SAMPLING-METHOD-INDUCED VARIABILITY AND ITS INFLUENCE ON INTERPRETATION OF NATURAL ATTENUATION OF HYDROCARBONS

James Armstrong, Komex International Ltd., Calgary, Alberta, Canada
Kevin Biggar, University of Alberta, Edmonton, Alberta, Canada
Dean Morin, University of Alberta, Edmonton, Alberta, Canada
Kimberley McLeish, University of Calgary, Calgary, Alberta, Canada

ABSTRACT

Current protocols for use of monitored natural attenuation (MNA) to address subsurface contamination issues use a ‘lines of evidence’ approach. This approach relies on collecting representative groundwater samples for a series of analytes exhibiting a range of chemical reactivities. A study was conducted to see how a variety of groundwater sampling methods and well constructions might affect the resulting analyses at two sites. The results showed how local and sampling-induced variability might change interpretation of MNA activity.

RÉSUMÉ

Les protocoles utilisés actuellement pour l’atténuation naturelle surveillée afin d’aborder les problèmes de contamination souterraine utilisent une approche dite ‘ligne de preuves’. Cette approche se fie à la collection d'échantillons typiques d’eau souterraine pour une série de paramètres d’analyse faisant preuve d’un éventail de réactivités chimiques. Une étude faite afin de voir comment différentes méthodes d’échantillonnage d’eau souterraine et de construction de puits peut affecter les analyses qui en résultent sur deux sites. Les résultats démontrent comment la variabilité locale et par échantillonnage peut affecter l’interprétation de l’activité de l’atténuation naturelle surveillée.

1. INTRODUCTION

The concept of using natural attenuation (NA) to manage groundwater contaminant situations has rapidly gained widespread acceptance throughout the world over the past decade (NRC, 2000). Natural attenuation refers to the reduction in contaminant mass and/or concentrations due to a variety of naturally occurring reactions. For petroleum hydrocarbon releases, biodegradation is a key process, in that contaminant mass is destroyed.

Protocols for NA often use the ‘line-of-evidence’ approach, whereby appropriate groundwater monitoring data are collected to demonstrate: reduction in contaminant concentrations over space and time; and, characteristic patterns of biodegradation ‘indicators’ associated with electron-accepting processes. The patterns of indicators include depleted dissolved oxygen, nitrate and sulphate, and enriched dissolved iron, manganese and methane in plume wells compared to background wells.

Inferences about natural attenuation are made based on quantitative assessment of the indicator patterns. Concentrations of these chemical indicators can vary with time, space , and sampling methodology (Cozzarelli et al., 1999); (Vroblesky and Chapelle, 1994) (Smith et al., 1991). In particular, the adverse effect of inappropriate sampling practice relative to sample variability needs to be understood. Primary concerns are related to allowing atmospheric oxygen to contact the water during well recharge or sampling, and use of inappropriate screen completions. Current protocols still include sampling 3 m long screened sections using bailer/Waterra methods. If NA potential is to be evaluated using these data, better understanding is required of the impacts of sampling variability relative to known temporal and local spatial variability on the contaminants and geochemical indicator species (Cozzarelli et al., 1999).

A research consortium, CORONA (Consortium for Research on Natural Attenuation), was formed at the University of Alberta. This program involves a variety of office-, laboratory- and field-based investigations to examine natural attenuation of hydrocarbon contamination associated with upstream oil and gas facilities. Three field research sites were selected for CORONA. Data from Sites 1 and 3 are discussed here.

The work focuses on assessing how monitoring well configurations and sampling methods might influence decisions regarding potential for natural attenuation to achieve remediation goals. The effects being considered relate to interpretation of NA processes based on dissolved contaminant concentrations, and the geochemical indicators commonly used as supporting evidence of natural attenuation (dissolved oxygen, nitrate, manganese, iron, sulphate and methane).

