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# An investigation of gas seeps and aquatic chemistry in Fisherman Lake, southwest Northwest Territories

I. Rod Smith, Stephen E. Grasby, and Larry S. Lane

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**Abstract:** Concerns about water quality in Fisherman Lake led to the discovery of 13 gas seeps. Analyses of <sup>13</sup>C isotope compositions of two gas samples ( $\delta^{13}C_{CH4}$ -73.1 and -70.9%;  $\delta^{13}C_{CO2}$ -19.4%) indicate that they are biogenic methane produced by CO<sub>2</sub> reduction. This rules out the possibility that the gas is thermogenic methane seeping through fractures connected to the underlying Pointed Mountain gas field. What is unknown is what effect, if any, methane produce winter anoxia. If this occurred in Fisherman Lake, it could produce the unpleasant water odour, taste and fish kills reported by residents. However, these same conditions could be the product of phytoplankton blooms and/or eutrophication, independent of methane generation. Further studies of seasonal and stratigraphic limnology, and paleolimnological records would be required to answer these and other questions.

**Résumé :** Des préoccupations quant à la qualité de l'eau du lac Fisherman ont mené à la découverte de 13 zones de suitement de gaz. L'analyse de la composition isotopique du <sup>13</sup>C dans deux échantillons de gaz  $(\delta^{13}C_{CH4} de -73, 1 et de -70, 9\%; \delta^{13}C_{CO2} de -19, 4\%)$  indique qu'il s'agit de méthane biogénétique produit par réduction de CO<sub>2</sub>. Il ne s'agit donc pas de méthane thermogénétique qui s'est infiltré le long de fractures reliées au champ de gaz sous-jacent de Pointed Mountain. Toutefois, on ignore l'effet éventuel de la production de méthane sur la chimie et l'écologie des eaux du lac Fisherman. Dans un lac eutrophe, le méthane peut engendrer l'anoxie hivernale. Dans le lac Fisherman, cette anoxie pourrait être à l'origine de l'odeur et du goût désagréables de l'eau et de la mortalité de poissons qui ont été signalés par les résidents. Toutefois, la prolifération phytoplanctonique ou l'eutrophisation peuvent produire ces mêmes effets, indépendamment de la production de méthane. Il faudrait entreprendre d'autres études de la limnologie stratigraphique et saisonnière et obtenir d'autres données paléolimnologiques avant de pouvoir répondre à ces questions et à d'autres.

# **INTRODUCTION**

This study was conducted as part of the Geological Survey of Canada's Central Foreland NATMAP project, in response to concerns raised by local residents of the Acho Dene Koe, Fort Liard, NWT, about water quality in Fisherman Lake (Fig. 1). Residents indicated that they perceived recent changes in water quality (bad taste, bad smell, fish kills in spring), and had questioned whether this was in some way caused by local petroleum resource development. In order to assess recent (<100 a) changes in aquatic ecology, two short (<70 cm) sediment cores were extracted from the central region of the lake. The two cores were subsampled in the field at 0.2 and 0.5 cm intervals, and have since been stored frozen, awaiting analyses.

While operating a boat on Fisherman Lake, several sites around the boat launch were found to have continuous streams of gas bubbles rising from point sources in the sediment (Fig. 2). Given the fact that Fisherman Lake sits atop and adjacent to the Pointed Mountain gas field, it was decided to focus our study on the gas seeps in order to determine whether they were related to natural processes, or instead, to petroleum resource development (fracturing of geological reservoirs) and what effect, if any, they might have on the ecology and limnology of Fisherman Lake.

# Study area

Fisherman Lake is a large  $(13.2 \text{ km}^2)$ , shallow lake (maximum depth <10 m), situated between two ridges at the southern terminus of the Liard Range, Mackenzie Mountains, 18 km northwest of the hamlet of Fort Liard (Fig. 1). It has a 380 km<sup>2</sup> catchment that drains the adjoining bedrock ridges and an otherwise gently sloping or flat-lying (boggy) terrain blanketed by till, glacial lake sediments and alluvium (Bednarski, 2003a, b). A prominent bird's foot delta has formed at the northwest end of the lake, where the largest stream enters the basin. Fisherman Lake drains southeastward via a small stream into the Liard River. The low rate of



*Figure 1.* Regional base map projected on a digital elevation model, outlining Fisherman Lake, its catchment, and surrounding region.

discharge and large volume of the basin indicates a long residence time of water, which in combination with its shallow depth and warm summer temperatures (~18°C) contribute to the lake's seemingly high productivity.

