Anaerobic microbial processes in a petroleum plume in fractured rock, Northern Canada

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ABSTRACT
The chemistry of petroleum-contaminated groundwater in fractured rock was investigated at a former mine in the Northwest Territories, Canada, within a zone of discontinuous permafrost. There was strong evidence that ongoing anaerobic microbial biodegradation of hydrocarbons has been occurring in the groundwater. This appears to be linked with microbial reduction of sulfate, iron, manganese and nitrate. Stable isotope data provided further information on sulfate reduction.

RÉSUMÉ
La chimie des eaux souterraines pétrole-souillées dans la roche fracturé a été étudiée à un terrain qui était précédemment une mine dans les Territoires du nord-ouest, Canada, dans une zone de pergélisol discontinu. Il y avait de preuve presque irréfutable que la biodégradation microbienne anaérobie des hydrocarbures s'était produite dans les eaux souterraines. Ceci semble être lié avec la réduction microbienne de sulfate, de fer, de manganèse et de nitrate. Les données d'isotopes stables ont fourni les informations supplémentaires sur la réduction de sulfate.

1 INTRODUCTION
Relatively little is known about microbial processes in fuel-contaminated groundwater under cold climate conditions (Van Stempvoort and Biggar, 2009). Based largely on studies at temperate climate sites, it is generally understood that anaerobic microorganisms may play dominant roles in the intrinsic biodegradation of petroleum hydrocarbons in groundwater (e.g. Wiedemeier et al., 1999). Hydrocarbon-oxidizing anaerobes use various electron acceptors such as sulfate, ferric iron, manganese (IV) and nitrate. These natural processes may significantly reduce the environmental impacts of such contaminant plumes.

The Canadian Shield region comprises nearly half the area of Canada. In general information about groundwater in the Canada Shield region is very sparse, and the resulting science gap is further complicated by the fact that permafrost occurs in the subsurface throughout much of this region. There are critical information gaps related to the fate of contaminant plumes in groundwater in this region. Fuel plumes are some of the most common groundwater contamination problems at contaminated sites throughout Canada, including the Canadian Shield region.

This study addresses some of the above important science gaps. Specifically this paper reports evidence for anaerobic microbial processes in fuel plumes in groundwater at a Canadian Shield site in the Northwest Territories, within a zone mapped as having extensive discontinuous permafrost (Natural Resources Canada, 1995). A previous paper (Bickerton et al., 2007) summarized hydrogeological conditions at the site. This paper takes a more focused look at redox-sensitive species in the groundwater, specifically iron, manganese, sulfate and nitrate. The data reported here are based on a sampling program conducted in September 2007.

2 STUDY SITE
The Colomac mine site (Figure 1) is located 220 km northwest of Yellowknife, Northwest Territories. The site operated as an open-pit gold mine from 1989 to 1997 and...
the site is currently in the custody of Indian & Northern Affairs Canada (INAC) as a Federal Contaminated Site. The natural topography of site is rugged, with large areas of outcropping bedrock at surface. Unconsolidated surficial material includes thin, discontinuous till and fill. At least 24 releases of fuel have occurred at the site, mostly diesel in and around the main fuel tank farm (Iwakun et al., 2008). The fuel has contaminated groundwater within the underlying fractured bedrock in the area of the former fuel tank farm and machine shop (Figure 1). Monitoring of water levels within boreholes in the fractured rock indicate that regional groundwater flow from the tank farm and machine shop areas is generally towards Steeves Lake (Figure 1: see Bickerton et al., 2007). In 2004 INAC contracted the construction of an engineered, subsurface “barrier wall” between the former fuel tank farm and Steeves Lake. Its intended role was to produce a shallow zone of permafrost that would limit seepage of contaminated groundwater from the tank farm area towards Steeves Lake.

Analyses of groundwater sampled from discrete intervals in fractured rock in boreholes in and around the former fuel tank farm, the shoreline of Steeves Lake, and the machine shop in 2006 and 2007 (e.g., Bickerton et al., 2007) revealed extensive contamination by petroleum hydrocarbons. Bickerton et al. (2007) found that thermistors installed at the site indicated much less permafrost in the tank farm and machine shop areas than had been assumed by previous investigators of this site. However, temperatures within the subsurface remain low year-round (typically < 5°C), and, with the exception of the Steeves Lake shoreline area, there is extensive seasonal freezing of the subsurface to depths of 15 m or more.