Site 1 is an actively producing facility located in a remote part of west central Alberta. The contaminant situation is related to a former flare pit that had been excavated before the CORONA program started. Remaining subsurface contamination is related to hydrocarbon and salt that had migrated out from the former pit. The soil generally comprises sand, silt and clay layers, with the sand layers located mainly near the former pit. There are no ecological receptors in the immediate area.

Site 3 is an active gas processing facility located in southeast Alberta. The contamination source is interpreted to be accidental gas condensate releases related to a nearby fire-training facility. Fire training is continuing in this area, thus the possibility exists for further hydrocarbon release. The soil consists of fine silty sand to sandy silt. There are no nearby groundwater users in the area.

2. FIELD PROGRAM

A series of test well configurations were constructed in 2003 adjacent to an existing monitoring well within an area approximately 2.5m square (one location at Site 1 and two locations at Site 3). Each series comprised:

- one 3 m screen monitoring well (original installation);
- three or four direct push (DP) wells (0.7 m long screen) completed at 1 m depth intervals near the top, middle and bottom of the 3 m long interval described above;
- three or four multilevel sampling points (ML) using the Solinst Model 403 CMT (continuous multichannel tubing) (0.6 m sand-backfilled interval) completed at similar levels as the direct push wells; and,
- two replicates of the original 3 m screen well.

All of the new wells were installed in early July 2003, using an auger rig equipped with solid stem or hollow stem augers, depending on the soil conditions. The auger rig was also used for the direct push installations. The ML series was strongly affected by drilling and completion operations (Kim, 2003), based on initial data. Results from these wells will not be discussed further.

Groundwater sampling from these well clusters was conducted in 2003 (July, October) and 2004 (February, June) using the sampling methods described in Table 1 below.

Table 1. Summary of sampled wells and methods.

Well Code	Sampler	Well Screen Type
BH (original well)	Bailer	3 m screen
MW-1	Waterra	3 m screen
MW-1A, 1C	Dialysis	
MW-2	Waterra	3 m screen
MW-2A, 2C	BarCad	
DP-1, 2, 3	Peristaltic	0.7 m screen intervals at various depths

Sampling was conducted to evaluate the effects of purging using the conventional sampling systems (bailer and Waterra). Preliminary testing showed that purging either did not noticeably affect the results (Site 1), or provided less conservative results. Therefore all sampling systems were standardized by minimizing purging, and sampling within the screened interval.

2.1 Sampling Method Description

Groundwater samples were collected from the well clusters using a variety of methods, including:

- Bailer (used for historical site monitoring);
- Waterra (sampler installed to well bottom);
- Dialysis membrane diffusion samplers (quasi-discrete interval);
- BarCad argon gas lift system (quasi-discrete interval); and,
- Peristaltic pump (dedicated vacuum lift ~ 2-3 m).

The dialysis membrane diffusion samplers comprised 0.6 m long tubes filled with de-oxygenated, de-ionized water. Three samplers were installed in wells with 3 m long screens, near the top, middle and bottom of the water column.

The BarCad sampling system was deployed below a packer system over the similar interval as the dialysis samplers.

Waterra-based samples were collected from near the bottom of the water column in the well being used. Peristaltic pump samples were recovered using dedicated polyethylene hose installed to the midpoint of the screened interval in each respective well.

Bailed samples were recovered from around the midpoint of the water column in the monitoring well.

When collecting discrete and quasi-discrete interval samples, drawdown was monitored to prevent sampled groundwater contacting atmospheric air. Such contact would likely affect results due to possible de-gassing (carbon dioxide, hydrogen sulphide) and oxidation-reduction reactions. Many publications discuss relevant sampling-related issues (Yeskis and Zavala, 2002).

2.2 Sampling Protocol Description

Protocols for using dedicated bailers and Waterra pumps are well known and not repeated here. Dialysis samplers were stored in de-oxygenated water until deployment at the site. Each sampler was isolated within the well by attaching an upper and lower annular seal constructed of a circle of flexible PVC liner (40 mil) sandwiched between two acetate discs cut to with slightly smaller diameters than the PVC well casing. Dialysis samplers were left in a well for three weeks to equilibrate (based on tests by Morin, 2004). Upon recovery, sampler water was decanted into laboratory-supplied sample bottles.

