

03-199

Environment Canada

Water Science and Technology Directorate

Direction générale des sciences
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Environnement Canada

Oxidation of Methane in Cold, Anaerobic Ground
Water, Linked to Bacterial Sulfate Reduction

By:

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NWRI Contribution # 03-199

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Water, Linked to Bacterial Sulfate Reduction

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Oxidation of Methane in Cold, Anaerobic Ground Water, Linked to Bacterial Sulfate Reduction

Dale Van Stempvoort, Harm Maathuis, Ed Jaworski, Bernhard Mayer, Kathleen Rich

Abstract

When fugitive methane migrates upward along boreholes of oil and gas wells to shallow ground water, this greenhouse gas may vent from adjacent water wells or pass through overlying soil to the atmosphere. In this field study near Lloydminster, Alberta, Canada, we found hydrogeochemical evidence that fugitive methane from an oil well impacted a shallow aquifer, but has been attenuated by bacterial sulfate reduction under low temperature (3 to 7°C), anaerobic conditions. The evidence includes spatial and temporal trends in concentrations of methane and sulfate in ground water, and associated trends in concentrations of bicarbonate and sulfide. The key evidence is stable isotope data: near the oil well methane was enriched in ^{13}C by up to 10 ‰, together with higher concentrations and ^{13}C -depletion of bicarbonate. Within 10 m of the oil well sulfate concentrations were lower and sulfate was enriched in both ^{34}S and ^{18}O . Sulfate concentrations had a strong positive correlation with $\delta^{13}\text{C}$ of bicarbonate, and sulfide was depleted in ^{34}S by 30 to 50 ‰, compared to sulfate. Together, these concentration and stable isotope data support an interpretation that in-situ bacterial reduction of sulfate to sulfide has occurred, and that higher concentrations of ^{13}C -depleted bicarbonate near the oil well were produced by oxidation of ^{13}C -depleted methane, linked to bacterial sulfate reduction as a terminal electron accepting process. Based on these results, bacterial sulfate reduction may play a major role in bioattenuation of fugitive natural gas in ground water in western Canada.

NWRI RESEARCH SUMMARY

Plain language title

Field study evidence that sulfate reducing bacteria break down the greenhouse gas methane in shallow groundwater at oil and gas sites in Alberta .

What is the problem and what do scientists already know about it?

At some oil and gas well sites in Canada and elsewhere, the shallow groundwater is contaminated by methane (natural gas) that has seeped upward along the well bores. If this greenhouse gas is not degraded in the subsurface, it will tend to migrate upward to the atmosphere. Research has shown that methane can be consumed by subsurface bacteria, but it has generally been assumed that these bacteria require oxygen (as an electron acceptor). However, recent studies have shown that in marine sediments, bacteria use sulfate in place of oxygen to degrade methane.

Why did NWRI do this study?

Based on the marine studies and other scattered evidence, the authors decided to investigate whether sulfate reducing bacteria may also have the potential to degrade methane in shallow groundwater at oil and gas sites in Canada.

What were the results?

This field study at an oil well site in Alberta provides strong evidence that bacteria are using sulfate to degrade methane in groundwater.

How will these results be used?

The findings are useful to estimate the quantitative effect of bacterial degradation processes in the subsurface that minimize the atmospheric impact of natural gas migrating upward at oil and gas sites in Canada. Further investigation may lead to a new remediation approach that utilizes and enhances the bacterial activity.

Who were our main partners in the study?

