography)	HACH Cadmium Reduction Method
Iron	SM3500-FeC (Ion Chromatography)	HACH 1, 10 Phenanthcoline (ferrous) HACH FerroVer Method
Sulfate	SM4500-SO_4^-B (Ion Chromatography)	HACH SulfaVer 4
Alkalinity	SM2320.B (Burette Thration Method)	SM2320.B (Field)

The iron sampling and analytical methodology merits discussion. In the context of characterizing intrinsic bioremediation, the difference in ferrous iron concentrations between background locations and locations geochemically influenced by a hydrocarbon release to the subsurface provides a measure of hydrocarbon degradation. The protocol used on this project was based on analysis of field-filtered samples for total iron. Field filtering is performed to eliminate suspended solids (e.g., ferric iron precipitates) that would contribute to total iron concentrations determined after sample digestion. With the micropurging method, filtering was accomplished with use of an in-line filter on the Grundfos® pump discharge tubing.

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 μg/L (Snoeyink and Jenkins, 1980). Given this low ferric iron solubility, it is assumed that the differences across the site in the concentration of total iron in field-filtered samples are essentially equal to the difference in the concentration of ferrous iron.

ANALYTICAL DATA

All DO probe measurements and analyses are summarized in Table 4-4 and Table 4-5. Analytical results for other geochemical parameters, including results for both the in-field methods and commercial laboratory, are summarized in Table 4-6. Evaluation of the data is presented in Section 6.

Table 4-4. Dissolved Oxygen Measurements - Colorado Gas Plant Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
04-WCGP					
	Profile	DO Probe			
			1	8.6	Prior to purge
			3	8.3	Prior to purge
			6	8.2	Prior to purge
	Micropurging	DO Probe	Not measured *in situ*	8.6	End of Purge
		Winkler	Not measured *in situ*	7.0	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	8.8	End of Purge
		Winkler	Not measured *in situ*	6.8	End of Purge
05-WCGP					
	Profile	DO Probe			
			1	2.2	Prior to purge
			3	1.8	Prior to purge
			6	1.6	Prior to purge
	Micropurging	DO Probe	Not measured *in situ*	2.8	End of Purge
		Winkler	Not measured *in situ*	<0.1	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	4.0	End of Purge
		Winkler	Not measured *in situ*	1.1	End of Purge
06-WCGP					
	Profile	DO Probe			
			1	7.5	Prior to purge
			5	6.8	Prior to purge
			8	6.4	Prior to purge
	Micropurging	DO Probe	Not measured *in situ*	5.2	End of Purge
		Winkler	Not measured *in situ*	2.7	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	4.0	End of Purge
		Winkler	Not measured *in situ*	2.0	End of Purge

Table 4-4. (Cont'd): Dissolved Oxygen Measurements - Colorado Gas Plant Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
08-WCGP					
	Profile	DO Probe			
			NA	NA	NA
	Micropurging	DO Probe	Not measured *in situ*	NA	NA
		Winkler	Not measured *in situ*	<0.1	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	4.1	End of Purge
		Winkler	Not measured *in situ*	<0.1	End of Purge
BH-02					
	Profile	DO Probe			
			NA	NA	NA
	Micropurging	DO Probe	Not measured *in situ*	NA	NA
		Winkler	Not measured *in situ*	<0.1	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	1.8	End of Purge
		Winkler	Not measured *in situ*		End of Purge
BH-03					
	Profile	DO Probe			
			1	2.0	Prior to purge
			3	1.8	Prior to purge
			6	1.6	Prior to purge
	Micropurging	DO Probe	Not measured *in situ*	0.8	End of Purge
		Winkler	Not measured *in situ*	<0.1	End of Purge
	Fast Purge	DO Probe	Not measured *in situ*	1.8	End of Purge
		Winkler	Not measured *in situ*	<0.1	End of Purge

Notes: [a]Elapsed time from start of slow-rate purging

Table 4-5. Dissolved Oxygen Measurements - Missouri UST Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
GMW-12					
	Profile	DO Probe			
			1	3.9	Prior to purge
			8	3.8	Prior to purge
			13	3.9	Prior to purge
	Continuous	DO Probe			
			Not measured *in situ*	4.21	2
			Not measured *in situ*	4.01	4
			Not measured *in situ*	3.86	6
			Not measured *in situ*	3.74	8
			Not measured *in situ*	4.00	10
			Not measured *in situ*	3.88	12
			Not measured *in situ*	3.41	14
			Not measured *in situ*	3.23	16
			Not measured *in situ*	3.62	20
			Not measured *in situ*	3.72	22
			Not measured *in situ*	3.68	24
			Not measured *in situ*	3.53	26
			Not measured *in situ*	3.57	28
			Not measured *in situ*	3.54	30
			Not measured *in situ*	3.53	32
	Micropurging	DO Probe	Not measured *in situ*	3.53	End of Purge
		Winkler	Not measured *in situ*	4.1	End of Purge
	Fast Purge	Winkler	Not measured *in situ*	4.2	End of Purge
GMW-8					
	Profile	DO Probe			
			1	3.92	Prior to purge
			8	0.34	Prior to purge
			14	0.10	Prior to purge
	Continuous	DO Probe			
			Not measured *in situ*	1.97	2
			Not measured *in situ*	1.80	4
			Not measured *in situ*	1.60	6
			Not measured *in situ*	1.80	10
			Not measured *in situ*	1.67	12
			Not measured *in situ*	1.52	14
			Not measured *in situ*	1.72	16
			Not measured *in situ*	1.66	18

Table 4-5. (Cont'd). Dissolved Oxygen Measurements - Missouri UST Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
GMW-	(continued)		Not measured *in situ*	1.67	20
			Not measured *in situ*	1.47	24
			Not measured *in situ*	1.18	26
			Not measured *in situ*	0.95	28
			Not measured *in situ*	0.76	30
			Not measured *in situ*	0.60	32
			Not measured *in situ*	0.51	34
			Not measured *in situ*	0.40	36
			Not measured *in situ*	0.31	38
			Not measured *in situ*	0.36	40
	Micropurging	DO Probe	Not measured *in situ*	0.36	End of Purge
		Winkler	Not measured *in situ*	1.0	End of Purge
			Not measured *in situ*		
	Fast Purge	Winkler	Not measured *in situ*	2.0	End of Purge
GMW-14					
	Profile	DO Probe			
			1	5.53	Prior to purge
			6	1.20	Prior to purge
			10	0.10	Prior to purge
	Continuous	DO Probe			
			Not measured *in situ*	1.69	2
			Not measured *in situ*	1.82	4
			Not measured *in situ*	2.64	6
			Not measured *in situ*	2.69	8
			Not measured *in situ*	2.58	10
			Not measured *in situ*	2.55	12
			Not measured *in situ*	2.58	14
			Not measured *in situ*	2.57	16
	Micropurging	DO Probe	Not measured *in situ*	2.57	End of Purge
		Winkler	Not measured *in situ*	2.5	End of Purge
	Fast Purge	Winkler	Not measured *in situ*	2.2	End of Purge
GMW-5					
	Profile	DO Probe			
			1	1.61	Prior to purge
			7.5	0.17	Prior to purge
			13.5	0.11	Prior to purge

Table 4-5. (Cont'd). Dissolved Oxygen Measurements - Missouri UST Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
GMW-5 (continued)					
	Continuous	DO Probe			
			Not measured *in situ*	1.05	2
			Not measured *in situ*	1.01	4
			Not measured *in situ*	0.89	6
			Not measured *in situ*	0.90	8
			Not measured *in situ*	0.86	10
			Not measured *in situ*	0.79	12
			Not measured *in situ*	0.93	14
			Not measured *in situ*	0.89	16
			Not measured *in situ*	0.77	18
			Not measured *in situ*	0.78	20
			Not measured *in situ*	0.72	22
			Not measured *in situ*	0.68	24
			Not measured *in situ*	0.64	26
			Not measured *in situ*	0.58	28
	Micropurging	DO Probe	Not measured *in situ*	0.58	End of Purge
		Winkler	Not measured *in situ*	1.1	End of Purge
	Fast Purge	Winkler	Not measured *in situ*	1.4	End of Purge
GMW-4					
	Profile	DO Probe			
			1	1.10	Prior to purge
			9	0.22	Prior to purge
			17	0.03	Prior to purge
	Continuous	DO Probe			
			Not measured *in situ*	0.87	2
			Not measured *in situ*	0.70	4
			Not measured *in situ*	0.49	6
			Not measured *in situ*	0.71	8
			Not measured *in situ*	1.40	10
			Not measured *in situ*	1.34	12
			Not measured *in situ*	1.02	14
			Not measured *in situ*	1.07	16
			Not measured *in situ*	0.55	18
			Not measured *in situ*	0.85	26
			Not measured *in situ*	0.78	28
			Not measured *in situ*	0.91	30
			Not measured *in situ*	0.83	32
			Not measured *in situ*	0.72	34

Table 4-5. (Cont'd). Dissolved Oxygen Measurements - Missouri UST Site

Well	Method	Measurement Technique	Feet Below Static Water Level	D.O. (mg/L)	Elapsed Time (minutes)[a]
GMW-4 (continued)			Not measured *in situ*	0.65	36
			Not measured *in situ*	0.59	38
			Not measured *in situ*	0.57	40
	Micropurging	DO Probe	Not measured *in situ*	0.57	End of Purge
		Winkler	Not measured *in situ*	0.63	End of Purge
	No Purge	Winkler		0.65	End of Purge
	Fast Purge	Winkler	Not measured *in situ*	0.13	End of Purge
	Argon Headspace	Winkler		0.33	End of Purge
GMW-3					
	Profile	DO Probe			
			1	0.55	Prior to purge
			8	0.15	Prior to purge
			12	0.08	Prior to purge
	Continuous	DO Probe			
			Not measured *in situ*	2.54	0
			Not measured *in situ*	1.73	15
			Not measured *in situ*	1.86	17
			Not measured *in situ*	1.58	19
			Not measured *in situ*	1.48	21
			Not measured *in situ*	1.38	23
			Not measured *in situ*	1.05	25
			Not measured *in situ*	1.09	27
	Micropurging	DO Probe	Not measured *in situ*	1.09	End of Purge
		Winkler	Not measured *in situ*	<0.1	End of Purge
	No Purge	Winkler		<0.1	End of Purge
	Fast Purge	Winkler	Not measured *in situ*	<0.1	End of Purge