The BarCad system operates as a gas lift system. A ceramic filter provides a 0.8 m long depth-discrete interval for water inflow. A one-way valve above the screen prevents the water surface from being drawn down into the screen. Mixing of the groundwater with atmospheric gases is further minimized by using pressurized argon to lift water in the riser pipe to ground surface. Care was taken to minimize any vigorous bubbling while using the gas lift system. These features overcome a potential deficiency of many sampling systems in slow recharge sediments (mixing of well recharge water with atmospheric oxygen). This system could not be used for winter sampling due to freezing potential (ambient temperature ~ -15 to -25°C).

2.3 Analytical Protocol

Dissolved oxygen (DO), electrical conductivity (EC), pH and temperature were measured in the field during initial sampling. Preliminary DO results indicated very little detectable DO, so these analyses were halted after the first sampling trip. Field-measured temperatures ranged from approximately 3 to 11 °C, depending on sampling date (typically, highest in early fall, and lowest in early spring).

All groundwater samples were immediately stored in ice-filled coolers prior to shipping to a commercial laboratory (Maxxam Analytics) for analysis. All samples were analyzed for major ions (calcium, magnesium, sodium, potassium, chloride, bicarbonate, carbonate and sulphate), general indicators (mineralization expressed as total dissolved solids, alkalinity, pH, electrical conductivity, total hardness), selected ions (nitrite+nitrate as N, dissolved iron and manganese) and target hydrocarbon compounds benzene, toluene, ethylbenzene and total xylenes (BTEX) and CCME hydrocarbon fraction F1 (C_6 to C_{10} – BTEX).

3. RESULTS

Chemical results were coded and tabulated according to Site, well location and sampling style. The data for each test area are reviewed in terms of spatial variability, local heterogeneity and lines of evidence supporting natural attenuation. In this paper, wells are compared using average values over the 3-4 sampling events for each of the well type-sampling method combinations.

Spatial variability is assessed using the three longer screen wells at each nest. Influence of sampling methodology is based on comparisons between samples collected using the different sampling methods.

Analytical results are presented as plots of multiple analytes for each well/sampling method combination. The plots are divided into three panels:
Left panel - discrete interval samples (DP, using peristaltic pump) are plotted from shallow to deep;
Middle panel - quasi-discrete interval samples are plotted for BarCad (shallow and deep) and dialysis membrane diffusion samplers (shallow and deep); and,
Right panel - integrated depth samples are plotted (two by Waterra (MW) and one by bailer (BH)).

3.1 Site 1

The data were assessed by comparing average values for each of the main ions and principal analytes used to assess natural attenuation by biodegradation. Data were collected approximately quarterly over one year.

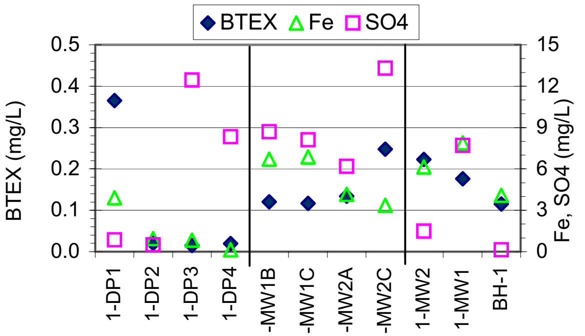

Figure 1. BTEX and indicator concentrations, BH-1 test area

The data in Figure 1 show that there is a relatively thin zone of hydrocarbon contamination identified only in the shallowest discrete interval sampler (1-DP1). Concentrations in the deeper discrete interval wells (1-DP2 to 1-DP4) were an order of magnitude lower. As is often seen during anaerobic biodegradation (Kennedy et al., 2001), the dissolved iron concentrations correlate directly with BTEX (high iron with high BTEX) and sulphate shows an inverse correlation (low sulphate with high BTEX).