Saskatchewan Research Council, University of Calgary, Alberta Environment

Oxydation du méthane dans de l'eau souterraine froide provenant de la réduction du sulfate par des bactéries en anaérobiose

Dale Van Stempvoort, Harm Maathuis, Ed Jaworski, Bernhard Mayer, Kathleen Rich

Résumé

Lorsque des vapeurs fugitives de méthane se retrouvent dans des nappes d'eau souterraine peu profondes en empruntant les trous de forage des puits de pétrole et de gaz, ce gaz à effet de serre peut passer dans des puits d'eau voisins ou diffuser à travers le sol jusque dans l'atmosphère. Dans la présente étude sur le terrain réalisée près de Lloydminster, en Alberta (Canada), nous avons obtenu des preuves hydrogéochimiques que des vapeurs fugitives de méthane provenant d'un puits de pétrole se retrouvent dans un aquifère peu profond, mais que la présence de bactéries sulfatoréductrices en atténue l'impact dans les conditions de basse température (3 à 7 °C) et d'anaérobiose qui y règnent. Ces preuves ont trait à des tendances observées dans les concentrations de méthane et de sulfate dans le temps et l'espace, associées à des tendances observées dans les concentrations de bicarbonate et de sulfure. Les principales données sont basées sur les isotopes stables : près du puits de pétrole, le méthane était enrichi en ^{13}C dans une proportion pouvant atteindre jusqu'à 10 %, alors que la concentration et l'appauvrissement en ^{13}C du bicarbonate augmentait. À moins de 10 m du puits de pétrole, les concentrations de sulfate étaient plus faibles et le sulfate était enrichi en ^{34}S et en ^{18}O . Les concentrations de sulfate présentaient une forte corrélation positive avec le $\delta^{13}\text{C}$ du bicarbonate, et le sulfure était appauvri en ^{34}S dans une proportion de 30 à 50 % comparativement au sulfate. Toutes ces données portant sur la concentration et le rapport des isotopes stables appuient l'hypothèse d'une réduction *in situ* du sulfate en sulfure par des bactéries et de concentrations plus élevées de bicarbonate appauvri en ^{13}C près du puits de pétrole provenant d'une oxydation du méthane appauvri en ^{13}C liée à la réduction du sulfate par des bactéries (processus agissant comme accepteur terminal d'électron). Ces résultats indiquent que la réduction du sulfate par des bactéries peut jouer un rôle important dans la bioatténuation des vapeurs fugitives de gaz naturel dans l'eau souterraine dans l'ouest du Canada.

Sommaire des recherches de l'INRE

Titre en langage clair

Des études sur le terrain indiquent que des bactéries sulfatoréductrices dégradent le méthane, un gaz à effet de serre, dans les nappes d'eau souterraine peu profondes près des puits de pétrole et de gaz en Alberta.

Quel est le problème et que savent les chercheurs à ce sujet?

Près de certains puits de pétrole et de gaz au Canada et ailleurs, les nappes d'eau souterraine peu profondes sont contaminées par du méthane (gaz naturel) empruntant les trous de forage des puits. Si ce gaz à effet de serre n'est pas dégradé en subsurface, il aura tendance à migrer jusque dans l'atmosphère. Des recherches ont montré que le méthane peut être dégradé par des bactéries en subsurface, mais il était généralement admis que ces bactéries exigent de l'oxygène (accepteur d'électron). Toutefois, des études récentes ont montré que des bactéries présentes dans des sédiments marins utilisent le sulfate à la place de l'oxygène pour dégrader le méthane.

Pourquoi l'INRE a-t-il effectué cette étude?

À partir de ces études marines et d'autres données éparses, les auteurs ont décidé d'amorcer des recherches visant à déterminer si des bactéries sulfatoréductrices peuvent également dégrader le méthane dans les nappes d'eau souterraine peu profondes près des puits de pétrole et de gaz au Canada.

Quels sont les résultats?

Les résultats de la présente étude sur le terrain près d'un puits de pétrole en Alberta nous indiquent fortement que des bactéries utilisent le sulfate pour dégrader le méthane dans l'eau souterraine.

Comment ces résultats seront-ils utilisés?

Ces résultats sont utiles pour déterminer l'effet quantitatif des processus de dégradation bactérienne en subsurface qui réduisent les effets atmosphériques du gaz naturel s'échappant des puits de pétrole et de gaz au Canada. Une recherche plus poussée pourrait nous permettre de proposer une nouvelle méthode de dépollution fondée sur l'utilisation et l'augmentation de l'activité bactérienne.

Quels étaient nos principaux partenaires dans cette étude?