Archaeological evidence suggests that Fisherman Lake has been the site of an active aboriginal fishery for more than 7000 years (Miller, 1968; Fedirchuk, 1975). Presently there are a small number of cabins located along the shore serving both seasonal and year-round residents. Fishing remains an important activity, and the lake supports populations of whitefish, walleye, pike, perch, and white sucker (Shultz, 1972).

Maps of the Fisherman Lake area bedrock geology (Lane, 2001, work in progress) indicate that the lake is underlain by a syncline composed of Lower Cretaceous Fort St. John Group shale. Ridges of the Liard Range to the east and west expose Lower Carboniferous and Permian rocks, primarily sand-stone and shale of the Mattson Formation. The western ridge comprises Pointed Mountain, which is a doubly plunging anticline with a broad crest and steeply dipping limbs. East of the lake, Mount Coty forms part of a west-dipping panel of Carboniferous sandstone, shale, and limestone and Permian calcareous siltstone, chert, and shale.

Since the 1960s, numerous (>10) wells related to the Pointed Mountain gas field have been drilled within the Fisherman Lake catchment area. Starting in 1971, the Amoco gas plant, northwest of the lake, fed an entrenched pipeline that passed 1 km west of the lake (Fig. 1). An airstrip was constructed southwest of the lake, as well as an accompanying work camp, during the development of the gas plant, pipeline and various well operations. The Amoco gas plant was taken out of service in the late 1990s and site reclamation is in progress.

#### **Previous studies**

In order to assess any immediate impact on Fisherman Lake caused by the construction of a pipeline in winter 1971 (connecting the Amoco gas plant with distribution networks to the south), baseline limnological studies were conducted in August 1971 and August 1972 (Schultz, 1971, 1972). Summaries of water quality analyses from these two studies are presented in Table 1. They show no discernible change in the lake environment beyond the range of analytical precision and accuracy, and of what would be considered typical seasonal variability.

In 1986, arising out of concerns by local residents about possible contamination of Fisherman Lake and the perception of petroleum-related off-flavours, eight whitefish and one walleye caught in Fisherman Lake were submitted for testing to the Department of Fisheries and Oceans (Lockhart et al., 1988). The fish were tested for proximate composition (moisture, ash, fat and protein content of muscle), lowboiling point hydrocarbons (toluene, ethylbenzene, ---, pand o-xylene, indicative of pollution from motor fuel exhaust), alkanes (assessing levels associated with microorganisms vs. pollution by petroleum), polycyclic aromatic hydrocarbons (PAH's), organochlorines (e.g., PCB's), liver microsomal enzymes (one of the most sensitive responses fish make to pollution by several PAH's and organochlorines), metals (Cr, Cu, Fe, Pb, Zn), and sensory evaluation (taste and odour of any petroleum or other environmental off-flavours). The conclusions of this study were that the fish were relatively unpolluted and in comparison to fish from elsewhere along the Mackenzie Valley, they were in similar or better condition (Lockhart et al., 1988; Trudeau, 1988).

# FIELD INVESTIGATIONS

On July 16, 2002, samples of the gas bubbling through the water column of Fisherman Lake were collected. Site 1 (Fig. 2, 3), identified in 2001, was sampled first, and then travelling by boat, the perimeter of the lake was inspected for additional gas seeps. A total of 13 sites with distinct bubble trains continuously rising to the surface were identified (Fig. 3). All of these sites were in areas of fairly shallow depth (<3 m). It is unlikely that seeps in deeper water would be



*Figure 2.* Photo of vertical stream of bubbles emanating from gas seep #1, Fisherman Lake.

**Table 1.** Limnological measurements of Fisherman Lake.

	Date	рН	Temp (°C)	Dissolved Oxygen (mg/l)	Conductivity (μS/cm)	Secchi depth (m)	HCO <sub>3</sub> <sup>°</sup> (mg/l)	SO₄²- (mg/l)
Schultz (1971)	8.28.71	8.5	16.7	9	376	2.70	194	69
Schultz (1972)	8.23.72	7.8	19.4	9	345	2.83	185	70
This study	7.16.02	8.12	17.9	12.2	443	1.88	243	83



*Figure 3.* Detailed map of Fisherman Lake showing location of gas seeps (numbered sample sites), sediment cores and adjacent gas plant and pipeline. Contour interval is 50 feet (15.2 m).

easily detected because waves and water currents would dissipate bubble streams. Gas samples were collected by filling 125 ml sample bottles with water, capping them with a large open funnel, and then inverting them in the water column above the bubble stream, allowing the collected gas to displace the water. Once the bottles were full, they were capped underwater and returned to the lab for analyses. Samples of gas from sites 1 and 2 (Fig. 3) were submitted for isotopic analyses in order to identify their composition, potential source and formation processes.