Analyses from the 3 m long screened wells show more variability. Total BTEX concentrations in all combinations of wells and samplers were typically between the range identified by the discrete samplers. The BarCad samples (1-MW2A/C) tended to show an opposite trend of increasing BTEX concentration with depth, but the differences were within a factor of 2. Notably, the deeper BarCad samples were similar to the Waterra-collected sample from the 3 m well. In contrast, the diffusion sampler results (1-MW1B/C) were nearly identical at both depths, and slightly lower than the Waterra-sample from this well. The bailed samples were lower than either of the other replicate wells, but remained within a factor of 2.

Dissolved iron concentrations in the longer wells were all within a factor of 2. The data did not show any consistent trend, but were generally higher than in the DP wells.

Sulphate concentrations in the newer wells (1-MW-series) tended to match concentrations in the two deepest discrete interval wells. The BarCad samples (MW2A/C) showed an increase with depth that was not seen in the diffusion samplers (MW1B/C). Waterra samples from MW1 had notably higher sulphate concentrations than either of the other two longer screen wells (bailer in BH-1 and in MW2, both <2 mg/L).

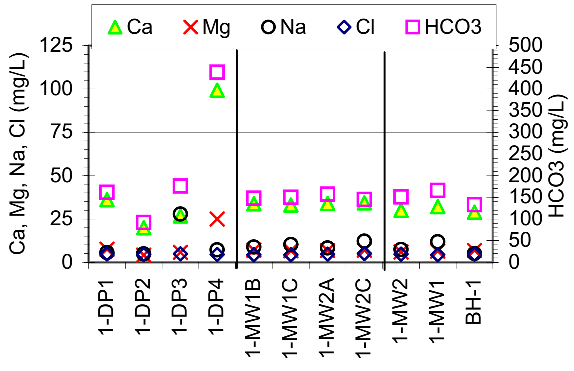

Figure 2. Main ion concentrations, BH-1 test area

The main ion data from the discrete interval samples (Figure 2) showed a notable increase in calcium, magnesium and bicarbonate in the deepest well (1-DP4). This well was in a deeper, different soil layer than the other wells. In contrast, all other samples (discrete interval, quasi-discrete and long screens) gave similar concentrations. As an aside, the higher sodium noted in 1-DP3 is mainly due to averaging with a relatively high value recorded in the first round of sampling. This effect is considered an artefact of geochemical stabilizing in the well after installation.

3.2 Site 3

This site had two detailed sampling locations. The BH-34 series of wells are located nearer the inferred contaminant source, with the BH-35 series located approximately 50 m downgradient. The sampling program at this site was conducted using a similar set of samplers and analyses as for Site 1. The sampling data are first assessed independently for each location (BH-34 and BH-35), and then in the context of plume movement. Data are presented using the same methodology as for Site 1.

3.2.1 BH-34 Test Area

The shallowest direct-push well had grout break through into the screened interval, so was left off the analytical program.

As at Site 1, BTEX samples showed a notable decrease with depth (34-DP2/3). Total BTEX concentrations obtained for the other sampling methods showed inconsistent concentration variations over a factor of 3, but within a similar order of magnitude as in the discrete interval samples (Figure 3). Dissolved iron concentrations were similar in almost all sampler/well combinations (3-6 mg/L), except the oldest well, BH-34 (increase by factor of 2 to 4). Historical monitoring data for this well showed much higher iron concentrations had been measured before the research program began.

Sulphate levels in the discrete interval samplers showed the inverse pattern from BTEX, characteristic of anaerobic biodegradation by sulphate reduction. The quasi-discrete samples showed somewhat consistent sulphate levels (factor of three), while concentrations in the longer-screened wells showed a wider range. Concentrations in these wells varied from 60 to 500 mg/L.