3 METHODS OF INVESTIGATION

Groundwater samples were collected from discrete intervals isolated between packers (cf Bickerton et al., 2007) in selected boreholes in September 2007. Samples were analyzed for volatile hydrocarbons, major ions, as well as dissolved metals using standard methods.

For δ34S analyses, sulfate was isolated from samples by precipitation as barium sulfate. δ34S values of the dried barium sulfate were determined by combustion with an Elemental Analyzer (EA) coupled to a Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS). Isotope ratios are reported in delta (δ) notation in units of per mil (‰) relative to the Vienna Caron Diablo Troilite (VCDT) isotope standard.

4 RESULTS AND DISCUSSION

4.1 Dissolved Petroleum Hydrocarbons

September 2007 data indicate the ubiquitous presence of aromatic hydrocarbons in all groundwater samples collected from discrete intervals in the vicinity of the gasoline storage area (BH13), the machine shop (BH14, BH40), and near the shoreline of Steeves Lake (BH15, BH24, BH29 and BH30) (Figure 2). The highest concentrations in profile BH13 likely have resulted from gasoline spills in the area. High concentrations near the shoreline (BH15, BH29, BH30) are apparently the result of fuel plume migration from the tank farm and/or adjacent gasoline storage areas (Figure 1).

4.2 Sulfate: An Abundant Electron Acceptor in the Fuel Plume

Analyses of the samples collected in 2007 indicate that sulfate is the dominant anion and a potential electron acceptor in the contaminated groundwater in the fractured rock. Several lines of evidence (some not discussed in this paper) indicate that the sulfate is likely derived from the oxidation of sulfide minerals along fractures and exposed surfaces of the bedrock. Various sulfide minerals are known to occur in the bedrock at the Colomac mine site (Hearn, 1990; Shelton et al., 2000). The near neutral pH values of the groundwater and the dominance of calcium as the major cation in the groundwater (unpublished data), suggests that calcite dissolution in response to acid generation associated with sulfide oxidation has been an important secondary reaction.

Stable sulfur isotope ratio analyses (δ34S/32S) provide key evidence for the origin of the sulfate. Figure 3 shows a plot of δ34S versus sulfate concentrations for
groundwater samples collected in 2007. Three general patterns can be discerned from this data:

- The highest sulfate concentrations are associated with $\delta^{34}S_{SO_4}$ values that cluster around 0 ± 2 ‰.
- Overall there is an increase in $\delta^{34}S_{SO_4}$ values (i.e., $^{34}$S enrichment) with a decrease in sulfate concentration.
- The trend of $\delta^{34}S_{SO_4}$ versus sulfate concentration is not linear; there are outliers that have relatively low sulfate concentrations but little $^{34}$S enrichment.

![Figure 3](image)

Figure 3. Plot showing the relationship between the concentrations and the stable isotope composition of the sulfate in groundwater (see Figure 1 for well locations).

The association of high sulfate concentrations with $\delta^{34}S_{SO_4}$ values that cluster around 0 ‰ (Figure 3) suggests that the main S source of the sulfate has a similar isotopic composition. These isotope data are compatible with an interpretation that the sulfate is derived from the oxidation of sulfide minerals, which are known to occur in the shallow subsurface at the site, as noted in a preceding paragraph of this section.

The $\delta^{34}S_{SO_4}$ values at the Colomac site are similar to most $\delta^{34}$S values reported for pyrite and other sulﬁdes present in a similar gold-bearing rock near Yellowknife, approx. 220 km from the Colomac site, which range from -5.4 to +9 ‰, with a mean of 1.6 ‰ (Shelton et al., 2004; excluding the “late Stage III” results). Typically environmental oxidation of sulﬁde minerals occurs primarily in the vadose zone (e.g., Bain et al. 2000), because here dissolved oxygen can be replenished at a relatively fast rate via the air phase.

It is interesting to note that the dissolved sulfate in Steeves Lake that we sampled in September 2007 had a $\delta^{34}$S of 1.9 ‰, similar to the values we found for the zones of high sulfate concentrations in groundwater. This similarity suggests that the sulfate in Steeves Lake is also derived primarily from the oxidation of sulfide minerals, via ongoing weathering of rock and exposed sediments throughout the lake catchment.