With the exception of site 2 (Fig. 3), all the seeps were observed to have a continuous flow of bubbles. Site 2 was unusual in that it occurred as a pulse of bubbles lasting 4 seconds, followed by a period of no bubbles for 23 seconds, a pattern and rate repeated for the 5 minute period of observation and sample collection. This implies that site 2 is being fed by a reservoir, where gas is accumulating until it reaches a threshold pressure, at which point it is vented through the sediment.

At the same time that gas samples were collected, water samples, filtered through a 0.45  $\mu$ m filter, were collected and submitted for geochemical analyses (Tables 1, 2). Dissolved oxygen, pH and conductivity were measured on site. Analyses of samples from an acidic spring (pH 2.9) emanating from the Middle Mattson Formation 62 km north of Fisherman Lake along the Liard Range (60°52.4'N, 124°03.0'W) are presented for comparative purposes (Table 2). The high acidity likely results from dissolution of iron pyrite within shale strata. Streams emanating from acidic springs in the Mattson Formation are widespread in the Liard Range, and are identifiable by pronounced rusty staining. Middle Mattson Formation strata also outcrop in the Fisherman Lake catchment, and thus surface and groundwater with similar chemistries may locally occur.

# RESULTS

Comparison of analytical results from Fisherman Lake (Tables 1, 2) and the Health Canada, Guidelines for Canadian Drinking Water Quality (2004) indicate all chemical parameters fall within acceptable guidelines. This is not the case for the acidic spring (situated well outside the Fisherman Lake catchment) where the waters have very low pH and unacceptably high levels of Al, Fe, Mn, and  $SO_4^{2^-}$ . A regional groundwater survey may therefore be useful in ruling out naturally occurring poor quality groundwater in the Fisherman Lake catchment.

Results of the isotopic analyses of gases from the two samples are shown in Table 3. Sample 1 was run through the Stable Isotope laboratory of the University of Calgary, while sample 2 was run through the Stable Isotope laboratory at the University of Alberta. Both gas samples were determined to be predominantly methane (CH<sub>4</sub>), with minor amounts of carbon dioxide (CO<sub>2</sub>). The isotopic composition ( $\delta^{34}$ S) of dissolved sulphate (SO<sub>4</sub><sup>2-</sup>) in sample 1 was also determined. A trace amount of ethane was detected in sample 2 ( $\delta^{13}$ C -43‰), but may have been derived from the plastic Nalgene<sup>®</sup> bottle used to trap the gas (Muehlenbachs, pers. comm. 2002).

	Fisherman Lake	Mattson spring		Fisherman Lake	Mattson spring	
рН	8.12	2.9	Mn μg/l	2.0	570.0	
Mg mg/l	19	27	Ca mg/l	72	110	
Na mg/l	5.70	1.60	K mg/l	2.00	1.80	
SO <sub>4</sub> mg/l	83	509	CI mg/l	0.486	0.249	
HCO <sub>3</sub> mg/l	243	0	Br μg/l	-50	-50	
NO₂ μg/l	-50	-50	NO <sub>3</sub> μg/l	-50	622	
F μg/l	114	142	Si mg/l	2.30	8.80	
Ti μg/l	-1	-1	Al μg/l	8.4	8400	
Fe µg/l	20	29000	Ag μg/l	-0.05	-0.05	
As μg/l	0.5	-0.2	Β μg/l	-16	-16	
Ba μg/l	44.00	2.80	Be μg/l	-1	-1	
Bi μg/l	-0.05	-0.05	Cd µg/l	-0.1	-0.1	
Co μg/l	0.16	22.0	Cr μg/l	-0.1	2.7	
Cs µg/l	-0.05	-0.05	Cu µg/l	1.0	7.2	
Ga µg/l	-0.05	-0.05	In μg/l	-0.05	-0.05	
Li µg/l	8	41	Mo μg/l	0.8	-0.1	
Ni μg/l	2.6	68.0	Pb μg/l	-0.05	0.38	
Rb μg/l	0.61	1.40	Sb µg/l	0.12	-0.05	
Sc µg/l	-1	2	Se µg/l	-1	-1	
Sr µg/l	130	40	Tl μg/l	-0.05	-0.05	
U μg/l	0.48	1.30	V μg/l	0.24	0.38	
Zn μg/l	-1	15				
*negative numbers indicate concentrations below limits of detection						