Notes: [a]Elapsed time from start of slow-rate purging

Table 4-6. Sample Results

Sample Number	No Purge	Minimal Aeration	Fast Purge	Argon Head-Space	Dissolved Oxygen (Winkler)	Nitrate		Sulfate		Alkalinity		Chloride	Iron		Methane		BTEX	TMB[1]
					Field	Field	Lab	Field	Lab	Field	Lab	Lab	Field	Lab	with HCl	no HCl	Lab	Lab
					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
04-WCGP																		
04-WCGP		X			7.0	21.0	48	1575	1600	234	230	82	0.35	<0.025		0.48	1.3	
04-WCGP-FP			X		6.8								0.17	<0.025		0.34		
09-WCGP																		
05-WCGP		X			<0.1	2.9	0.9	425	380	908	840	190	17	36		10990	<1	
05-WCGP-FP			X		1.1								15	22		4970		
06-WCGP																		
06-WCGP		X			2.7	5.9	13	125	110	590	570	100	0.02	<0.025		9.32	2.4	
06-WCGP-FP			X		2.0								0.1	<0.025		6.04		
08-WCGP																		
08-WCGP		X			<0.1	3.1	0.1	<2	12	852	1000	140	18	33		630	4910	
08-WCGP-DUPL		X				2.0	0.1	<2	12	884	960	150	11	15		575	10300	
08-WCGP-TRIPL		X				2.0		<2		856			14			650		
08-WCGP-FP			X		<0.1								25	34		370		
08-WCGP-FP-DUPL			X											36		405		
08-WCGP-FP-TRIPL			X													365		
BH-02																		
BH-02		X			<0.1	2.1	<0.01	26	42	854	860	200	1.29	13		537	55300	
BH-02-FP			X											9.6		507		
BH-03																		
BH-03		X			<0.1	<0.5	<0.1	238	170	1130	1333	46	16	15		2050	40400	
BH-03-DUPL		X			<0.1	<0.5	<0.1	238	150	1160	1100	48	16	16		1910	38900	
BH-03-TRIPL		X			<0.1	<0.5		238		1140			16			2030		
BH-03-FP			X		<0.1	<0.5	<0.1	275	220	1200	1200	42	16	16		1450		
BH-03-FP-DUPL			X		<0.1	<0.5		288		1210			14			1340		
BH-03-FP-TRIPL			X		<0.1	<0.5		300		1180			15			1410		

[1]-Trimethyl Benzene

Table 4-6. Sample Results

Sample Number	No Purge	Minimal Aeration	Fast Purge	Argon Head-Space	Dissolved Oxygen (Winkler)	Nitrate		Sulfate		Alkalinity		Chloride	Iron		Methane		BTEX	TMB[1]
					Field	Field	Lab	Field	Lab	Field	Lab	Lab	Field	Lab	with HCl	no HCl	Lab	Lab
					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
GMW12																		
G12-XX-1		X			4.1		1.8		29.9		228	262		0.076		0.25	<4.0	<3.0
G12-XX-2		X			4.1	1.8		40		222			0.36					
G12-MA-4		X				1.5	1.7	30	28.5	222	225							
G12-MA-5		X				1.6	1.7	30	25.9	222	232							
G12-MA-6		X				1.8	1.7	31	26.5	218	239							
G12-FP-1			X		4.2									0.129		<0.53		
GMW8																		
G8-MA-1		X			1.0		1.2		32.2		180	127		<0.05		41.6	<4.0	<3.0
G8-MA-2		X				1.6		42		184			0.05					
G8-FP-1			X		2.0									<0.05		14.9		
GMW14																		
G14-XX-1		X			2.5		<2.0		44		355	9.6		2.83		<0.26	<4.0	<3.0
G14-XX-2		X				0.7		1		354			2.2					
G14-FP-1			X		2.2									3.41		1552		
GMW5																		
G5-XX-1		X			1.1		<0.2		59.2		379	285		2.51		69.2	16	<3.0
G5-XX-2		X				0.6		72		414			2.3					
G5-FP-1			X		1.4									2.99		36.8		
GMW-4																		
G4-NP-1	X				0.65									2.40		1001		
G4-NP-2	X				0.70									2.41		788		
G4-NP-3	X				0.60									2.39		890		
G4-MA-1		X			0.80		<0.2		0.5		399	245		5.62		4089	6393	75.2
G4-MA-2		X			0.60		<0.2		0.4		435			5.48	2316			
G4-MA-3		X			0.50		<0.2		0.3		391			5.79	2806			

[1]-Trimethyl Benzene

Table 4-6. Sample Results

Sample Number	No Purge	Minimal Aeration	Fast Purge	Argon Head-Space	Dissolved Oxygen (Winkler)	Nitrate		Sulfate		Alkalinity		Chloride	Iron		Methane		BTEX	TMB[1]
					Field	Field	Lab	Field	Lab	Field	Lab	Lab	Field	Lab	with HCl	no HCl	Lab	Lab
					mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
G4-MA-4		X				<0.5		<0.5		392			6.0		2515			
G4-MA-5		X				<0.5		<0.5		392			5.8			3145		
G4-MA-6		X				<0.5		<0.5		390			6.9			3366		
G4-FP-1			X		0.20		<0.2		0.6		416			4.22		3764		
G4-FP-2			X		0.10		<0.2		0.2		370			4.24		3412		
G4-FP-3			X		0.10		<0.2		0.3		430			1.36		3239		
G4-AH-1				X	0.60		<0.2		0.3		414			5.16		3152		
G4-AH-2				X	0.10		<0.2		<0.2		411			5.10		3087		
G4-AH-3				X	0.30		<0.2		<0.2		416			5.05		3356		
GMW-3																		
G3-NP-1	X				<0.1									4.52		15.8		
G3-NP-2	X				<0.1									4.54		15.4		
G3-NP-3	X				<0.1									4.48		13.7		
G3-MA-1		X			<0.1									5.93		49.1	20850	2236
G3-MA-2		X			<0.1		<0.2		0.5		261			5.99	53.1			
G3-MA-3		X			<0.1		<0.2		0.5		273			6.02	44.6			
G3-MA-4		X				<0.5		<1		252			7.2		75.9			
G3-MA-5		X				<0.5		<1		256			7.0			58.4		
G3-MA-6		X				<0.5		<1		248			6.5			49.7		
G3-FP-1			X		<0.1		<0.2		0.5		415					179		
G3-FP-2			X		<0.1		<0.2		0.3		280					209		
G3-FP-3			X		<0.1		<0.2		0.6		462					185		

[1]-Trimethyl Benzene

Section 5

DISCUSSION

SAMPLING METHODOLOGY

Laboratory Study

The micropurging sampling method using the Grundfos® pump produced the most representative results. However, even this method resulted in some loss of methane (13 percent) and iron (24 percent). A possible explanation for these losses is the exchange between the synthetic groundwater and the atmosphere in the well, with a subsequent loss of methane through volatilization and of iron through reaction with oxygen and subsequent removal of ferric iron precipitates in the in-line filter. Another potential mechanism of these losses is exchange of gases through the pump discharge tubing. However, this explanation is considered unlikely, considering the thickness of tubing (5/8-inch) and the short residence time in the tubing.

The greatest loss of methane occurred with the method employing the peristaltic pump. This is apparently a result of the sample degassing in the pump inlet tubing, evidenced by the formation of gas bubbles.

The method employing the high purge rate and bailer resulted in the most unrepresentative DO measurements. This is not surprising, given the increased opportunities for exposure of the groundwater to the atmosphere with this method in comparison with the micropurging methods. Such opportunities result from the greater drawdown in the well, the mixing that occurs with entry of the bailer into the water column, and the pouring of bailer contents into the sample container.

Field Study

On the basis of the laboratory studies, the baseline sampling method used in the field studies was the micropurging method, employing a downhole Grundfos® pump. The primary alternative method examined in the field studies was the fast purge/bailer technique, since this is the most commonly employed groundwater sampling method. The manner in which the bailer was used was not evaluated as a variable. All use of the bailer (for purging and sample collection) involved rapid lowering of the bailer into the well, resulting in splashing and agitation of water within the well bore. This was intended to be representative of commonly employed field techniques, in which minimizing the labor and overall project costs is often a primary consideration.

In conjunction with both the micropurging and fast purge/bailer sampling methods, samples were collected and analyzed for DO, iron, and methane, which are the parameters most susceptible to the effects of artificial aeration. Results are summarized in Figures 5-1 through 5-3.

With respect to DO measurements in the field studies, there was no clear trend between the micropurging and bailer methods (see Figure 5-1). The trend observed in the laboratory study (higher DO with the bailer method than with the micropurging method) was not consistently evident in the data from the two field study sites. Potential explanations for these results are:

- The drawdown in the wells (although limited) caused as much artificial aeration as purging/sampling with a bailer. Variability resulting from the accuracy and precision of the DO measurements exceeded any bias introduced with the different field methods.

- The sample with the fast purge/bailer method produced a significant amount of solids, and the oxygen introduced into the sample may have been consumed by these solids (e.g., through oxidation of geochemically reduced compounds, such as ferrous iron).

For iron concentrations greater than approximately 5 mg/L, the micropurging method consistently resulted in higher concentrations than the fast purge/bailer method (see Figure 5-2). Methane concentrations were generally, but not in every case, higher with the micropurging method than with the fast purge/bailer method (see Figure 5-3).