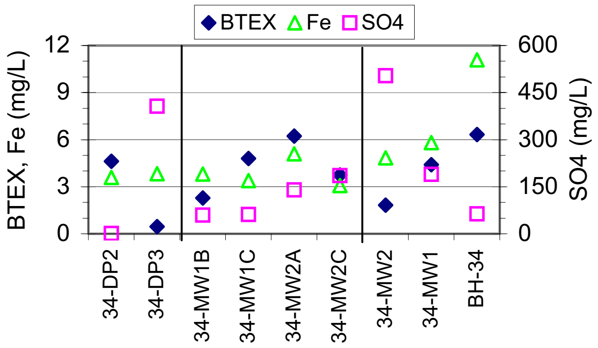

Figure 3. BTEX and indicator concentrations, BH-34 test area

The dialysis samplers (34-MW1B/C) and BarCad samples (34-MW2A/C) did not identify the same depth-dependent patterns or concentrations identified by the discrete interval samplers (34-DP2/3).

As an aside, recent additional sampling in BH-34 (July 2004) found that samples collected by bailer (1 pre-purge and 2 post-purge) and low-flow sampling methods all had similar concentrations of dissolved iron (7-8 mg/L) and sulphate (95 mg/L), except for one notably lower sulphate concentration (12 mg/L in the pre-purge bailed sample). In contrast all three bailed samples had higher total BTEX concentrations (up to a factor of 2) than the six, low-flow samples.

The other major ions from the BH-34 series showed several similar patterns (Figure 4). Chloride concentrations were relatively consistent for all samples, except a slightly lower concentration in the shallower discrete interval well. Calcium and magnesium (to a lesser degree) concentrations tended to show the same patterns as sulphate, possibly indicating a mineralogical control. All of the ions showed show some degree of vertical variation, increasing with depth in the discrete interval samplers. Except for the calcium-sulphate correlation, main ions in the other samples did not show any consistent pattern. Concentrations were generally within the range bounded by the discrete interval samples, except for a higher sodium level in the shallow BarCad samples (34-MW2A).

The bailer and Waterra samples typically also showed intermediate values, although the bailed samples (BH-34) had a lower calcium concentration than either of the Waterra samples (34-MW1 and 2).

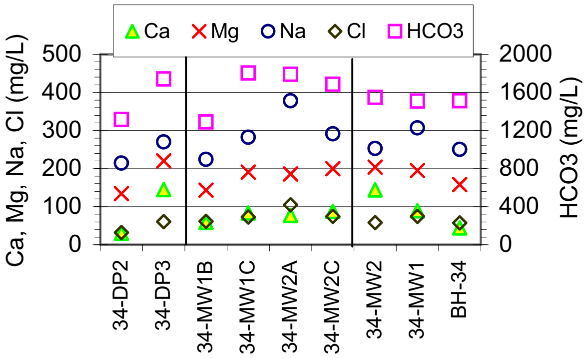

Figure 4. Main ion concentrations, BH-34 test area

3.2.2 BH-35 Test Area

Sampling data collected at the BH-35 area are shown below in Figure 5. As with the BH-34 well nest, the BTEX, iron and sulphate data show clear and consistent evidence of decreasing contamination and associated biological activity with depth. The three discrete interval samples in order of increasing depth (35-DP1, -2 and –3) show decreasing BTEX and iron concentrations, and increasing sulphate concentrations. In contrast samples collected from the longer screen wells show varying BTEX, iron and sulphate concentrations, but no clear patterns. As at the B34 well nest, the bailed sample had the highest BTEX and iron and lowest sulphate concentrations.

Compared to the discrete interval samples, the quasi-discrete interval samples (35-MW1B, 1C, 2A, 2C) had dissolved BTEX concentrations typically near the upper range of values. Dissolved iron and sulphate levels tended to be near the lower range. In contrast, the longer-screen samples (bailer > Waterra) varied over the full ranges of BTEX and dissolved iron concentrations expressed by the discrete interval well samples. These samples all had low sulphate levels.