**Table 2.** Geochemistry of Fisherman Lake waters, andMiddle Mattson acidic spring.

# DISCUSSION

# Limnology of Fisherman Lake

Based on what must be recognized as very limited surveys, the limnological parameters presented in Table 1 do not suggest dramatic changes in Fisherman Lake. Differences in pH are well within the range of precision of past analytical techniques, and temperature and dissolved oxygen may simply reflect seasonal variations. Conductivity, bicarbonate (HCO3-) and sulphate  $(SO_4^{2-})$  appear to be slightly increased, but again this could be related to seasonal variability. Perhaps the greatest measured change is a decrease in Secchi depth - which is a measure of transmissivity (reflecting concentrations of algal and inorganic particulate matter suspended in the water column), and serves as a proxy indicator of trophic status. Decreases in Secchi depth reflect increased eutrophication, suspended sediment inputs, or both. However, before Fisherman Lake were to be declared a eutrophic lake, other limnological analyses, including phosphorus and nitrogen concentrations, would need to be conducted.

# **Table 3.** Stable isotope compositions of gas samples.

	δ <sup>13</sup> C <sub>CH4</sub> ‰	δ <sup>13</sup> C <sub>co2</sub> ‰	δ <sup>34</sup> S <sub>so4</sub> ‰
Sample 1	-70.9		-6.1
Sample 2	-73.1	-19.4	

### Biogenic or thermogenic methane determination

Once the gas samples were determined to be principally methane, two hypotheses were tested regarding their possible source:

- The methane was biogenic in origin, and was related to the natural decomposition of sedimentary organic matter. Methane gas production is commonly associated with freshwater lakes and swamps where anaerobic decomposition of organic matter takes place. It can also be produced from decomposition in organic-rich shales.
- 2) The methane was thermogenic in origin, and therefore represented a seep from geological strata of the Pointed Mountain gas field below the lake. Naturally occurring seeps of natural gas (largely methane) are widespread, and include the "Hot Pot," a continuously burning seep of gas in northwest Alberta, as well as seeps that have been linked to the discovery and development of many economically significant natural gas deposits (e.g. Turner Valley, AB). Seeps can also be artificially created through human-induced fracturing of geological reservoirs.

Biogenic gas is generally formed at shallow depths and low temperatures by anaerobic bacterial decomposition of sedimentary organic matter, and is almost entirely composed of methane. Thermogenic gas forms at deeper depths by either thermal cracking of organic matter into hydrocarbon liquids and gas, or thermal cracking of oil at high temperatures into gas. Thermogenic gas is also largely methane, but depending on maturity levels it can also contain significant concentrations of ethane, propane, and butanes. Because of their different formative processes and associated fluids, it is possible to use stable isotope geochemistry to distinguish between biogenic and thermogenic gas (Schoell, 1980, 1988; Whiticar et al., 1986; Kaplan et al., 1997; Rowe and Muehlenbachs, 1999). Thermogenic methane has a  $\delta^{13}$ C of between -60 and -20%, while biogenic methane tends to be much more isotopically light, ranging from -100 to -40% (Fig. 4). The central overlap area between -60 and -40% is where "mixed gases" are found: biogenic and thermogenic gases that have been altered chemically and isotopically during migration to the surface. The  $\delta^{13}C_{CH4}$  values of -70.9 and -73.1% recorded for the Fisherman Lake gas samples would therefore place them in the biogenic field. In contrast, the Pointed Mountain gas field has been determined to be an overmature thermogenic gas deposit, with  $\delta^{13}C_{CH4}$  values of around -33% (Muehlenbachs, pers. comm., 2002). Thus we can conclusively rule out that the source of the Fisherman Lake gas seeps is the result of fracturing of geological reservoirs, and direct passage of gas to the surface. Additional



Figure 4. Generalized distributions of  $\delta^{13}C$  and  $\delta D$  values for methane (CH<sub>4</sub>) generated by biogenic CO<sub>2</sub> reduction, biogenic fermentation and thermogenic processes. Shaded areas (mixed gases) represent methane that can be formed by any of the three processes. While  $\delta D_{CH4}$  was not determined, the  $\delta^{13}C_{CH4}$  values of -73.1 and -70.9% clearly place the methane gas samples from Fisherman Lake in the biogenic CO<sub>2</sub> reduction field. (after Kaplan et al., 1997, their Fig. 1).

support of this assertion is the  $\delta^{34}$ S isotopic value of -6.1‰ from sample 1, which were it to have been derived from waters associated with the Pointed Mountain gas field (Devonian Manetoe facies), would measure around +20‰. Experiments (cf. Zhang and Krooss, 2001) have indicated that methane can undergo significant isotopic fractionation by molecular diffusion through tight shale caps giving an apparent biogenic signature. However, we consider this an improbable scenario given the amount of fractionation that would be required, the local geological setting, and the likely age of the Pointed Mountain gas formation.