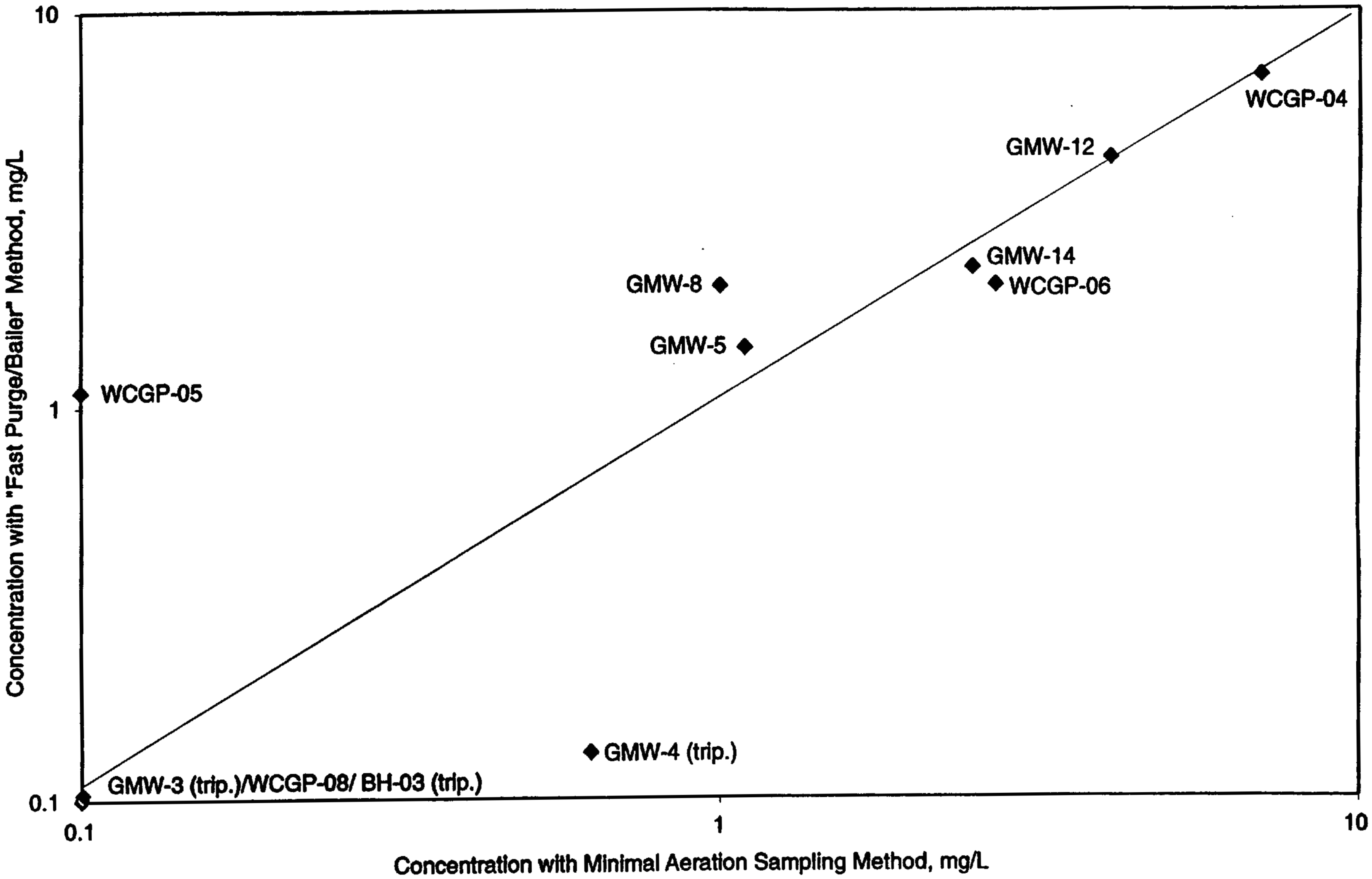


Figure 5-1. Field Evaluation of Sampling Methods - Dissolved Oxygen

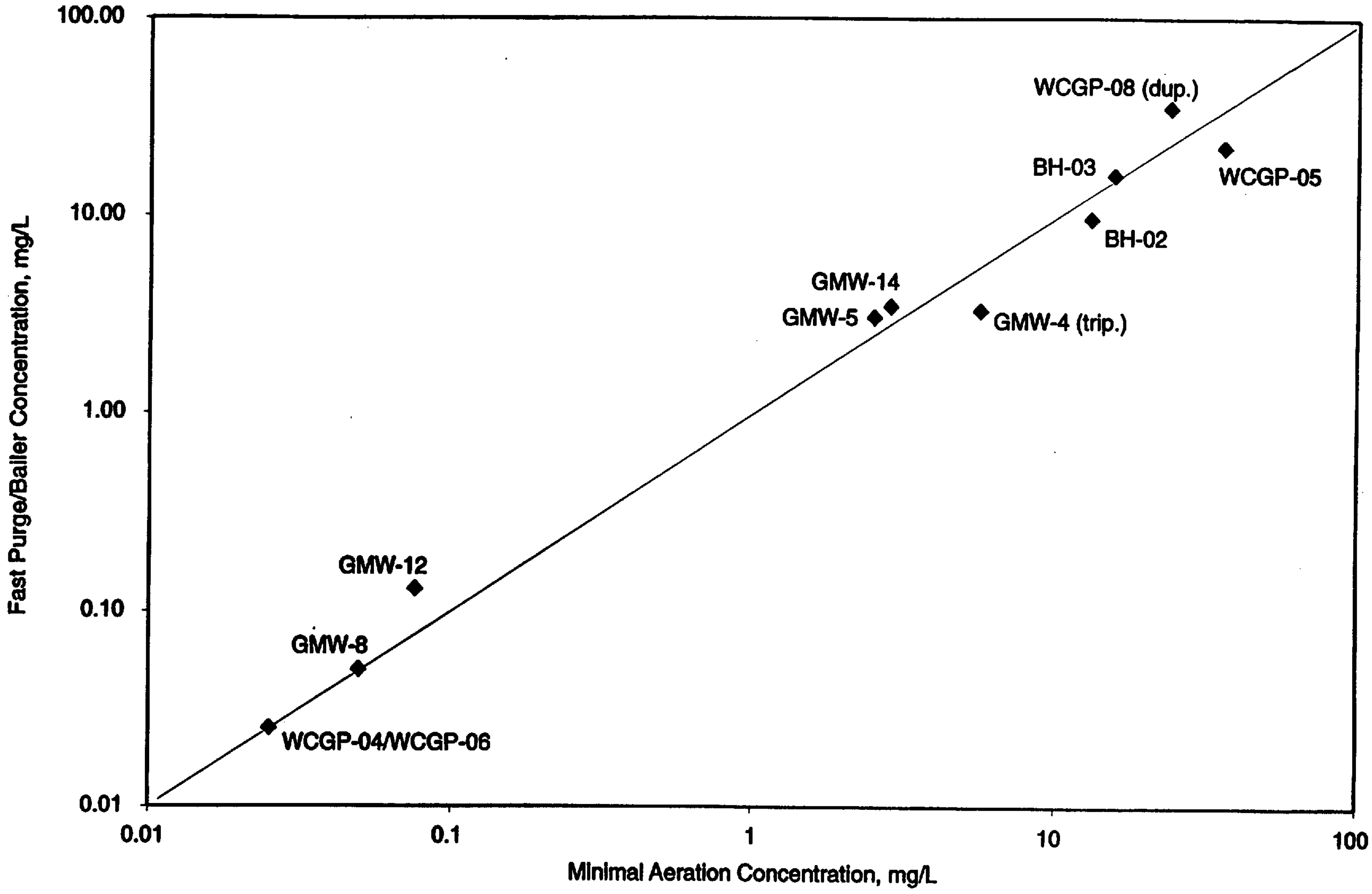


Figure 5-2. Field Evaluation of Sampling Methods - Iron

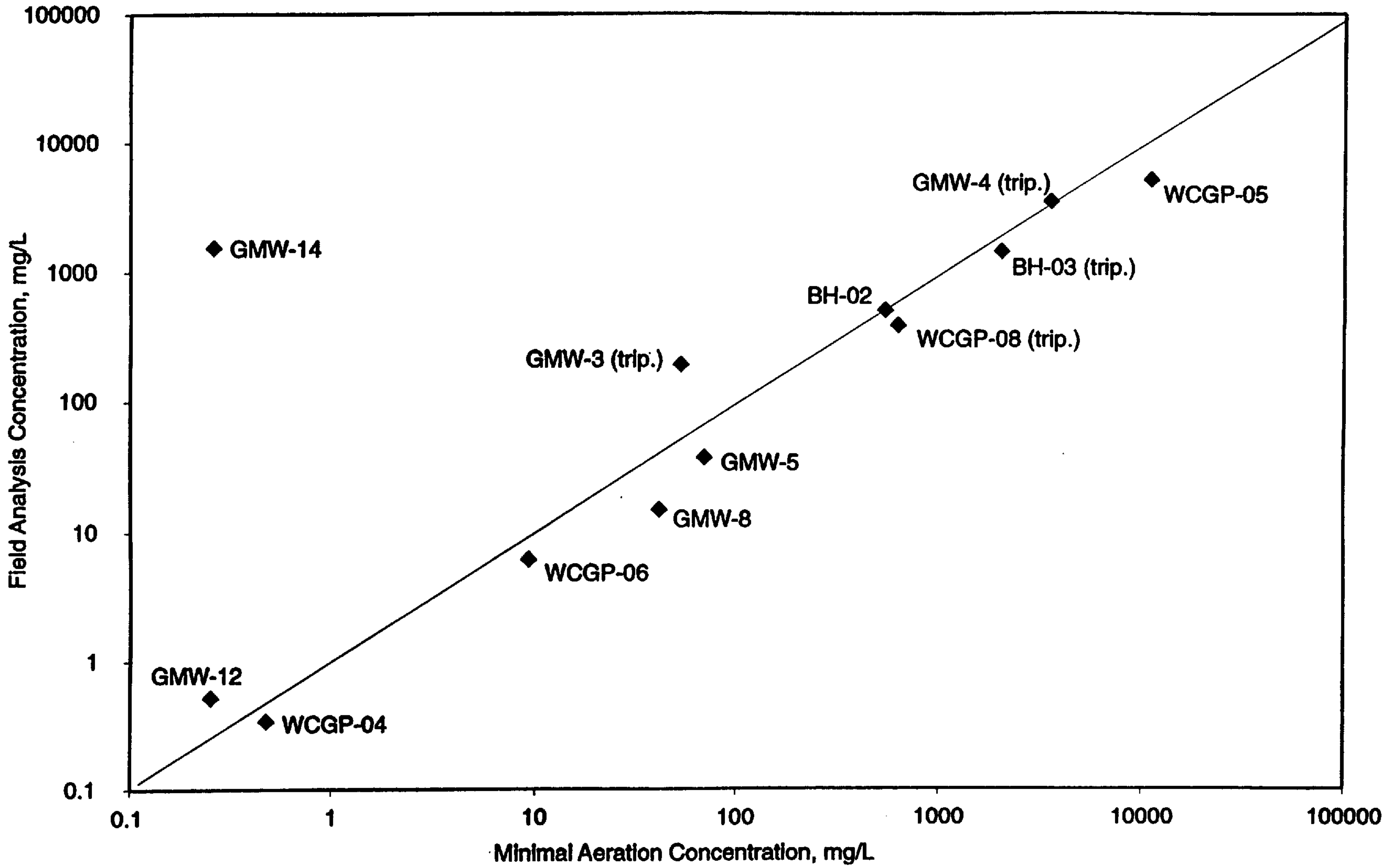


Figure 5-3. Field Evaluation of Sampling Methods - Methane

Triplicate samples for key geochemical parameters were collected from Well GMW-4 using four different sampling methods: no purge, micropurging, argon headspace, and fast purge/bailer. Results are summarized in Table 5-1. Sampling of Well GMW-4 with the argon headspace sampling technique was implemented with the expectation that there would be significant drawdown of the water level in this well during purging, and that the well would recharge at a very slow rate. In such a case, the argon head-space sampling technique will, reportedly, significantly reduce artificial aeration of the groundwater cascading into the well.

Table 5-1. Triplicate Sample Results for GMW-4

	Results of GMW-4 Triplicate Sampling[a]			
Parameter	No Purge	Micropurging	Fast Purge	Argon Headspace
Dissolved Oxygen, mg/L	0.65 +/- 0.046	0.63 +/- 0.14	0.13 +/- 0.053	0.33 +/- 0.23
Iron, mg/L	2.40 +/- 0.00924	5.63 +/- 0.143	3.27 +/- 1.53	5.10 +/- 0.0509
Methane, µg/L	893 +/- 98.4	3533 +/- 456	3472 +/- 247	3198 +/- 130
Nitrate[b], mg/L	-	<0.2	<0.2	<0.2
Sulfate [c], mg/L	-	0.4 +/- 0.09	0.4 +/- 0.2	0.1 +/- 0.2
Alkalinity, mg/L	-	408 +/- 21.7	405 +/- 29.0	414 +/-2.33

Notes:
[a] Results presented are the average values (of triplicate analyses) and the 95% confidence level.
[b] All results were below detection limits.
[c] There were two samples for sulfate/argon headspace that had results below detection limits; these were averaged as 0.