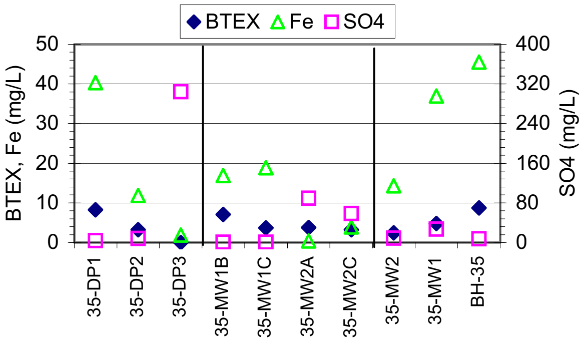

Figure 5. BTEX and indicator concentrations, BH-35 test area

The other main ions are plotted for the BH-35 nest in Figure 6. Relatively consistent concentrations were observed for chloride, sodium, and magnesium in all of the samples. In contrast, calcium and bicarbonate results show greater variability. In the discrete interval samples, calcium increases and bicarbonate decreases with depth. Greater variability is evident for both ions in the longer-screened wells, but not in the quasi-discrete samples collected from those same wells.

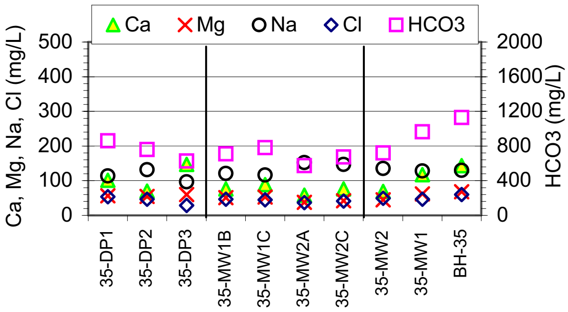

Figure 6. Main ion concentrations, BH-35 test area

Although the BH-34 and -35 nests are ostensibly in the same plume, there are numerous geochemical differences. The BH-34 wells typically had higher sulphate, bicarbonate, magnesium and sodium, but lower BTEX and iron concentrations. Further soil characterization is planned to improve understanding of local soil-groundwater geochemical interactions (Cozzarelli et al., 2001).

4. INTERPRETATION

As might be expected, chemical analyses collected from the discrete interval samplers provided greater vertical definition of the plume and related geochemical relationships. The results at both sites confirmed that the plumes are relatively thin vertically, are not getting pushed deeper by infiltration in downgradient areas, and have the characteristic geochemical indicator patterns for anaerobic biodegradation.

Samples collected from ‘conventional’ 3 m long screened wells were able to reproduce the same general patterns of hydrocarbon contamination and geochemical indicators of biodegradation. These results indicated thicker plumes than identified by the depth-discrete samplers.

Consistent patterns in main geochemical indicators of biodegradation (enriched iron and depleted sulphate relative to background) in all samples at each well nest meant that general inferences regarding natural attenuation were not affected. However, indicator concentrations varied locally (up to factor of 4 over 3 m) for similar well screen and sampling configurations. As an example, background levels at Site 3 are on the order of

10^3 mg/L sulphate and 10^{-1} mg/L iron. Samples from the BH-34 wells showed average sulphate levels ranging from 60-500 mg/L, and dissolved iron ranging from 3-11 mg/L. This range exceeded acceptable analytical variability of 10-50%, and may help bound what constitutes a locally-significant change in analyte concentrations in MNA assessments. This variability might also strongly affect geochemical modelling, particularly in regard to longterm MNA performance. Testing of mineralogy (Kennedy et al., 2001) and microbiology (Lovley and Anderson, 2000) might help explain these results.

Bailed samples generally provided a similar hydrocarbon concentration as the maximum level from the nest of discrete samplers, while Waterra samples tended to give lower values. This result is likely because of the sampling methodology used. The bailed samples were typically recovered from approximately 0.5 to 1 m below the groundwater surface, while the Waterra pumps had been installed to the bottom of the wells. As a result, bailed samples represented an averaged sample from within the water column, while Waterra samples extracted groundwater preferentially from the bottom of the well.

Sampling methodologies used to try and identify depth-discrete features in these same longer-screened wells were generally unsuccessful in this regard. Some of the samples showed vertical variability, but the patterns were inconsistent.