4.3 Evidence for Microbial Reduction of Sulfate

The overall trend shown in Figure 3, an increase in $\delta^{34}S_{SO_4}$ values with a decrease in sulfate concentrations in groundwater, can most easily be explained as a result of microbial sulfate reduction. Many studies have shown that microbial sulfate reduction leads to $^{34}$S enrichment of the residual sulfate (e.g., Chambers and Trudinger, 1979). Sulfate reduction is known to be an important electron accepting process linked to degradation of hydrocarbon plumes in groundwater (e.g., Wiedemeier et al., 1999; Van Stempvoort and Biggar, 2008). It appears that this is also the case at the Colomac mine site.

![Figure 4](image)

Figure 4. Regression of all data in Figure 3 except the BH14 and BH24 data (outliers, see text for discussion).

If, during microbial sulfate reduction, the fuel-contaminated groundwater at the study site behaved as a closed system with respect to sulfate, with a uniform isotopic fractionation associated with this process, then the trend of $\delta^{34}S_{SO_4}$ versus sulfate concentrations would be expected to follow a Rayleigh-type fractionation equation (Hoefs, 1987), which would yield a linear trend in a plot such as shown in Figure 4 (excludes BH14, BH24 data). The departure of some of the field samples from the general trend (compare Figures 3 and 4) indicates that the sulfate in groundwater at our study site does not behave uniformly within a closed system. It appears that at least one other process has taken place concurrently with microbial sulfate reduction, resulting in...
some relatively low concentrations of sulfate which are less enriched in $^{34}$S that they would be under closed-system conditions.

Consistent with our conceptual model of the site, a process that could explain such a pattern is as follows: ongoing downward displacement of $^{34}$S-depleted “fresh” sulfate that had formed by sulfide oxidation from the vadose zone that mixes with “older” sulfate that has been undergoing reduction in the groundwater. Such ongoing replenishment of groundwater sulfate by recharge from the vadose zone has been reported in other hydrogeological settings (e.g., Van Stempvoort et al., 2007).

Based on the 2007 data reported here, the effect of the sulfate reduction process has been more pronounced in the shallowest groundwater in the machine shop area. For this reason, the groundwater sampled at BH40 has probably behaved more like a closed system with respect to sulfate than groundwater sampled from other boreholes, which may have received sulfate from the vadose zone locally via vertical recharge. This contrast in hydraulic setting may explain why BH40 has exceptionally positive $\delta^{34}$S values associated with some of the lowest sulfate concentrations.

The fact that sulfate concentrations are generally elevated in groundwater samples in the shoreline area (Figures 3 and 5) in spite of high petroleum hydrocarbon concentrations (Figure 2) suggests that this area is prone to significant ongoing vertical influx of sulfate from the vadose zone, or that microbial sulfate reduction is limited in this area. Perhaps such an influx is related to the presence of “a relatively extensive and permeable vertical feature” (fractured-related) in this nearshore area, as reported by Bickerton et al. (2007). Overall the unevenness of sulfate concentrations and isotope patterns in the shoreline area (Figures 3 and 5) indicates that the processes that affect the sulfate in this area are spatially variable in terms of rates and/or fluxes.

Estimation of microbial sulfate reduction rates in the groundwater at the study site is outside the scope of this paper. Given the complexity of the sulfate behavior in the fractured rock, a relatively open system (influx from vadose zone, losses by reduction), with seasonal temperature variations, and the fact that variable groundwater flow rates in the fracture rock are poorly understood, the task of estimating sulfate reduction rates would be very challenging.

4.4 Dissolved Iron and Manganese

Relatively high levels of dissolved iron and manganese were present in the groundwater sampled from discrete intervals in the fractured bedrock at the site, ranging up to 9.7 and 12.9 mg/L respectively (Figure 6). Given the near-neutral pH conditions of the groundwater, the dissolved iron and manganese are inferred to be mainly the reduced forms, ferrous ion and Mn(II), respectively. These data suggest that reduction of ferric iron and Mn(VI) are important electron-accepting processes in the groundwater, probably associated with microbial degradation of hydrocarbons in these fractures.