While the gas seeps sampled from Fisherman Lake can be clearly distinguished as relating to natural biogenic sources, questions remain as to what is controlling the formation of methane in Fisherman Lake, and whether the methane production can be related to changes in water quality perceived by local residents. The remaining discussion attempts to answer these questions.

#### *Methanogenesis*

The production of methane, or methanogenesis, occurs as a result of anaerobic decomposition of organic matter in sediments, and is driven by one of two pathways, each of which creates different isotopic fractionations. In the fermentation process (aceticlastic methanogenesis), fermenting bacteria break down cellulose into acetate (CH<sub>3</sub>COOH), which is then converted by methanogenic bacteria into carbon dioxide and methane.

$$CH_3COOH \rightarrow CO_2 + CH_4$$
 (1)

The  $\delta^{13}C_{CH4}$  produced by fermentation ranges from -40 to -65% (Woltemate et al., 1984; Whiticar et al., 1986; Cicerone and Oremland, 1988), and therefore is not the dominant process operating in Fisherman Lake, at least as it pertains to the two gas samples analyzed in this study.

The second pathway occurs by the reduction of carbon dioxide (in which the  $CO_2$  may be found as  $HCO_3^-$ ), which serves as an electron acceptor (Schlesinger, 1991).

$$\mathrm{CO}_2 + 4\mathrm{H}_2 \to \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{0},\tag{2}$$

Methane produced by this process is highly depleted in <sup>13</sup>C with  $\delta^{13}C_{CH4}$  of -60 to -100% (Whiticar et al., 1986; Lansdown et al., 1992). This is therefore interpreted to be the dominant methanogenic process operating in Fisherman Lake. Globally, methanogenesis in freshwater sediments occurs predominantly by acetate reduction (70:30 compared to CO<sub>2</sub> reduction); in marine systems, CO<sub>2</sub> reduction predominates (Rudd and Taylor, 1980; Whiticar, et al. 1986). In freshwater sediments where sulphate is present in sufficient quantity, acetate-oxidizing organisms can out-compete methanogens for acetate, producing CO<sub>2</sub> that is then reduced to produce methane (Winfrey and Zeikus, 1977; Rudd and Taylor, 1980; Coleman et al., 1988). Given the sulphate concentrations measured in Fisherman Lake water (Table 1; likely sourced from sulphide oxidation), this may well be favouring  $CO_2$  reduction methanogenesis. Alternatively, the methane may be sourced from organic-rich, Cretaceous Fort St. John Group marine shale, or potentially even overlying Tertiary sediments. However, there are insufficient data to characterize these potential sources.

Methanogenesis will produce methane dissolved within the formation, or sediment, porewater. When methane production in sediments reaches supersaturation (exceeding atmospheric and hydrostatic pressures), bubbles begin to form and escape through the sediment to the lake water surface, a process called ebullition. Ebullition can be aided by the roots of aquatic plants and internal structure of stems, which can act as conduits (Dacey, 1981; Sebacher et al., 1985). This may be occurring at some sites in Fisherman Lake as several (but not all) gas seeps were found in areas of submerged aquatic vegetation.

#### Limnological properties of methane

As methane diffuses upward through sediment porewater, it passes the oxic-anoxic boundary. At this point it is readily consumed in the sediment column and/or overlying lake waters by aerobic methanotrophic bacteria, converting it into bacterial cell material and  $CO_2$  in about a 50:50 ratio (Rudd and Taylor, 1980).

$$2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O \tag{3}$$

Where lakes become stratified, forming seasonally anoxic bottom waters (hypolimnia), methane released from the sediments can accumulate in the water. This is not usually problematic as thermally induced seasonal overturn and/or wind mixing with overlying oxygenated waters quickly leads to aerobic bacterial oxidation of the methane (the absolute rate of which is in part dependent on nitrogen nutrient levels; Rudd et al., 1976; Welch et al., 1978), producing  $CO_2$ , which is then respirated by aquatic plants. In this manner, carbon is recycled through the system with very little lost to the atmosphere.

