

API SOIL & GROUNDWATER RESEARCH BULLETIN

*A summary of research
results from API's Soil
and Groundwater
Technical Task Force.*

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Evaluation of Sampling and Analytical Methods for Measuring Indicators of Intrinsic Bioremediation

Evaluating intrinsic bioremediation at a particular site often involves sampling and analysis of groundwater for geochemical indicators of naturally occurring biodegradation. This project was initiated by the American Petroleum Institute (API) to evaluate and compare the sampling and analytical methods used to characterize intrinsic bioremediation, with the ultimate objective of providing insight into preferred sampling methods and analytical procedures. Performance data on various sampling and analytical methods were generated in laboratory and field studies. A laboratory study was conducted to determine the effects, if any, of several commonly employed sampling techniques on the geochemistry of the associated groundwater samples. Field studies were then performed to provide further insight into potential biases associated with the sampling techniques. During these field studies, analytical methods were also evaluated by comparing results obtained from an off-site commercial laboratory with results obtained through use of in-field test kits.

Data from API studies and other studies were then used in the development of two documents that compare the various methods. These documents provide assistance in 1) selecting methods that best meet site-specific and project-specific needs, 2) implementing procedures to improve representative quality of data collected, and 3) interpreting data with respect to the potential biases introduced through the sampling and analytical methods used. This bulletin summarizes the information presented in API Publication Numbers 4657, *Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies* and 4658, *Methods for Measuring Indicators of Intrinsic Bioremediation: Guidance Manual*.

SAMPLING METHODS

Background

Removing several casing volumes of groundwater from monitoring wells prior to sampling (i.e., purging) has long been a standard practice. The underlying assumption has been that, owing to volatilization from stagnant well water, concentrations in samples collected without benefit of prior purging will be reduced; and that contaminant concentrations in samples collected subsequent to purging will be more representative of concentrations in the formation groundwater. A number of recent studies have examined this assumption.

Williams *et al.* (1996) compared purged and unpurged samples from 164 monitoring wells at 69 service station underground storage tank (UST) sites in southern California. Statistical t-test and Sign test procedures indicated that, within a 5% probability of error, BTEX and TPH concentrations in unpurged samples tended to be greater than in purged contrary to the standard assumption. Williams *et al.* (1996) also reference preliminary findings from a concurrent Western States Petroleum Association study of 101 UST sites, showing a similar result. Serlin and Kaplan (1996) compared volatile chlorinated organic concentrations in ten samples

collected after micropurging with corresponding concentrations collected after standard purging of two wells at a southern California site. Statistical paired t-test and Wilcoxon rank sum tests indicated no significant difference between the two data sets, again contrary to the assumption underlying the standard purging technique.

Four different sampling methods are evaluated and compared in the API Publication 4657 and 4658. These four groundwater sampling methods are briefly described and discussed below (See Table 1).

Conventional Purge/Bailer Method

The conventional purge/bailer method consists of purging the well of three to five well volumes (if possible), and then collecting groundwater samples through use of a bailer. An EPA guidance document (EPA, 1986) contributed to the establishment of this method as a widely practiced sampling method. The state-of-the-practice for groundwater sampling has been evolving away from this sampling method, based partly on data quality considerations and partly on the desire to reduce purge water volumes and groundwater monitoring costs (Shanklin *et al.*, 1995).

Micropurging Method

A micropurging method for collection of geochemical indicator data was adapted from EPA's micropurging protocol (EPA, 1992; Puls and Paul, 1995). API Publication Numbers 4657 and 4658 contain a standard operating procedure for this method. The key components of the micropurging sampling method are intended to reduce the potential for artificial aeration of, and entrainment of particulates in, the groundwater sample. This is accomplished by purging and sampling from the screened portion of the well, at a flow rate that approaches the natural flux of groundwater flow through the well, thereby avoiding excessive drawdown in the well. With this method, purging proceeds until the extracted groundwater exhibits steady-state measurements of key groundwater quality parameters (DO, pH, temperature, and ORP). When the extracted groundwater exhibits steady-state conditions for these parameters, it is assumed that the groundwater is representative of formation groundwater, and groundwater samples are then collected.

No Purging

As implied in the title, the no purging sampling method involves no purging of the well prior to sample collection or downhole measurements. The method is based on the following assumptions:

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

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

When done properly, the "no purging" method is very similar to the micropurging method. The most significant difference is that in no purging, it is assumed that the water initially present within the screened interval is representative of the formation groundwater; whereas with the micropurging method, actions are taken to confirm and document that water being sampled is representative of the formation groundwater.