However, the drawdown created by well purging was only 5 percent of the wetted screen length, and the well recharged to the prepurging water level in a relatively short period of time. Results obtained with the argon headspace, micropurging, and bailer sampling techniques were generally comparable. The no purge sampling method produced lower iron concentrations and much lower methane concentrations than the other sampling methods.

Considering both the laboratory and field studies, there is evidence that the micropurging sampling methodology generally provides more representative geochemical results than the fast purge/bailer sampling technique. This is particularly true for ferrous iron and methane—two parameters that are particularly susceptible to artificial aeration. To evaluate whether the differences in results obtained with the micropurging and bailer methods are significant, it is necessary to consider the way the geochemical data are used in an intrinsic bioremediation evaluation.

As discussed in Section 2, geochemical data may be used qualitatively for consistency with predicted geochemical consequences of petroleum hydrocarbon biodegradation (see Figure 2-2, p. 2-4). Concentrations of key geochemical parameters for wells within and downgradient of a petroleum hydrocarbon source area are compared to background concentrations in Table 5-2. As indicated in Table 5-2, there was no significant difference between the micropurging and fast purge/bailer methods when the data are interpreted qualitatively for consistency with expected geochemical trends. The data produced using the micropurging and fast purge/bailer techniques at the two field sites were also used quantitatively for calculation of the expressed assimilative capacity (see Tables 5-3 and 5-4). The greater loss of iron and methane that occurs with the fast purge/bailer sampling method results in an underestimation of the expressed assimilative capacity relative to the micropurging method. At the Colorado Gas Plant site, the expressed assimilative capacity based on iron reduction and methanogenesis was 15.9 mg/L using the minimal aeration results, compared to 7.6 mg/L using the fast purge/bailer results, a difference of approximately 50 percent. However, the magnitude of the difference in the total expressed assimilative capacity was small, approximately 3 percent, because iron reduction and methanogenesis were not the dominant bioattenuation processes at the site. The differences between the two sampling methods with respect to the expressed assimilative capacity was even less pronounced for the Missouri UST site, owing to the similarity of methane concentrations obtained using the two sampling methods on the well exhibiting the greatest methanogenic impact.

It should be noted that bias introduced by sampling technique into the calculation of the expressed assimilative capacity is conservative because the bias results in an underestimation of the expressed assimilative capacity.

Table 5-2. Qualitative Data Evaluation-Micropurging Method Versus Bailer Method

		Micropurging Method			Bailer Method		
Well	Parameter	Background Conc. (mg/L)	Conc. in Plume (mg/L)	Conc. in Plume Relative to Background	Background Conc. (mg/L)	Conc. in Plume (mg/L)	Conc. in Plume Relative to Background
BH-03	DO	7.0	<0.1	↓	6.8	<0.1	↓
	Iron	<0.025	15.5	↑	<0.025	16	↑
	Methane	0.0005	2.0	↑	0.0003	1.4	↑
BH-02	DO	7.0	<0.1	↓	6.8	---	---
	Iron	<0.025	13	↑	<0.025	9.6	↑
	Methane	0.0005	0.54	↑	0.0003	0.51	↑
08-WCGP	DO	7.0	<0.1	↓	6.8	<0.1	↓
	Iron	<0.025	24	↑	<0.025	35	↑
	Methane	0.0005	0.62	↑	0.0003	0.38	↑
06-WCGP	DO	7.0	2.7	↓	6.8	2.0	↓
	Iron	<0.025	<0.0025	↔	<0.025	<0.025	↔
	Methane	0.0005	0.009	↑	0.0003	0.006	↑
05-WCGP	DO	7.0	<0.1	↓	6.8	1.1	↓
	Iron	<0.025	36	↑	<0.025	22	↑
	Methane	0.0005	11.0	↑	0.0003	5.0	↑
GMW-3	DO	4.1	<0.1	↓	4.2	<0.1	↓
	Iron	0.076	6.9	↑	0.129	---	---
	Methane	0.0003	0.05	↑	<0.0005	0.19	↑
GMW-8	DO	4.1	1.0	↓	4.2	2.0	↓
	Iron	0.076	<0.05	↓	0.129	<0.05	↓
	Methane	0.0003	0.04	↑	<0.0005	0.01	↑
GMW-4	DO	4.1	0.63	↓	4.2	0.17	↓
	Iron	0.076	5.6	↑	0.129	3.3	↑
	Methane	0.0003	3.5	↑	<0.0005	3.5	↑
GMW-5	DO	4.1	1.1	↓	4.2	1.4	↓
	Iron	0.076	2.3	↑	0.129	3.0	↑
	Methane	0.0003	0.07	↑	<0.0005	0.04	↑
GMW-14	DO	4.1	2.5	↓	4.2	2.2	↓
	Iron	0.076	2.8	↑	0.129	3.4	↑
	Methane	0.0003	<0.0003	↔	<0.0005	1.5	↑

Notes: Background for BH-03, BH-02, 08-WCGP, 06-WCGP, and 05-WCGP is 04-WCGP
Background for GMW-3, GMW-8, GMW-4, GMW-5, and GMW-14 is GMW-12.
DO results are Winkler Method results, Iron results are commercial laboratory results, Methane results are unpreserved samples.

Table 5-3. Expressed Assimilative Capacity—Colorado Gas Plant Site[a]

Parameter	Conversion Factor[b]	Micropurging				Bailer Method			
		Background[c]	Geochemically Reduced Zone	Difference	BTEX Equivalent	Background[b]	Geochemically Reduced Zone	Difference	BTEX Equivalent
Dissolved Oxygen	0.32	7.0	<0.1[e]	7.0	2.2	6.8	<0.1	6.8	2.2
Nitrate	0.25	21	<0.1[e]	21	5.3	—	—	—	5.3[f]
Iron	0.046	<0.025	36[d]	36	1.6	<0.025	22[d]	22	1.0
Sulfate	0.21	1575	42[e]	1533	321.9	—	—	—	321.9[f]
Methane	1.3	0.0005	11.0[d]	11.0	14.3	<0.0003	5.0[d]	5.0	6.5
TOTAL					345.3				336.9

[a] All concentrations in mg/L.

[b] Mass of toluene mineralized per mass of electron acceptor consumed or metabolite produced.

[c] Well 04-WCGP

[d] Well 05-WCGP

[e] Well BH-02

[f] Results for micropurging method.

Table 5-4. Expressed Assimilative Capacity—Missouri UST Site[a]

Parameter	Conversion Factor[b]	Micropurging				Bailer Method			
		Background[c]	Geochemically Reduced Zone	Difference	BTEX Equivalent	Background[c]	Geochemically Reduced Zone	Difference	BTEX Equivalent
Dissolved Oxygen	0.32	4.1	<0.1[d]	4.1	1.3	4.2	<0.1[d]	4.2	1.3
Nitrate	0.25	1.7	<0.2[d]	1.7	0.4	---	---	---	0.4[f]
Iron	0.046	0.076	6.2[e]	6.2	0.3	0.129	3.3[e]	3.2	0.1
Sulfate	0.21	27	0.4[e]	26.6	5.6	---	---	---	5.6[f]
Methane	1.3	0.0003	3.5[e]	3.5	4.6	<0.0005	3.5	3.5	4.6
TOTAL					12.2				12.0

[a] All concentrations in mg/L.

[b] Mass of toluene mineralized per mass of electron acceptor consumed or metabolite produced.

[c] Well GMW-12

[d] Well GMW-3

[e] Well GMW-4

[f] Results for micropurging method.

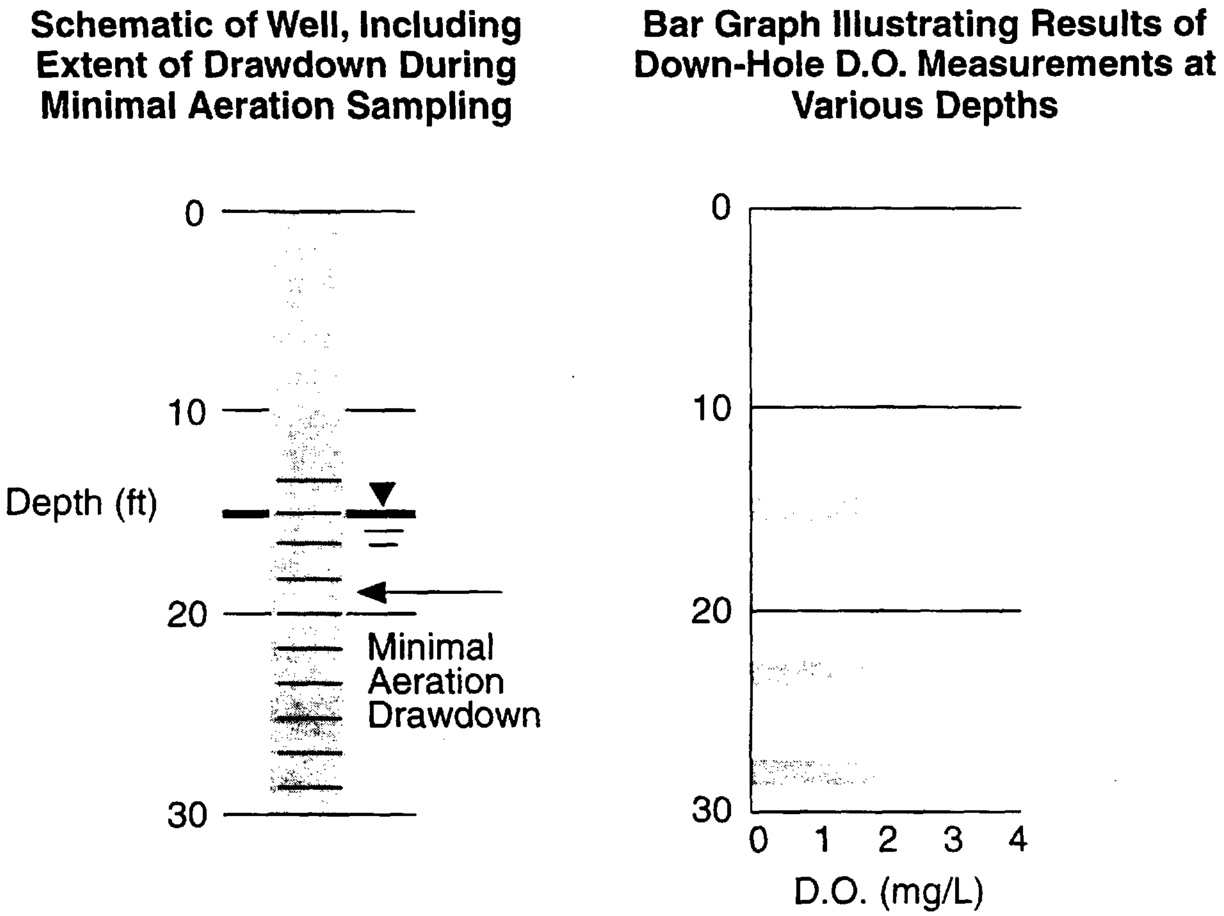
DO DETERMINATIONS

In the field studies, three methods for DO determinations were examined: (1) downhole DO surveys using a DO meter; (2) flow cell DO meter readings on groundwater produced using the micropurging method; and (3) Iodometric-Winkler analyses of groundwater samples produced using the micropurging method.