Where ebullition is occurring, studies have demonstrated that <10% of methane gas re-dissolves during passage through a 10 m water column (Robertson, 1979), and thus in well-oxygenated waters, such as were measured in Fisherman Lake, methane seeps would not likely be seen as detrimental to the aquatic ecology. However, it has also been shown that in eutrophic lakes with high hypolimnetic methane concentrations (and by implication, non-stratified lakes with high ebullition of methane), which undergo rapid winter freezeup, methane oxidation can carry on through the winter, leading to anoxic conditions (Rudd and Hamilton, 1978). Indeed, the study of Rudd and Hamilton (1978) in an artificially eutrophied lake basin in the Experimental Lakes Area, Ontario, demonstrated that methane oxidation consumed 110% of the oxygen present in the lake at freeze-up during one winter observation period. Since the ice and snow cover effectively cut off any interchange with the atmosphere, the anoxic waters resulted in widespread suffocation of fish, zooplankton and zoobenthos. If the same situation were to occur in Fisherman Lake, varying degrees of winter lake water anoxia (and its effects on lake water chemistry, including the formation of odorous hydrogen sulphide (H<sub>2</sub>S) gas from anaerobic bacterial reduction of sulphate  $(SO_4^{2-})$ , could explain observations by local residents of mass fish kills, and bad smelling and tasting water. It should be noted, however, that Rudd and Hamilton's study (1978) also demonstrated that under more protracted fall lake water overturn, methane in the lake was entirely oxidized prior to freeze-up, and no winter anoxia was produced - thus high annual variability in basins may occur.

In oligotrophic (nutrient-poor) lakes, even high volumes of methane released into a lake through winter may not be enough to generate anoxic conditions. Welch et al. (1979) artificially dissolved 280 kg of methane into an ice-covered arctic lake, with little effect on dissolved oxygen concentrations. This experiment was designed to test the implications of a buried pipeline rupture in the arctic, and demonstrated that arctic lakes do not contain methane-oxidizing bacteria, and/or do not have enough nutrients (particularly nitrogen) to sustain their activity in the water column to the point of creating anoxic water conditions.

Methane production in Fisherman Lake is only one component of a complex limnological system operating in what may be a eutrophic lake. While total methane production has been positively linked to carbon sedimentation rates (aquatic carbon production and detrital carbon from the catchment; Robertson, 1979), high organic accumulation, and its decomposition can lead to benthic lake water anoxia, independent of methanogenesis. Also, the shear volume of gas entering the lake as continuous point source streams, and apparent stability of these point sources, belies the notion that it is largely the product of simple decomposition of sedimentary organic matter in the lake sediments. The underlying organic-rich shale of the Fort St. John Group may well be the ultimate source of the methane.

#### **RECOMMENDATIONS FOR FUTURE STUDY**

The one study with surface-to-sediment transects of temperature and dissolved oxygen (Schultz, 1971) suggests Fisherman Lake does not support an anoxic hypolimnion in the summer. This is not surprising given the size and shallow depth of the lake, and the effective fetch and wind-induced mixing it would be subject to. However, in order to gain a proper understanding of Fisherman Lake limnology we advocate the seasonal collection of water samples across the basin, and from surface to bottom.

It would also be useful to establish the degree of eutrophication in Fisherman Lake. In general, eutrophication can occur naturally when there are high nutrient inputs from catchment runoff, or can be the result of nutrient loading brought about by the actions of humans, such as when large concentrations of sewage are discharged into a basin. It can also be related to changes in water level and climatic change (Melack, 1991; Carpenter et al., 1992).

Subsequent to collection of the gas samples used in this study, the authors were told by a local resident that one of the ponds along the margin of Fisherman Lake (Fig. 3, site 3) had copious amounts of gas bubbling through it –so much so, that the pond never froze over completely in the winter – and that there was often a "rotten-eggs" smell ( $?H_2S$ ). It would be worth returning to this site to sample the gas in order to identify its composition and source, and compare it to the two seeps investigated in this study.

Further refinement of the gas source and generation interpretation could be achieved by measuring the  $\delta^{13}$ C,  $\delta$ D (hydrogen) and  $\delta^{34}$ S compositions of methane, carbon dioxide, water, H<sub>2</sub>S, and sulphate in the gas seeps, lake water and sediment porewaters.