Use of Inert Gas in the Well Bore

This method is a variant of other sampling methods in which an inert gas atmosphere is maintained in the headspace of the well during well purging and sampling. This method is based on the recognition that the formation groundwater is often in dramatic disequilibrium with the atmosphere, and that the presence of oxygen in the well headspace can result in artificial aeration of the groundwater both prior to and during well purging and sampling. Argon is used because it is heavier than air and will "sit" in the well at the air/water interface. As described by Borden *et. al.*, (1995), the inert gas method involves filling monitoring wells with argon gas before purging multiple well volumes using a submersible pump. Groundwater is then pumped through tubing to the surface and collected directly into sample bottles.

Summary Comparison

A comparison of the four sampling methods is summarized in Table 1. The methods vary in terms of data quality, complexity, level of effort, and cost.

Any of the methods will generally produce geochemical data of adequate representativeness, particularly when both of the following apply:

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

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

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

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

Summary Comparison of Sampling Methods				
Method	Data Quality	Level of Effort	Complexity	Cost
Micropruging	Generally yields more representative data than conventional purge/bailer method, particularly in low permeability formations where fast purging results in excessive drawdown	Increased level of effort compared to fast purge/bailer method; however, this may be offset by smaller purge volumes required. Dedicated pumps also decrease the level of effort for this method. The level of effort increases significantly on very low permeability sites.	More complex than conventional purge/bailer method. More equipment is required (e.g., a flow cell, a DO meter, a submersible pump, etc.) May also require some additional training of technicians.	This method generally requires more equipment and time than conventional purge/bailer approach. However, these factors can be offset by decreased purging and purge water disposal requirements.
Conventional Purge/Bailer	Generally yields data adequate for trend analyses. However, this sampling method cause increased aeration and turbidity of groundwater sample, which may significantly affect DO, iron, and methane data.	Generally requires a minimal level of effort. The time required to purge the required 3 to 5 well volumes and purge water disposal requirements are important considerations.	Generally requires the least amount of equipment and training of technicians.	Generally less expensive than other methods given minimal equipment and training requirements. However, purge time and purge water disposal costs can be reduced with other methods.
No Purge	Generally yields data adequate for qualitative (trend) analysis. DO, iron, and methane data may not be representative of formation groundwater.	Equipment requirements similar to the micropurging method. Does not require purging wells before sampling.	This sampling method is slightly less complex than the micropurging method, because it eliminates the monitoring required to determine completion of well purging.	This method is generally less costly than micropurging, because of reduced well purging and purge water disposal requirements.
Inert Gas in the Well Bore	Yields the most representative geochemical data, particularly at low permeability sites.	Requires the most equipment. May be faster than micropurging method on low permeability sites (Excessive drawdown not a concern.)	Requires the most equipment and the most training of technicians.	Generally the most costly due to increased equipment costs and the additional training of technicians required.

ANALYTICAL METHODOLOGY

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

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

outliers and the potential need for additional sampling and/or analyses to provide a complete and representative data set. Selection of a field or analytical laboratory should be based on individual project needs and constraints, considering the advantages and disadvantages discussed above.

For the geochemical parameters that seem to be most commonly included in characterizing intrinsic bioremediation at petroleum hydrocarbon sites, available methods for measurement and analyses are presented in Table 2.

CONCLUSIONS

Generally, there is no single sampling or monitoring method that will be the most appropriate method in every situation. Selecting the most appropriate method will depend on project-specific and site-specific considerations. Factors to be considered in selection of sampling and analytical methods include intended data use (e.g, qualitative versus quantitative), and the associated factors of complexity, level of effort, and cost. In many cases, selection of methods will involve a balancing of data quality and cost control objectives. API implemented a project to evaluate and compare various methods. The insights gained through this project are presented in API Publication Numbers 4657 and 4658.