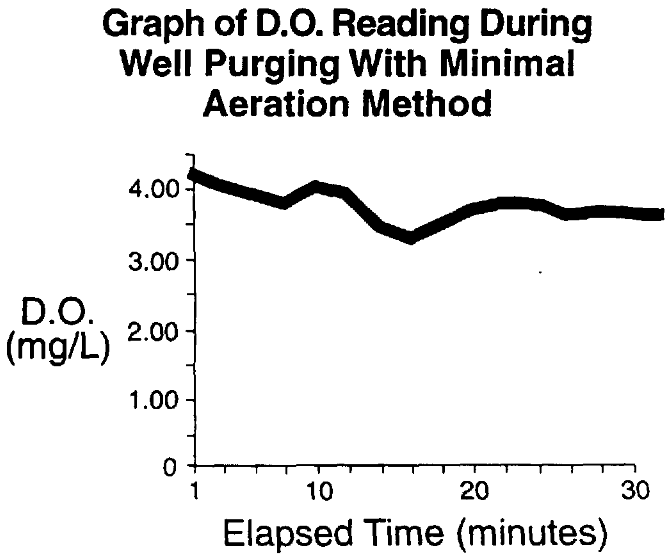
Representative results from the Missouri UST site are summarized in Figures 5-4 through 5-6, which present results for wells upgradient, within, and downgradient of the NAPL zone, respectively.

Representative Quality of Downhole Measurements with No Purging

Pre-purge, downhole DO surveys were conducted on several monitoring wells in the field studies. A DO gradient was consistently observed in wells within the plume of detectable concentrations of benzene, toluene, ethylbenzene, and/or xylene (BTEX). For these wells, the highest DO concentrations were measured just below the top of the water column, and measured DO concentrations decreased with depth. In addition, flow cell DO meter readings for these wells consistently showed a decline in DO as purging proceeded (see Figures 5-5 and 5-6). Collectively, these data indicate that for groundwater monitoring wells in geochemically reduced zones (i.e., within and immediately down-gradient of the BTEX plume), groundwater comprising the water column within a monitoring well typically contains higher DO than formation groundwater. This phenomenon was not observed for wells outside the geochemically altered zone surrounding the hydrocarbon release, as illustrated in Figure 5-4, summarizing DO data for a monitoring well located up-gradient of the fuel release at the Missouri UST site. For this well, DO meter readings remained relatively constant with depth, and flow cell DO readings remained relatively constant during purging. While the data suggest that water initially present in a monitoring well may contain higher DO than groundwater in the surrounding formation, downhole measurements in unpurged wells still appear valid for DO trend analysis, as long as the measurements are made at a consistent depth (see Figures 5-7 and 5-8).


Schematic of Well, Including Extent of Drawdown During Minimal Aeration Sampling

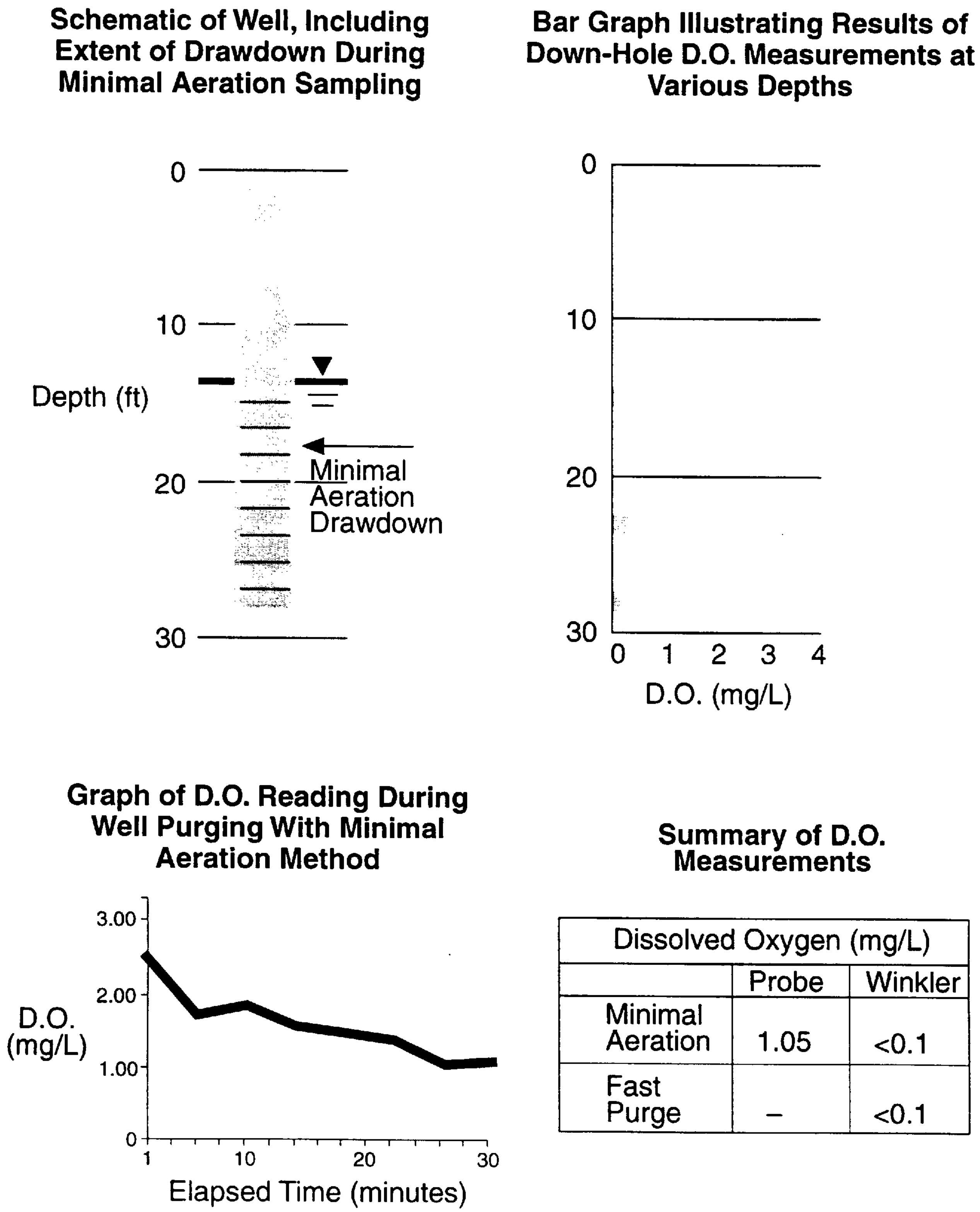
Bar Graph Illustrating Results of Down-Hole D.O. Measurements at Various Depths


Graph of D.O. Reading During Well Purging With Minimal Aeration Method

Summary of D.O. Measurements

Dissolved Oxygen (mg/L)		
	Probe	Winkler
Minimal Aeration	3.53	4.1
Fast Purge	–	4.2

Figure 5-4. Dissolved Oxygen Measurements - Up-gradient Well



Schematic of Well, Including Extent of Drawdown During Minimal Aeration Sampling

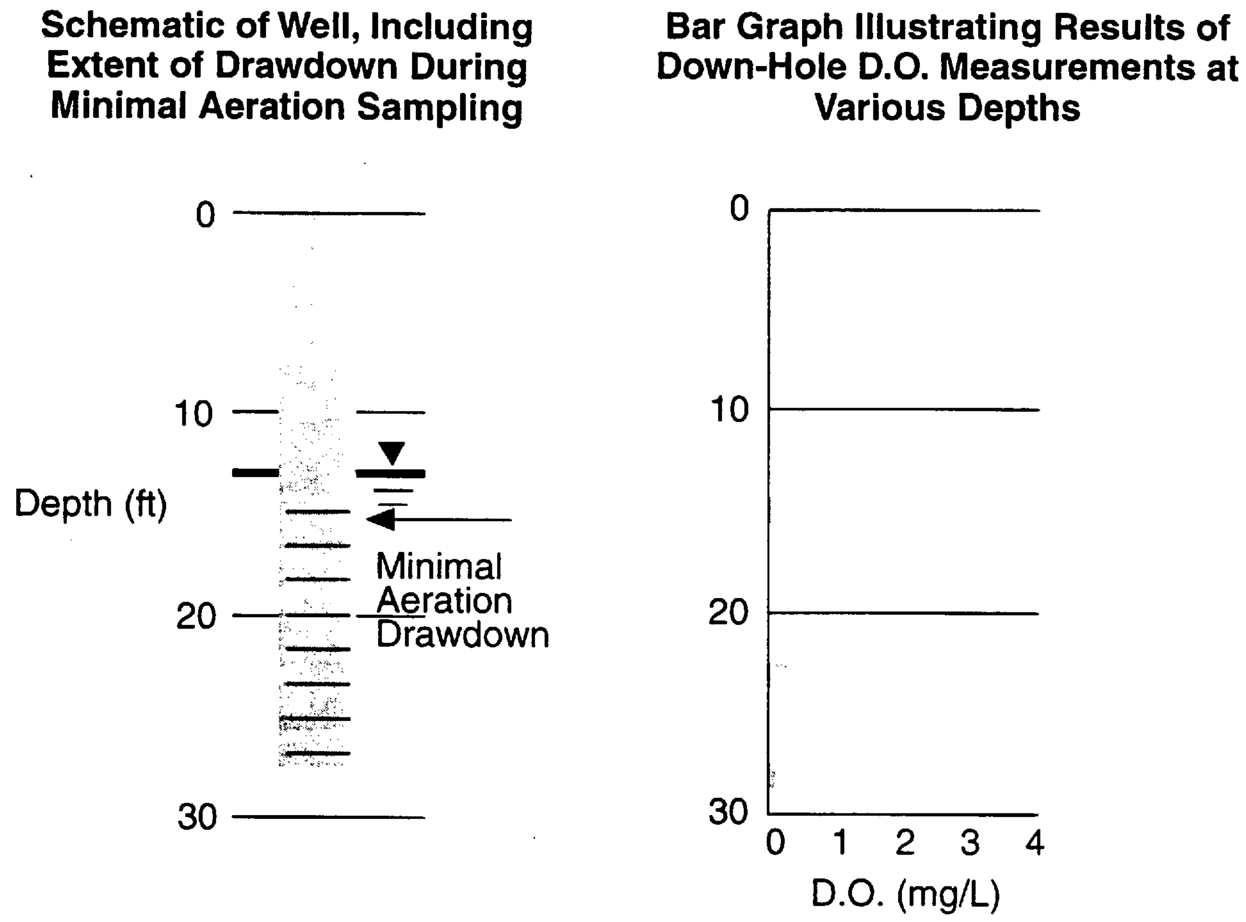
Bar Graph Illustrating Results of Down-Hole D.O. Measurements at Various Depths