Independent of the creation of anoxic water, studies of bad tasting and smelling water have been documented in lakes elsewhere in the world, and have generally been linked to extracellular organic compounds produced by phytoplankton blooms (Smol, 2002). These phytoplankton blooms can occur in both oligotrophic lakes (often associated with certain chrysophyte and diatom algae; Nicholls and Gerrath, 1985; Paterson et al., 2004) and in eutrophic lakes (often involving Cyanobacteria), both of which would leave fossil records preserved in the lake sediment. There is a rich literature on proven techniques and various proxy indicators that can be used to reconstruct qualitative, quantitative, and temporal changes in lakes (cf. Smol, 1987, 2002; Smol et al., 2001). Therefore, a paleolimnological study of the recent (<100 a year) sedimentary record of Fisherman Lake is likely to provide the most definitive answer on what, if any, changes have occurred, and when these took place.

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#### REFERENCES

#### Bednarski, J.M.

- 2003a: Surficial Geology, Fisherman Lake (95B/5), Northwest Territories; Geological Survey of Canada Open File map 4360, scale 1: 50 000.
- 2003b: Surficial geology, Mount Flett, Northwest Territories (NTS 95B/12); Geological Survey of Canada, Open File map 4481, scale 1.50,000

Carpenter, S.R., Fisher, S.G., Grimm, N.B., and Kitchell, J.F.

- 1992: Global change and freshwater ecosystems; Annual Review of Ecology and Systematics, v. 23, p. 119-139.
- Cicerone, R.J., and Oremland, R.S.
- 1988: Biogeochemical aspects of atmospheric methane; Global Biogeochemical Cycles, v. 2, p. 299-327.
- Coleman, D.D., Liu, C-L., and Riley, K.M.
- Microbial methane in the shallow Paleozoic sediments and glacial 1988: deposits of Illinois, U.S.A.; Chemical Geology, v. 71, p. 23-40.
- Dacey, J.W.H.
- 1981: Pressurized ventilation in the yellow waterlily; Ecology, v. 62, p. 1137-1147.
- Fedirchuk, G.J.
- Functional analysis of the Julian technology, Fisherman Lake, 1975: Northwest Territories; Ph.D. thesis, University of New Mexico, Socorro, NM, 164 p.

#### Health Canada

2004: Summary of Guidelines for Canadian Drinking Water Quality. www.hc-sc.ca/waterquality

#### Kaplan, I.R., Galperin, Y., Lu, S-T., and Lee, R-P.

- Forensic environmental geochemistry: differentiation of fuel types, 1997: their sources and release times; Organic Geochemistry, v. 27, p. 289-317.
- Lane, L.S.
- 2001: Geology, Fisherman Lake, Northwest Territories (95B/5); Geological Survey of Canada, Open File map 4161, scale 1:50 000.
- Lansdown, J.M., Quay, P.D., and King, S.L.
- CH<sub>4</sub> production via CO<sub>2</sub> reduction in a temperate bog: A source of 1992: <sup>13</sup>C<sup>4</sup>depleted CH<sub>4:</sub> Geochimica et Cosmochimica Acta, v. 56, p. 3493-3503.

#### Lockhart, W.L., Metner, D.A., Danell, R.W., Billeck, B.N.,

- Murray, D.A.J., Muir, D.C.G., Hunt, R.V., York, R.K.,
- and Deegan, A.
- 1988: Data on proximate composition, contaminants, and tainting for fish from Fisherman Lake, N.W.T.; Report prepared for D.M. Trudeau, Department of Indian Affairs and Northern Development, Department of Fisheries and Oceans, Central and Arctic Region Freshwater Institute, Winnipeg, MB. 14 p.
- Melack, J.M.
- Reciprocal interactions among lakes, large rivers, and climate; in 1991: Global Climate Change and Freshwater Ecosystems, (ed.) P. Firth and S.G. Fisher; Springer-Verlag, New York, p. 68-87.
- Miller, J.V.F.
- Archeology of Fisherman Lake, western District of Mackenzie, 1968: N.W.T.; Ph.D. thesis, University of Calgary, 496 p.
- Nicholls, K.E., and Gerrath, J.F.
- The taxonomy of Synura (Chrysophyceae) in Ontario with special 1985: reference to taste and odour in water supplies; Canadian Journal of Botany, v. 63, p. 1482-1493.