The main problem is likely related to installation of the sampling equipment leading to uncontrolled vertical mixing in the well and surrounding sandpack. This mixing would tend to average any vertical heterogeneity established in the well. The option of using a longer interval between installation and sampling was impractical for removing this effect. Although testing is not yet complete, it is anticipated that dialysis membrane deterioration would occur over the course of several months. The BarCad system was also not left in a given well, because of the expense of buying dedicated BarCad pumps.

The BarCad and dialysis membrane diffusion samplers appeared to give similar dissolved BTEX concentrations (same order of magnitude) as the other sampling methods. Dissolved iron concentrations were similar at two of the three areas tested, but were lower in the 35-MW1B/C (dialysis membrane) samples compared to the 35-MW1 (Waterra). Further effort is being applied to investigate if oxygenation of the de-ionized water placed in the sampler might cause this negative bias.

Use of argon as the compressed gas source for the Barcad sampling system reduced negative biases caused by oxygenation during sampling. However, this sampling system did not appear to provide any advantages for the sites investigated.

Main ion analyses (excluding sulphate) were generally quite insensitive to the sampling methods used. The discrete interval samplers showed some vertical heterogeneity, but similar scales of variability were provided by samples collected from the multiple longer-screen wells at each location.

5. CONCLUSIONS

Several combinations of groundwater sampling methods and well configurations were tested to evaluate potential influences on supporting evidence for natural attenuation. The use of short-screen wells provides better definition of vertical plume extent and concentration gradients than ‘conventional’ 3 m long screened wells.

Use of ‘quasi-discrete’ sampling methods in 3 m screened wells did not provide any better depth delineation than sampling directly from the wells. Longer equilibration times between installation and sampling might improve application of this approach.

Overall assessment of biodegradation potential with respect to natural attenuation was not affected by any of the sampling methods. However, relatively large variability between samples may cause difficulty if the data will be used for model-based projections regarding natural attenuation processes and possible changes.

6. REFERENCES

Cozzarelli, I.M., Bekins B.A, Baedecker M.J, Aiken G.R, Eganhouse R.P and Tuccillo M.E, 2001. "Progression of natural attenuation processes at a crude-oil spill site - I. Geochemical evolution of the plume." Journal of Contaminant Hydrology **53**(3): 369-385(17).

Cozzarelli, Isabelle M., Janet S. Herman, Mary Jo Baedecker and Jeffrey M. Fischer, 1999. "Geochemical heterogeneity of a gasoline-contaminated aquifer." Journal of Contaminant Hydrology **40**: 261-284.

Kennedy, Lonnie, Jess Everett and James Gonzales, 2001. Aqueous and Mineral Intrinsic Bioremediation Assessment (AMIBA) Protocol. Brooks Air Force Base, Texas, Air Force Centre for Environmental Excellence - Technology Transfer Division.

Kim, Kangjoo, 2003. "Long-term disturbance of ground water chemistry following well installation." Ground Water **41**(6): 780-789.

Lovley, D. R. and R. T. Anderson, 2000. "Influence of dissimilatory metal reduction on fate of organic and metal contaminants in the subsurface." Hydrogeology Journal **8**(1): 77-88.

Morin, Dean M., 2004. MSc Thesis, in preparation, University of Alberta.

NRC, (National Research Council), 2000. Natural Attenuation for Groundwater Remediation. Washington. DC, National Academy Press.

Smith, Richard L., Ronald W. Harvey and Denis R. LeBlanc, 1991. "Importance of closely spaced vertical sampling in delineating chemical and microbiological gradients in groundwater studies." Journal of Contaminant Hydrology **7**: 285-300.

Vroblesky, Don A. and Francis H. Chapelle, 1994. "Temporal and spatial changes of terminal electron-accepting processed in a petroleum hydrocarbon-contaminated aquifer and the significance for contaminant biodegradation." Water Resources Research **30**(5): 1561-1570.

Yeskis, Douglas and Bernard Zavala, 2002. Groundwater sampling guidelines for superfund and RCRA project managers. Chicago, IL, U.S. EPA**:** 53.