Graph of D.O. Reading During Well Purging With Minimal Aeration Method

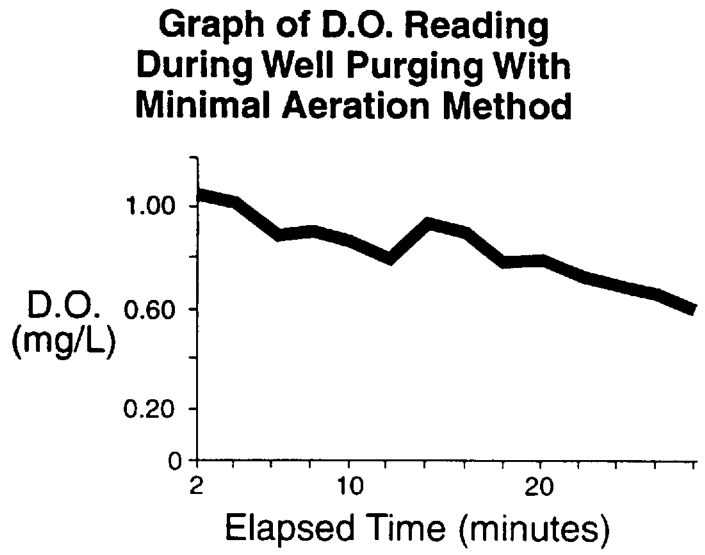
Summary of D.O. Measurements

Dissolved Oxygen (mg/L)		
	Probe	Winkler
Minimal Aeration	1.05	<0.1
Fast Purge	–	<0.1

Figure 5-5. Dissolved Oxygen Measurements - Well in Anaerobic Core of Plume


Schematic of Well, Including Extent of Drawdown During Minimal Aeration Sampling

Bar Graph Illustrating Results of Down-Hole D.O. Measurements at Various Depths


Graph of D.O. Reading During Well Purging With Minimal Aeration Method

Summary of D.O. Measurements

Dissolved Oxygen (mg/L)		
	Probe	Winkler
Minimal Aeration	0.58	1.1
Fast Purge	–	1.4

Figure 5-6. Dissolved Oxygen Measurements - Down-gradient Well

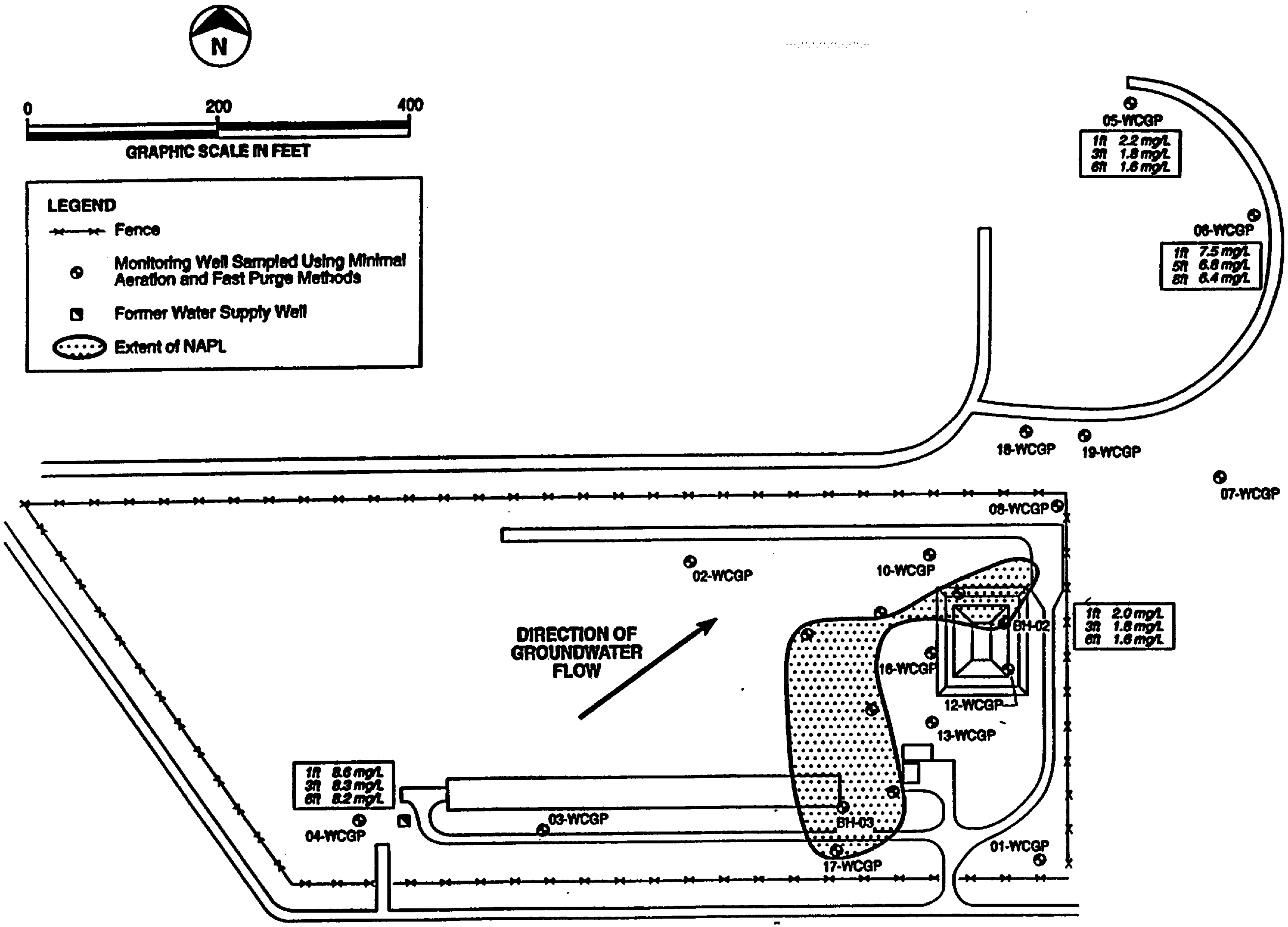


Figure 5-7. Dissolved Oxygen Profile - Colorado Gas Plant Site

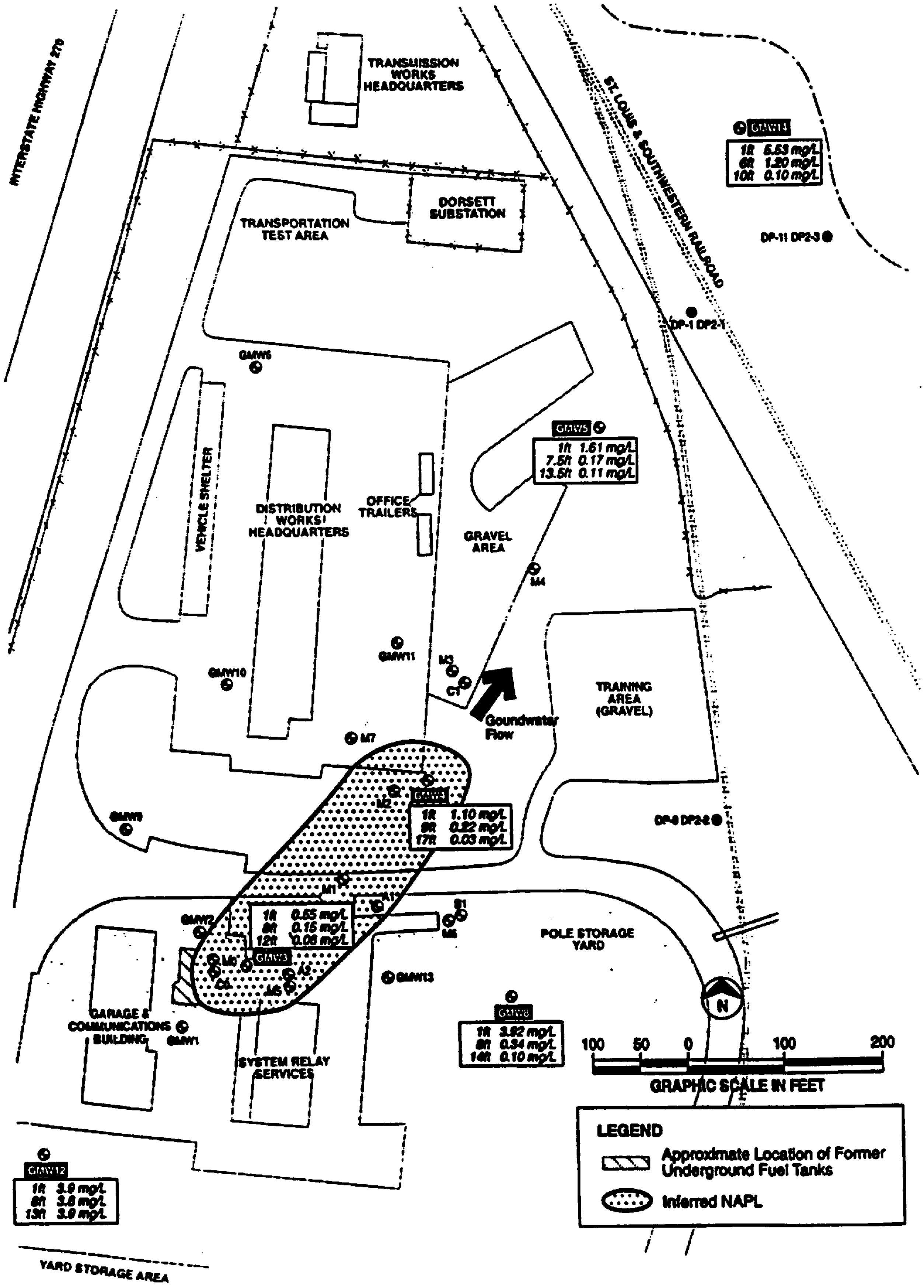


Figure 5-8. Dissolved Oxygen Profile - Missouri UST Site

Effect of Purging on DO

An assumption underlying the development of the micropurging methodology is that drawdown in a monitoring well will cause groundwater entering the well to cascade along the well screen, create a relatively high degree of contact between the groundwater and atmospheric air, and result in artificially high DO. This assumption was tested by varying the drawdown during purging and observing the effect on DO readings. This was performed on Well GMW-8 at the Missouri UST site. Because this well is within the BTEX plume, the DO in formation groundwater is anticipated to be very low. Results show a clear relationship of increasing DO with increasing drawdown, providing evidence that drawdown does result in groundwater aeration and alteration of sample geochemistry (see Table 5-5). However, in this case, the magnitude of the DO increase was not great. At maximum drawdown of 15 percent of the wetted screen length, the DO was still less than 1 mg/L.

Table 5-5. Dissolved Oxygen as a Function of Drawdown

Steady-State DO Measurements - Micropurging Sampling at MW-B1			
	Drawdown		
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

ANALYTICAL METHODOLOGY

Comparisons of field analytical methods with commercial laboratory methods for various geochemical parameters are graphically presented in Figures 5-9 through 5-12. The micropurging sampling technique was used to generate the samples for this comparison.