Saskatchewan Research Council, Université de Calgary, ministère de l'Environnement de l'Alberta.

1
2 **1. Introduction**

3 To address growing concerns about global warming, researchers are probing the
4 global carbon cycle and the fate of greenhouse gases, such as methane. In Canada, both
5 provincial and federal governments have committed to reduce greenhouse emissions, in
6 part by introducing new technologies and innovation. The oil and gas industrial sector in
7 western Canada is an active participant in the research and development of new
8 technologies to address greenhouse gas emissions. As part of this effort, over the past
9 decade both industry and regulators of the oil and gas sector in western Canada have
10 probed the occurrence, migration pathways and fate of fugitive natural gas, primarily
11 methane, in soils and ground water at petroleum production sites (e.g., Erno and Schmitz
12 1994; Van Stempvoort et al. 1996).

13 Some of the methane that occurs in shallow ground water may be vented from water
14 wells, or migrate upwards through the overlying soil, contributing to the global
15 atmosphere load of this greenhouse gas. For example, it is estimated that migration of
16 methane from landfills accounts for approximately one quarter of the total anthropogenic
17 emissions of methane to the atmosphere in developed countries (USEPA 2001). Leakage
18 from oil and gas production, processing and transmission systems contributes more than
19 one quarter of the total methane emissions to the atmosphere in developed countries
20 (USEPA 2001), and some of this migration occurs through the shallow ground water
21 environment.

22 Unintentional vertical movement of natural gas is a concern in western Canada (Erno
23 and Schmitz 1994; Van Stempvoort et al. 1996, 2000; Rowe and Meuhlenbachs 1999).

1 Dyck and Dunn (1986) found elevated concentrations of methane in ground water in
2 southwestern Saskatchewan associated with oil and gas fields. Highest methane
3 concentrations tended to be associated with higher densities of exploration holes. They
4 suggested that the anomalies might be due to either leakage along the exploration holes,
5 or natural migration along faults and fracture zones. Erno and Schmitz (1994)
6 documented leakage of natural gas from oil and gas wells to soils in the Lloydminster
7 area, along the Saskatchewan/Alberta border. Subsequently, Van Stempvoort and co-
8 workers documented leakage of natural gas from oil production wells to shallow ground
9 water at several sites in the Lloydminster area (Van Stempvoort and Jaworski 1995, Van
10 Stempvoort et al. 1996, 2000). Other recent studies have provided information on various
11 sources of methane in the shallow subsurface of the Prairies region of western Canada
12 (Rowe and Muehlenbachs 1999; Taylor et al. 2000).

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13 This paper contributes to the research at "upstream" petroleum sites in western
14 Canada. Specifically, this paper examines the fate of methane that has unintentionally
15 migrated upward to shallow ground water along the borehole of an oil well. Following
16 on earlier research, this paper examines the potential that bacterial sulfate reduction may
17 act as an important terminal electron accepting process (TEAP) in the natural attenuation
18 of fugitive methane in ground water.

19 As indicated in Section 2.1, recent studies of marine sediments have indicated an
20 important linkage between methane oxidation and sulfate reduction in marine sediments,
21 mediated by consortia of bacteria. Though other studies have suggested that there is a
22 coupling of the same two redox processes in ground water (Section 2), the evidence has

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1 generally been inclusive. Further, only a few of the pertinent ground water studies were
2 at cold climate sites, characteristic for western Canada.

3 In this study, we probed the potential relationship between methane oxidation and
4 sulfate reduction using an array of field procedures and laboratory techniques, including
5 stable isotope analyses of inorganic sulfur species, and of both organic and inorganic
6 carbon species.

7

8 2. Background

9 2.1 Sources and Fate of Methane in Ground Water

10 Globally, a significant portion of the methane that occurs in shallow ground water (<
11 200 m below ground) has migrated from the deeper subsurface, where it formed via
12 thermogenic ("thermocatalytic" or "thermal") processes. Upward migration from natural
13 gas reservoirs occurs via geologic conduits, such as fracture zones. Upward migration of
14 natural gas, largely methane, may also occur along exploration holes or defective
15 production wells in active oil and gas fields, impacting shallow soils, ground water or
16 surface water bodies (Rose and Alexander 1945; Preston 1980; Kelly et al. 1985; Chafin
17 et al. 1993; Chafin 1994). Figure 1 is a schematic of this process of unintentional natural
18 gas migration.