Table 2. Methods for Key Geochemical Parameters

Parameter	Method Description	Typical Reporting Limits	Discussion
Dissolved Oxygen	Membrane Electrode Method, SM4500-0-G or EPA 360.1, Field Technique	0.6 mg/L	Most interfering substances experiences with other methods have little or no effect. Use flow through cell or down hole measurement. Polarographic probe requires constant flow through cell or gentle movement of probe during down hole measurement.
	Winkler Azide Modification, SM4500-0-C or EPA 360.2, Field Technique	0.2 mg/L	Many interferences, including ferrous iron above 1 mg/L and atmospheric oxygen. Requires field titration.
	HACH, EM Science or Equivalent; Winkler Azide, HRDO, Indigo Carmine, Field Technique	varies	Various interferences, including reduced compounds. Requires field spectrophotometer or titration.
	Headspace equilibration; GC-TCD, KS Kerr-175, Laboratory Technique	0.5 mg/L	Very difficult to prevent or limit atmospheric contamination of sample (sampling, storage, and analysis). Also provides methane and carbon dioxide data.
Nitrate	Ion Chromatography, SM 4110 or EPA 300, Laboratory Technique	0.2 mg/L	Very high concentrations of other ions can increase reporting limit. Lab pretreatment for organic removal may be required.
	SM 4500-NO ₃ ; Cadmium, titanous chloride, Hydrazine reduction. Field kits available from HACH, EM, Science or equivalent; Cadmium reduction. EPA 353.1, 353.3, Laboratory or Field Technique	0.2 mg/L	Requires nitrite compensation. Multiple interferences including ferric iron, chloride, oil and grease, chlorine. Field studies have demonstrated significant matrix interferences at hydrocarbon sites. Requires spectrophotometer.
	Nitrate ion specific electrode. SM 4500-NO ₃ -D. HACH or Equivalent, Laboratory or Field Technique	varies	Several interferences at varying concentrations, including: chloride, carbonate, bicarbonate, nitrite, sulfide, and organic acids. Sensitive to pH, use of buffer required.
Ferrous Iron	Inductively Couple Plasma (ICP) with acid digestion, SM 3120 B or EPA 200.7, Laboratory, Technique	0.04 mg/L	Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron.
	Flame Atomic Absorption Spectrometry (AA) with acid digestion, SM 3111 B or EPA 236.1, Laboratory Technique	0.12 mg/L	Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron. Typically more expensive than ICP. Susceptible to matrix interferences.
	Phenanthroline Method; Color Development. SM 3500 Fe-D, Laboratory or Field Technique	0.01 mg/L	Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron. Requires digestion by boiling sample. Color or organic matter requires drying, ashing and acid dissolving steps. Color development is pH dependent. Requires spectrophotometer or Nessler tubes.
	Ferrozine Method; Color Development. HACH Ferrozine, Laboratory or Field Technique		Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron. Digestion suggested if precipitate present. Color development is pH dependent. Requires spectrophotometer or Nessler tubes.
	Ferover Method; Color Development, HACH Ferover		Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron. Digestion required. Excess iron will inhibit color development. Extreme pH requires adjustment. Iron oxides require digestion. Requires spectrophotometer or Nessler tubes.
	TPTZ Method; Color Development HACH TPTZ		Total iron analysis performed on field filtered sample. Reasonably equivalent to soluble ferrous iron. Color development is pH dependent. Several metal elements interfere at low ppm levels to inhibits color development or create precipitate.

Table 2. Methods for Key Geochemical Parameters

Parameter	Method Description	Typical Reporting Limits	Discussion
	Ferrous Iron, HACH Phenanthroline, Field Technique		Requires dilution of sample to below 3 mg/l. Ferrous iron converts to ferric iron (not measured by test) within minutes. Requires spectrophotometer or Nessler tubes.
Manganese	Inductively Coupled Plasma (ICP with acid digestion), SM 3500-MnC or EPA 200.7, Laboratory Technique	0.04 mg/L	Total manganese analysis performed on field filtered sample. Represents soluble manganese.
	Flame Atomic Absorption Spectrometry (AA) with acid digestion, SM 3500-MnB or EPA 243.1, Laboratory Technique	0.12 mg/L	Total manganese performed on field filtered sample. Represents soluble Mn ⁴⁺ Typically more expensive than ICP. Susceptible to matrix interferences.
	PAN Method; Color Development, HACH, Laboratory or Field Technique		Total manganese analysis performed on field filtered sample. Represents soluble Mn ⁴⁺ Digestion required. Requires spectrophotometer or Nessler tubes.
Sulfate	Ion Chromatorgraphy, SM 4110 or EPA 300, Laboratory Technique	0.2 mg/L	Very high concentrations of other ions can increase reporting limit. Lab pretreatment for organic removal may be required.
	Turbidimetric Method. SM 4500-SO ₄ ^{-E} . HACH Sulfaver EPA 375.4, Laboratory or Field Technique	1 mg/L	Large quantities of organic or solids material may interfere.
Carbon Dioxide	Headspace equilibrium; GC-TCD, RS Kerr-175, Laboratory Technique	0.5 mg/L	Also provides oxygen and methane data.
Methane	Headspace equilibrium; GC-TCD, RS Kerr-175, Laboratory Technique	0.125 mg/L	Also provides oxygen and carbon dioxide data. Detection limit generally acceptable.
	Headspace equilibrium; GC-FID, Laboratory Technique	0.0005 mg/L	Superior sensitivity. Sensitive to all carbon containing compounds, creating possible test interference.
Alkalinity	Titration Method, SM 2320-B or EPA 3101, Laboratory or Field Technique	1 mg/L	Use pH probe or indicator. Phenolphthalein alkalinity end point is 8.3, total alkalinity end point is 4.5. Oily matter may coat pH electrode, creating interference to test.
Redox Potential	Electrometric probe measurement, SM 2580-B, Field Technique	NA	ORP reading is converted to Eh. Measure using flow cell or as down hole measurement. Use standard redox solutions to calibrate electrode system at the expected temperature of measurement.
	Bold indicates preferred method		

The documents provide information of value in method selection, method implementation, and data interpretation.

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