#### Paterson, A.M., Cumming, B.F., Smol, J.P., and Hall, R.I.

Marked recent increases of colonial scaled chrysophytes in boreal lakes: implications for the management of taste and odour events; Freshwater Biology, v. 49, p. 199-207.

#### Robertson, C.K.

- Quantitative comparison of the significance of methanogenesis in 1979: the carbon cycle of two lakes; Archiv für Hydrobiologie ergbenis der Limnologie, v. 12, p. 123-135.
- Rowe, D., and Muehlenbachs, K.
- 1999: Isotopic fingerprints of shallow gases in the Western Canadian sedimentary basin: tools for remediation of leaking heavy oil wells; Organic Geochemistry, v. 30, p. 861-871.
- Rudd, J.W.M. and Hamilton, R.D.
- 1978: Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism; Limnology and Oceanography, v. 23, p. 337-348. Rudd, J.W.M. and Taylor, C.D.
- Methane cycling in aquatic environments; in Advances in Aquatic 1980: Microbiology, Volume 2, (ed.) M.R. Droop and H.W. Jannasch; Academic Press, Toronto, p. 77-145.
- Rudd, J.W.M., Furutani, A., Flett, R.J., and Hamilton, R.D.
- Factors controlling methane oxidation in shield lakes: The role of nitrogen fixation and oxygen concentration; Limnology and Oceanography, v. 21, p. 357-364.
- Schlesinger, W.H.
- 1991: Biogeochemistry: an analysis of global change; 2<sup>nd</sup> Ed., Academic Press, San Diego, CA. 588 p.
- Schoell, M.
- 1980: The hydrogen and carbon isotopic composition of methane from natural gases of various origins; Geochimica et Cosmochimica Acta, v. 44, p, 649-661.
- 1988: Multiple origins of methane in the Earth; Chemical Geology, v. 71, p. 1-10.
- Schultz, C.D.
- Ecological and economical impact of the Pointed Mountain natural gas line. 1971: Supplement to Section III, III/7 Liminology and Biology of Fisherman Lake, Northwest Territories; Westcoast Transmission Company Limited, Vancouver, Right-of-way application B Beaver River gas field to Pointed Mountain gas field. Schultz International Limited, Vancouver, BC, 27 p.
- 1972: Limnology of Fisherman Lake NWT; Report prepared for Westcoast Transmission Company Limited, Vancouver, by Schultz International Limited, Vancouver, BC, 26 p.
- Sebacher, D.I., Harriss, R.C., and Bartlett, K.B.
- 1985: Methane emissions to the atmosphere through aquatic plants; Journal of Environmental Quality, v. 14, p. 40-46.
- Smol, J.P.
- Methods in Quaternary Ecology #1. Freshwater Algae; Geoscience 1987: Canada, v. 14, p. 208–217.
- 2002: Pollution of Lakes and Rivers: A Paleoenvironmental Perspective; Arnold Publishers, London. 280 p

#### Smol, J.P., Birks, H.J.B., and Last, W.M. [Editors]

- 2001: Tracking Environmental Change Using Lake Sediments Volume 3: Terrestrial, Algal, and Siliceous Indicators; Kluwer Academic Publishers, Dordrecht, 371 p.
- Trudeau, D.M.
- Report on fish quality at Fisherman Lake, N.W.T.; Water Resource 1988: Officer, Northern Affairs Program, Department of Indian Affairs and Northern Development. 4 p.
- Welch, H.E., Rudd, J.W.M., and Schindler, D.W.
- 1979: Methane addition to an arctic lake in winter; Department of Fisheries and Environment, Arctic Islands Pipelines Program, Report A1-29, 33 p.
- Whiticar, M.J., Faber, E., and Schoell, M.
- 1986: Biogenic methane formation in marine and freshwater environments: CO<sub>2</sub> reduction vs. acetate fermentation Isotope evidence; Geochimica et Cosmochimica Acta, v. 50, p. 693-709.

#### Winfrey, M.R. and Zeikus, J.G.

- Effect of sulfate on carbon and electron flow during microbial 1977: methanogenesis in freshwater sediments; Applied and Environmental Microbiology, v. 33, p. 275-281
- Woltemate, I., Whiticar, M.J., and Schoell, M.
- Carbon and hydrogen isotopic composition of bacterial methane in a shal-1984: low freshwater lake; Limnology and Oceanography, v. 29, p. 985-992.
- Zhang, T. and Krooss, M.
- Experimental investigation on the carbon isotope fractionation of 2001: methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure; Geochimica et Cosmochimica Acta, v. 65, p. 2723-2742.

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