19 In other cases, methane in shallow ground water (< 200 m below ground) is produced
20 *in-situ* as a byproduct of anaerobic biodegradation of organic matter by microorganisms.
21 This is often referred to as "biogenic" methane (Barker and Fritz 1981b). Some aquifers
22 have natural occurrences of high concentrations of biogenic methane (> 10 mg/L) for
23 example as the result of in-situ degradation of buried peat beds (Aravena and Wassenaar

1 1993). Elsewhere, high concentrations of biogenic methane in ground water result from
2 degradation of anthropogenic organic wastes, such as municipal landfill materials (Barker
3 and Fritz 1981b), or petroleum hydrocarbon plumes derived from fuel leaks and spills
4 (Vrobley et al. 1996).

5 Methanogenic (methane-producing) bacteria require anaerobic conditions, and they
6 tend to thrive in the absence of sulfate (Barker and Fritz 1981b; Vrobley et al. 1996).
7 Typically, microbial communities tend to utilize alternative terminal electron accepting
8 processes (TEAPs) in sequence: methanogenesis follows the reduction of sulfate, after
9 other preferred electron acceptors (oxygen, nitrate, Fe^{3+} , Mn^{2+}) have been depleted
10 (Azadpour-Keeley et al. 2001). During microbial methanogenesis, the electron accepting
11 process is often the reduction of dissolved CO_2 , though in other cases, methanogens
12 produce methane from other precursors such as acetate or methanol (Thauer 1998). The
13 typical sequence of TEAPs, which is explained in terms of energy yield considerations
14 (e.g., Appelo and Postma 1993), is not always strictly followed. For example,
15 methanogenesis concomitant with slow bacterial reduction of sulfate and/or Fe^{3+} has been
16 reported (Vrobley et al. 1996; Hansen et al. 2001).

17 Biogenic and thermogenic methane can be distinguished by their chemical
18 association and isotopic signatures. Thermogenic methane is typically associated with a
19 range of other light hydrocarbons, such as ethane, propane and butane, and it has
20 relatively high $^{13}\text{C}/^{12}\text{C}$ ratios (Barker and Fritz 1981b; Taylor et al. 2000). Biogenic
21 methane with $\delta^{13}\text{C}$ values between -60 and -90 ‰ is generally distinguishable from
22 thermogenic methane, which has higher $\delta^{13}\text{C}$ values. However, methane $\delta^{13}\text{C}$ values in
23 the range -50 to -60 ‰ are not diagnostic for either biogenic or thermogenic methane

1 (Taylor et al. 2000). *In-situ* microbial oxidation of methane will tend to enrich the
2 residual methane in ^{13}C , and this potentially obscures the source identification by isotopic
3 techniques (Barker and Fritz 1981a; Rowe and Meuhlenbachs 1999; Taylor et al. 2000).
4 Biogenic methane may have measurable ^{14}C content (Barker and Fritz 1981b; Aravena
5 and Wassenaar 1993).

6 High methane concentrations in shallow ground water may present an explosion
7 hazard for domestic or municipal supply wells (Aravena and Wassenaar 1993. There is
8 some potential for methane to be degraded by microorganisms in the shallow subsurface,
9 thus reducing the emissions of this greenhouse gas. Field investigations that have probed
10 such processes have focused on the aerobic oxidation of upward migrating methane in
11 landfill cover soils (e.g., Whalen et al. 1990; Chanton et al. 1999; Boerjesson et al. 2000;
12 Christophersen et al. 2000). In the presence of dissolved oxygen, methane will tend to be
13 degraded by aerobic methanotrophs, microorganisms that oxidize methane, which utilize
14 enzymes referred to as methane monooxygenases (Hanson and Hanson 1996).