The dissolved iron may have formed by the reduction of iron oxide “stains” which were commonly observed on fractures/joints during drilling of rock at the site (e.g., EBA Engineering Consultants Ltd., 1988). These iron oxides
apparently formed as a result of oxidative surficial weathering processes.

Patterns of dissolved iron concentrations were different in the various boreholes – increasing with depth in some (e.g., BH13, BH14, BH15), decreasing with depth in others (e.g., BH30, BH40). These differences suggest there is more than one hydro/bio/geochanical process controlling ferrous iron concentrations in the groundwater.

Figure 6. Total dissolved iron and manganese in groundwater samples. (see Figure 1 for sample locations).

In boreholes where ferrous iron concentrations tend to be highest at shallow depths, iron reduction has apparently been a key electron accepting process in shallow groundwater, probably associated with microbial degradation of hydrocarbons. In contrast, in boreholes with increasing dissolved iron with depth, precipitation of ferrous iron may be occurring in the shallow zone, perhaps associated with sulfate reduction (cf. Section 4.3), which generates sulfide that may precipitate as FeS. In other places, ferrous iron may be reoxidized to ferric iron in shallow zones possibly coupled with denitrification (e.g., Tesfay and Korom, 2006). We suggest that this redox pair of reactions might have been important at BH15, where a significant plume of nitrate was observed in 2006, and in borehole BH8, which is located between the former fuel tank farm and the lake (Bickerton et al., 2007). In contrast, by 2007 much lower concentrations of nitrate were observed in discrete interval samples taken from the two shoreline boreholes (BH15, BH30; Figure 7, note that BH8 was not resampled in 2007). The anomalous high concentrations of nitrate in these boreholes in 2006 are inferred to be derived from explosives that were used to break up the bedrock during excavation of the “barrier trench” (near BH8) in September 2004. This interpretation is supported by detection of perchlorate in samples that had elevated nitrate (Figure 8, Bickerton et al., 2007).

Manganese concentrations in the groundwater increase upwards in most boreholes, suggesting it has been reduced and mobilized in shallow hydrocarbon plumes associated with microbial degradation of hydrocarbons. Manganese reduction has apparently been especially important in (or upgradient of) the shoreline area, based on the high concentrations observed in most samples from BH15, BH29 and BH30 (Figure 6).

4.5 Nitrate – Evidence for Denitrification

Very high nitrate concentrations were observed in discrete interval samples of groundwater from boreholes BH15 and BH30 near the shoreline of Steeves Lake in 2006, and in borehole BH8, which is located between the former fuel tank farm and the lake (Bickerton et al., 2007). In contrast, by 2007 much lower concentrations of nitrate were observed in discrete interval samples taken from the two shoreline boreholes (BH15, BH30; Figure 7, note that BH8 was not resampled in 2007). The anomalous high concentrations of nitrate in these boreholes in 2006 are inferred to be derived from explosives that were used to break up the bedrock during excavation of the “barrier trench” (near BH8) in September 2004. This interpretation is supported by detection of perchlorate in samples that had elevated nitrate (Figure 8, Bickerton et al., 2007).
this nitrite is uncertain. Perhaps it formed along with nitrate by partial oxidation of explosive-derived NH$_3$. Some of the nitrite may have formed during denitrification, though generally denitrifying bacteria will also use nitrite as an electron acceptor, rather than releasing it to the environment. In any case, the near absence of nitrate (and nitrite) in 2007 in the same wells that had high concentrations in 2006 (Figure 8) suggests that denitrification was an important process in the groundwater in 2006-07. It is also possible that advection flushed a significant amount of nitrate from the fractures downgradient of the barrier trench by 2007.

5 SUMMARY

The data provided in this paper give strong evidence that anaerobic microorganisms are active in fuel-contaminated groundwater in fractured rock (Canadian Shield) at the study site. The evidence indicates that these microbial processes include the reduction of the following electron acceptors: sulfate, ferric iron, manganese (IV) and possibly nitrate. It is likely that such anaerobic processes play an important role in the biodegradation of dissolved petroleum hydrocarbons in the groundwater at this site. Further information and analysis would be required in order to infer rates of these processes in the groundwater at the study site, and to understand the specific relationship of these processes to degradation of the fuel plume.

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