Iron

No clear trend is evident in the iron data (see Figure 5-9). There is a fair correlation between the methods. In some cases, the field method yielded a higher concentration than the commercial laboratory method; in other cases, the converse was true.

Sulfate

There was generally good agreement between field and commercial laboratory analyses for sulfate (see Figure 5-10). For sulfate concentrations above 1 mg/L, determined by field analyses, the field method generally yielded higher concentrations than the commercial laboratory, although there were some exceptions to this trend.

Nitrate

Overall, there was generally good agreement between field and commercial laboratory analyses for nitrate (see Figure 5-11). However, when commercial laboratory analyses indicated nondetectable nitrate concentrations, the field method in several instances indicated the presence of nitrate at concentrations in the range of approximately 0.5 to 2 mg/L.

Interference with the nitrate field method was observed for several samples. In several cases, the addition of the required reagent caused solids in the sample to precipitate out of solution, thus altering the degree of color in the sample and interfering with the color-based analytical process. In these cases, the obvious method interference led the field chemist to reject the data. Interference was also noted in some of the samples exhibiting the greatest discrepancy between field and commercial laboratory data (e.g., samples from BH-02 and WCGP-08).

Alkalinity

There was excellent agreement between field and commercial laboratory analyses for alkalinity (see Figure 5-12).