15 The amount of oxygen in ground water is limited by its low solubility, its slow
16 diffusion from the overlying soil, and its consumption by biogeochemical and abiotic
17 processes in the presence of electron donors, such as organic compounds or sulfide
18 minerals. Consequently, the ground water in many shallow environments is anaerobic,
19 particularly in zones that are contaminated by organic contaminants, such as landfill
20 wastes or hydrocarbon plumes.

21 Until recently, it was generally assumed that methane is essentially biologically inert
22 in anaerobic environments (Higgins et al. 1981). However, research over the past few
23 decades has shown that the coupling of the oxidation of methane with the reduction of

1 sulfate (Equation 1) is a key relationship in anaerobic marine sediments (Iversen and
2 Blackburn 1981; Devol and Ahmed 1981; Iversen and Jørgensen 1985, Niewöhner et al.
3 1998; Aharon and Fu 2000; Boetius et al. 2000; DeLong 2000; D'Hondt et al. 2002;
4 Nauhaus et al. 2002). Equation 1 is a summary reaction that represents the net effect of
5 an array of stepwise redox reactions, which involve various enzymes, intermediate
6 valence sulfur species, such as sulfite (Trudinger 1969), and intermediate valence carbon
7 species, such as methanol (Hanson and Hanson 1996).



9 Bacterial sulfate reduction is probably the dominant terminal electron accepting
10 process that consumes methane throughout the oceans globally (D'Hondt et al. 2002),
11 including large upward fluxes of methane in submarine seeps associated with natural gas
12 reservoirs in the Gulf of Mexico (Aharon and Fu 2000). The microorganisms responsible
13 for the redox process summarized in Equation 1 appear to be symbiotic consortia of
14 sulfate reducing bacteria and methane-oxidizing Archaea (Boetius et al. 2000; Orphan et
15 al. 2001). There is also evidence that sulfate may be an important electron acceptor for
16 anaerobic oxidation of methane by microorganisms in surface sediments of a freshwater
17 lake in Minnesota (Panganiban et al. 1979; Zhender and Brock 1980), and in saline lakes
18 with abundant sulfate (Oremland and Des Marais 1983).

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19 Relatively few studies have examined the microbial degradation of methane in
20 ground water under anaerobic conditions. Smith et al. (1991) tracked the fate of methane
21 injected into an unconfined sand and gravel aquifer at Cape Cod, Massachusetts. Within
22 the aquifer, the methane was oxidized in an aerobic zone, and also within a sewage-
23 contaminated, anaerobic zone. On the basis of the available data, Smith et al. suggested

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1 that denitrification (nitrate reduction) was the main TEAP linked to anaerobic methane
2 oxidation in the aquifer. A recent study of a landfill leachate plume in the Netherlands
3 also suggested that anaerobic methane oxidation might be linked to nitrate reduction (van
4 Breukelen et al. 2001).

5 A few studies have suggested that the redox coupling of sulfate reduction and
6 methane oxidation, which is now well documented as an important process in marine
7 sediments, may also be important in ground water environments. One of the earliest
8 indications was a unique laboratory study by Davis and Yarborough (1966), which
9 reported slow oxidation of methane by sulfate reducing bacteria isolated from ground
10 water sampled from an oil-field aquifer at 1.3 km depth in southern Texas. In the mid-
11 1980s, a study of ground water impacted by a blow-out in Ohio associated with gas
12 exploration indicated that sulfate reduction appeared to be the principal reaction involved
13 with methane oxidation and alkalinity production (Kelly et al. 1985). Research in the
14 mid-1990s showed that methane oxidation coupled to sulfate reduction may also be
15 important in anaerobic rice paddy subsoils in Japan (Murase and Kimura 1994a,b).