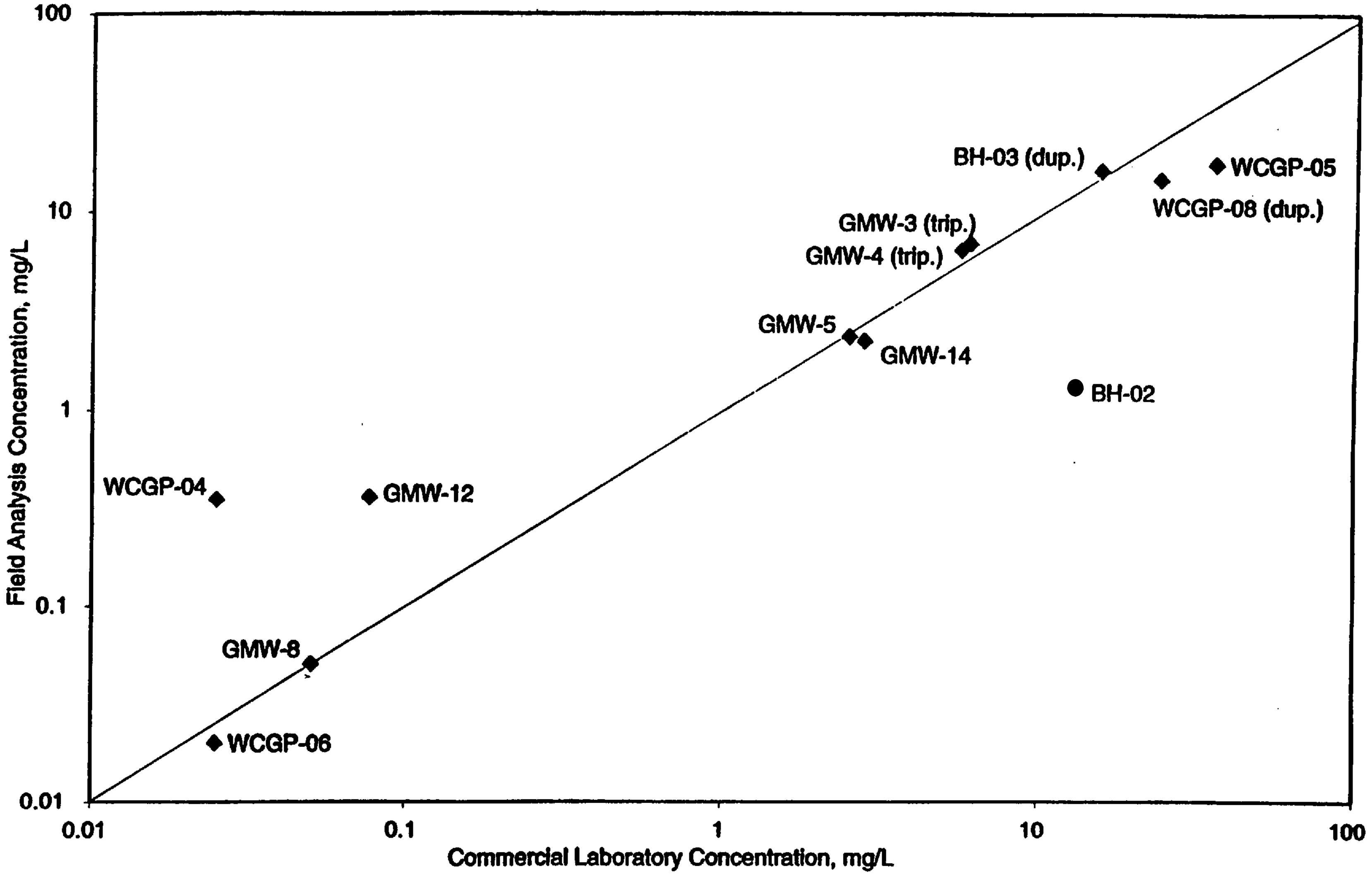


Figure 5-9. Comparison of Analytical Methods - Iron

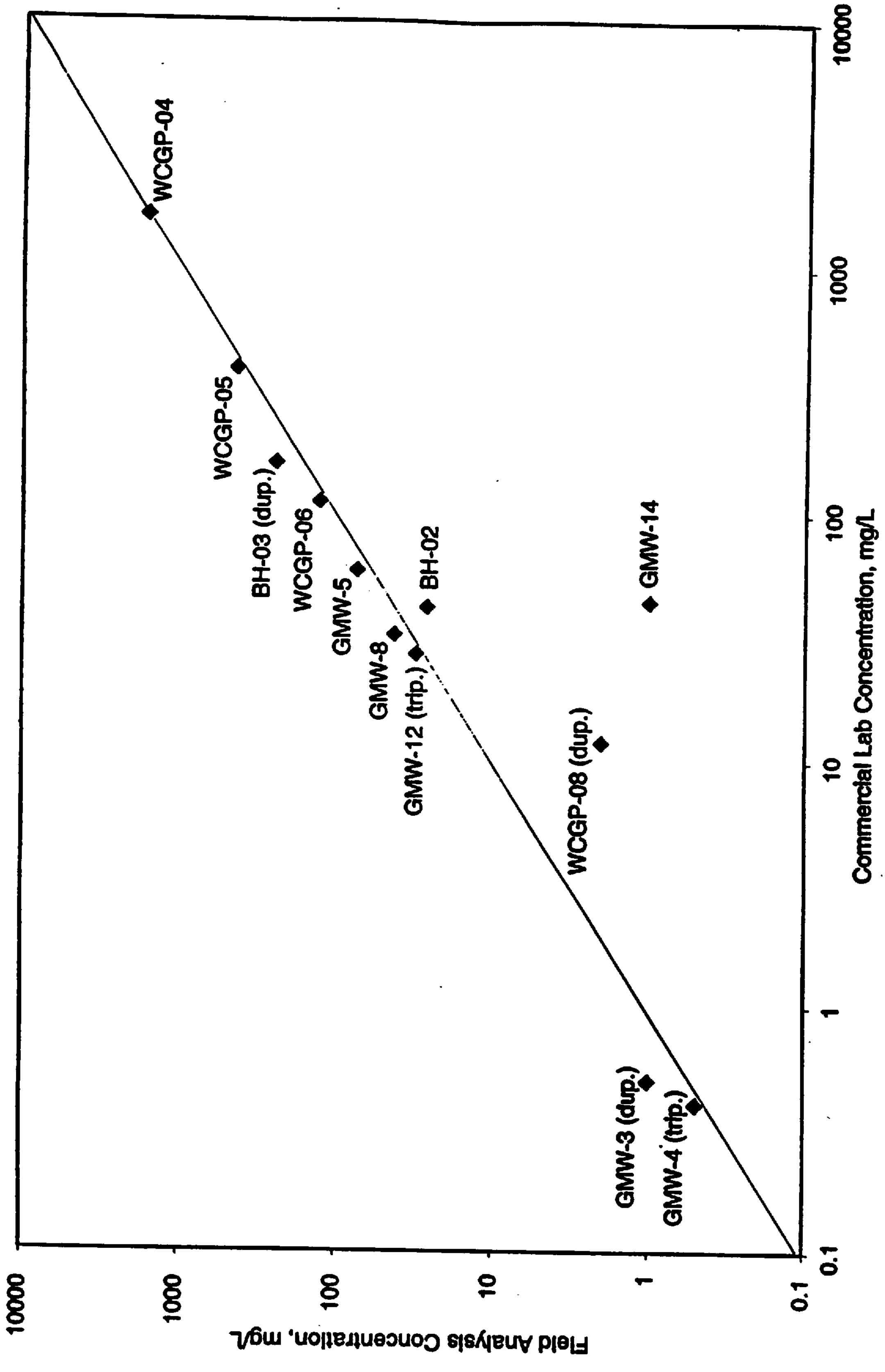


Figure 5-10. Comparison of Analytical Methods - Sulfate

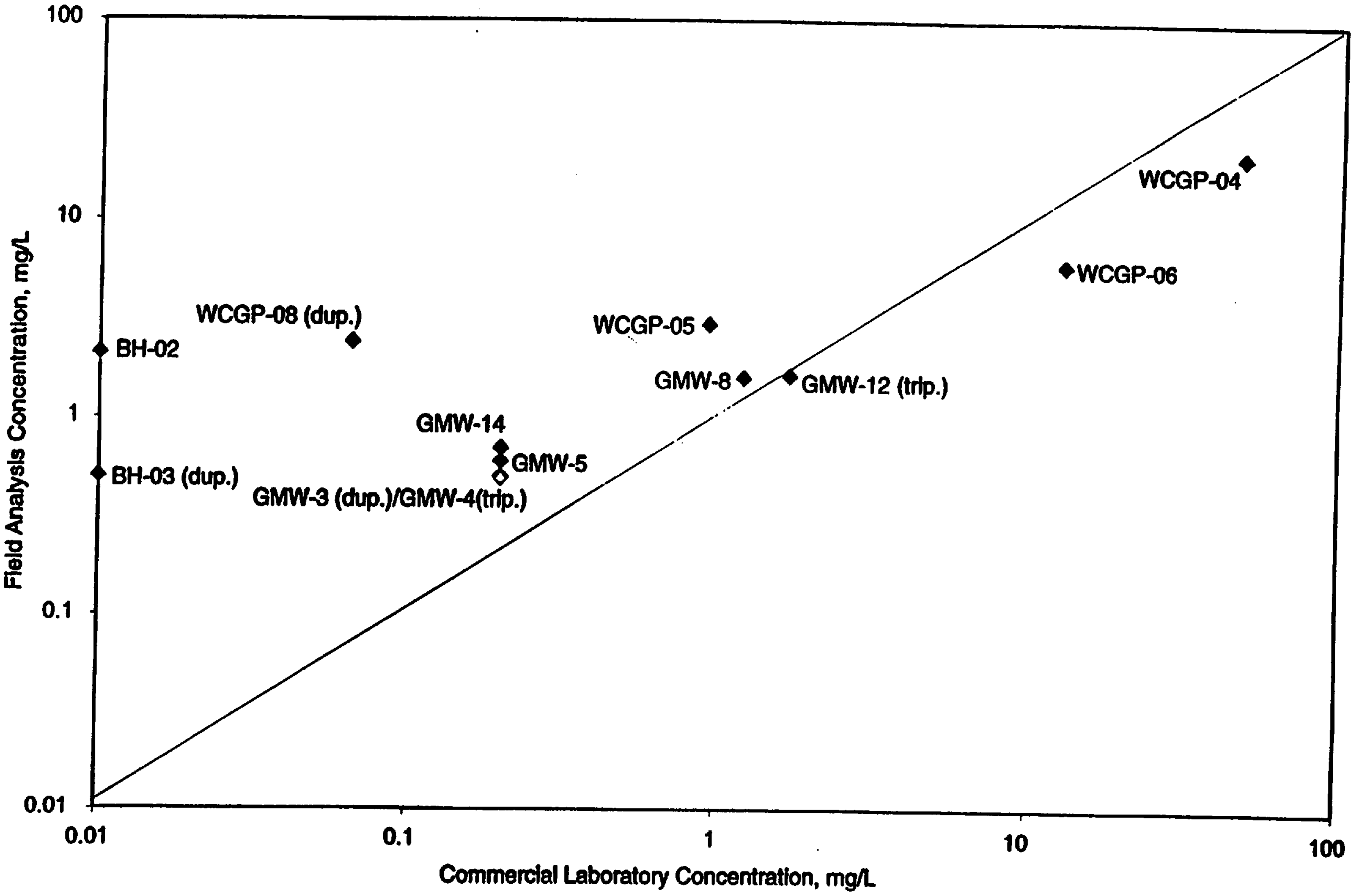


Figure 5-11. Comparison of Analytical Methods - Nitrate

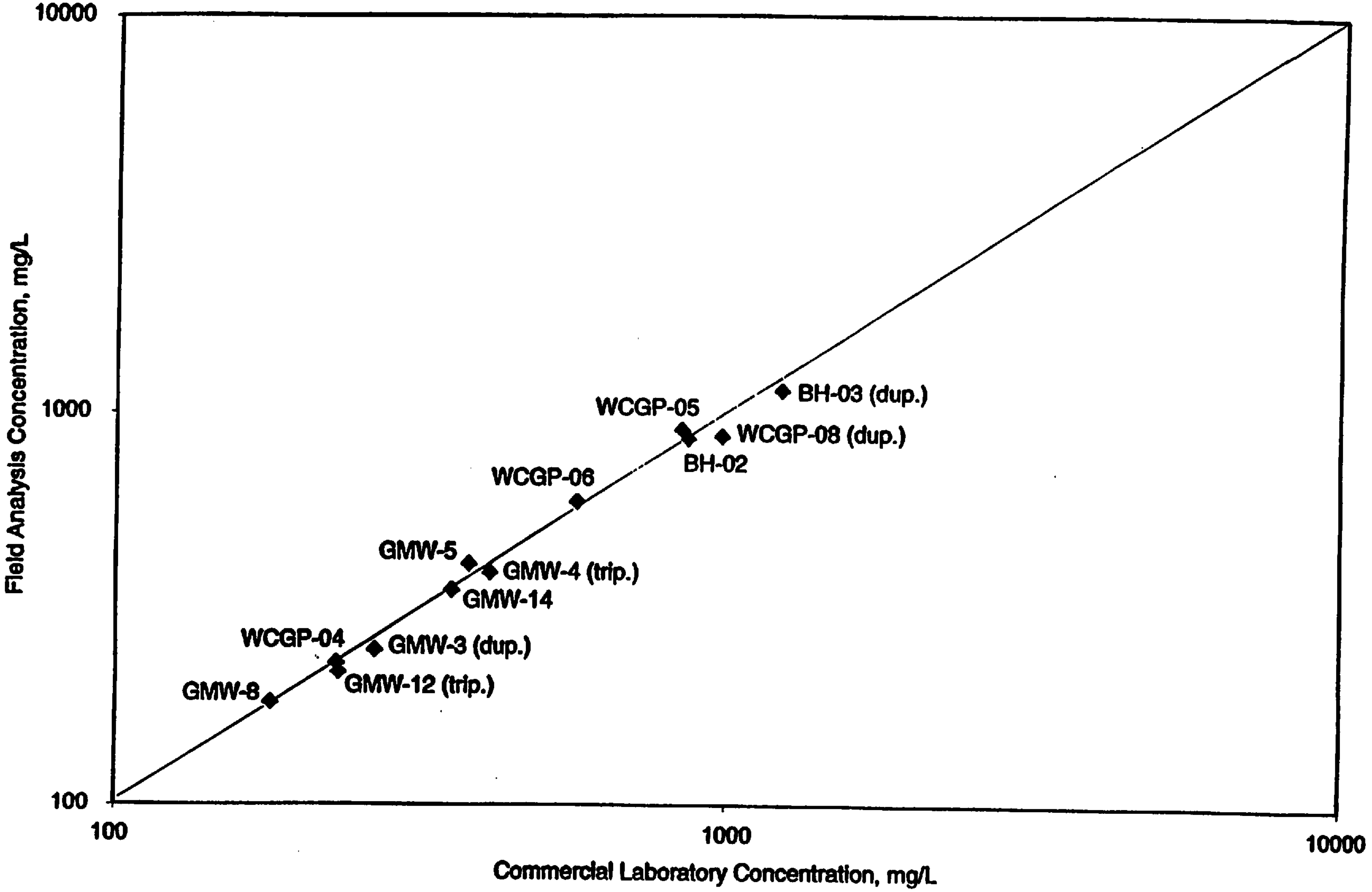


Figure 5-12. Comparison of Analytical Methods - Alkalinity

Discussion

Under certain conditions, there was an apparent trend of higher nitrate and sulfate concentrations reported with the field analyses relative to the commercial laboratory analyses. There are two potential explanations for this apparent trend:

- There was a microbially mediated loss of nitrate and sulfate during the longer sample holding time associated with the commercial laboratory analyses.
- The differences in reported concentrations reflect a difference between methods (colorimetry in the field analyses versus ion chromatography in the laboratory analyses) and/or the variability resulting from different chemists performing the analyses. In this case, there would have been no difference in the actual concentration of the sulfate or nitrate in the samples at the time of the analyses.

The data are not conclusive on which was responsible, or another possible explanation, for the apparent trend.

Assuming loss of nitrate and sulfate during sample storage actually occurred, the apparent nitrate loss was most pronounced in wells located within the BTEX plume. The commercial laboratory reported no detectable nitrate and the field analysis showed nitrate at concentrations of up to 2 mg/L. If there truly were up to 2 mg/L nitrate in the sample, using the commercial laboratory results would slightly overestimate the mass of hydrocarbon removed through microbiological nitrate reduction. When sulfate concentrations, determined through laboratory analysis, were higher than 1 mg/L, the field analytical results generally, but not always, yielded a higher sulfate concentration. Field analyses yielded sulfate concentrations that were from 10 to 40 percent higher than those reported by the commercial laboratory.

If there truly were loss of sulfate during shipment and storage of samples awaiting commercial laboratory analysis, the use of the commercial laboratory data could result in overestimation of the mass of hydrocarbon removed through biological sulfate reduction.

If, on the other hand, the geochemical data are used qualitatively as evidence of naturally occurring hydrocarbon biodegradation (as described in Section 2), the magnitude of the potential changes seen in nitrate and sulfate concentrations during sample shipment and storage would not be significant.

Section 6

FINDINGS AND RECOMMENDATIONS

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. This was confirmed during the project by both the laboratory and field studies.

The geochemical parameters of interest in characterizing intrinsic bioremediation that are most affected by contact with the atmosphere are DO, ferrous iron, and methane.

While certain groundwater sampling techniques can alter the samples' geochemistry, these changes may or may not significantly affect data interpretation. Based on the sites evaluated in this project, qualitative evaluations of geochemical data (e.g., spatial trend analyses) are not very sensitive to groundwater sampling techniques, as long as they are consistently applied at a given site.

If the data are used in quantitative projections of plume migration (e.g., input parameters in numerical modeling), results could be significantly affected. The potential for sampling methodology to significantly affect results will be highest for sites where the dominant biodegradation mechanisms are aerobic respiration, iron reduction, and/or methanogenesis.

The bias introduced by the sampling technique will generally be a conservative bias. The loss of iron and methane would result in an underestimation of the rate and/or magnitude of microbial activity (e.g., in the calculation of the expressed assimilative capacity).

Obtaining representative DO measurements is often one of the most challenging aspects of intrinsic bioremediation characterizations. For wells in zones geochemically affected by hydrocarbon releases, downhole DO measurements on unpurged monitoring wells often yield DO readings that are higher than the DO of formation groundwater. The minimal aeration method generally provides more representative DO measurements. However, in low-yield formations with unavoidable drawdown during purging, the minimal aeration method will also yield DO readings that are higher than the DO of formation groundwater.

In addition to the above sampling complications, there are idiosyncrasies with DO measurements and analyses. All methods used to measure DO in the field studies showed the presence of DO in groundwater produced from zones in which DO should have been absent, based on thermodynamic considerations (e.g., in zones exhibiting sulfate-reducing and/or methanogenic activity). Potential explanations for this observation include the following: (1) contact between groundwater and atmospheric air in the well; (2) mixing of groundwater from aerobic and geochemically reduced zones in the well; and (3) analytical interferences associated with high levels of dissolved iron. In many cases, the best evidence of anaerobic conditions is not near zero DO levels, which are hard to measure, but rather the presence of elevated concentrations of iron and methane.

The manner in which DO data will be used should be considered in determining the labor expended to obtain representative DO measurements. If the DO data are to be used for comparison with the expected trend of depressed DO within the aqueous phase hydrocarbon plume, a number of methods may suffice, including downhole DO readings on unpurged wells. If this method is used, DO readings should be taken at consistent depths. More quantitative uses of DO data merit consideration of more intensive DO measurement methods.

The project produced some evidence of apparent nitrate and sulfate loss during sample shipment and storage; however, the evidence generated in this project is not conclusive on this point. The difference in nitrate and sulfate concentrations reported in the field versus commercial laboratory analyses could be due to the differences in the analytical methods. As with the effects of sampling methodology, if loss of nitrate and sulfate truly occurs during sample storage, such loss may or may not be significant depending on data use. The most significant benefit of in-field analyses may not be reduced loss of electron acceptors during sample storage, but rather real-time data generation and evaluation that allow identification of data outliers and the potential need for re-sampling and/or re-analysis to provide a complete set of representative data.

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