16 In a recent study of aquifers in east-central Texas, abundant methane (> 10 mM) was
17 only present where sulfate levels were low (< 1 mM) (Zhang et al. 1998). This
18 relationship suggested that methanogenesis was only important in the absence of sulfate
19 in the Texas aquifers (Zhang et al. 1998). The methane $\delta^{13}\text{C}$ values indicated that
20 bacterial oxidation of this hydrocarbon had occurred, and there was a significant positive
21 correlation between $\delta^{13}\text{C}$ of methane and sulfate concentration. With other
22 considerations, this suggested that methane oxidation was associated with bacterial
23 sulfate reduction (Zhang et al. 1998).

1 In a detailed study of a landfill leachate plume in Oklahoma, Grossman et al. (2002)
2 reported evidence for anaerobic degradation of the methane. On the basis of methane
3 concentration and $\delta^{13}\text{C}$ trends along a 210 m transect of the plume, they concluded that
4 80-90 % of the methane was degraded under anaerobic conditions, associated with sulfate
5 reduction (Grossman et al. 2002). With reference to recent marine sediment studies,
6 Grossman et al. suggested that perhaps a consortium of sulfate reducing bacteria and
7 Archaea is responsible for the oxidation of methane in the ground water, linked to sulfate
8 reduction.

9 10 2.2 Methane and Sulfate in Ground Water at Oil and Gas Sites in Western Canada

11 The methane that occurs in the shallow subsurface in oil and gas producing areas of
12 western Canada is often thermogenic in origin, though it may have an ambiguous or
13 biologically altered isotopic signature (Rowe and Meuhlenbachs 1999). Similar to the
14 pattern observed in Texas (Zhang et al. 1998), a survey of private water wells in the
15 Lloydminster area, along the border of the provinces Alberta and Saskatchewan in
16 western Canada (Maathuis and Jaworski 1997), indicated a marked inverse relationship
17 between sulfate concentrations and methane in ground water (Figure 2). This relationship
18 suggests that elevated methane concentrations may persist only in the absence of sulfate,
19 and conversely, that the presence of sulfate may result in bacterial sulfate reduction,
20 linked to degradation and depletion of methane in the subsurface (Van Stempvoort et al.
21 2000). This would be analogous to the inverse relationship between sulfate and methane
22 concentrations observed in marine sediment profiles, which has been shown to be related
23 to coupling of bacterial sulfate reduction and methane oxidation.

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1 In more detailed studies of ground water chemistry at petroleum production sites in
2 the Lloydminster area, Van Stempvoort and co-workers found further evidence that
3 suggested bacterial sulfate reduction was linked to microbial degradation of methane that
4 had leaked from production wells into the ground water (Van Stempvoort and Jaworski
5 1995; Van Stempvoort et al. 1996).

6 7 **3. Research Site**

8 The research site (Figure 3) is located approximately 50 km northwest of
9 Lloydminster (53°17' N; 110°00' W) near the border between the Provinces of Alberta
10 and Saskatchewan in western Canada, in a rural setting, where the dominant land uses are
11 agriculture and oil and gas production. This site is in the Aspen Parkland region of central
12 Alberta, transitional between semi-arid grassland to the south, and humid, boreal forest to
13 the north. Seasonal changes in temperature are large; selected climate normals are shown
14 in Table 1.

15 The surface elevation at the site is approximately 625 meters above mean sea level.
16 The topography of the site is relatively level, whereas the surrounding area slopes
17 moderately toward the south. There is a large alkaline/saline slough located in a
18 depression within several hundred meters to the south of the study site.

19 The oil production well at this site was completed by Amoco Canada in December,
20 1983. The total depth drilled was approximately 640 m below ground surface. The oil
21 producing zones occur between 510 and 580 m below ground. Oil was produced from
22 this well from February, 1984 to November, 1987. The cemented surface casing extends
23 from ground to approximately 100 m.

1 Leakage of natural gas to surface along the well casing was first noted in 1988
2 (Ulrich 1994). This non-producing well is relatively remote from other oil wells in the
3 area. In close vicinity, shallow aquifers in the drift (largely glacial till) and in the bedrock
4 (Cretaceous Judith River Formation) had been documented (Ozaray et al. 1994; records
5 of private water wells retained by Alberta Environmental Protection). Given the above
6 factors, this was one of the first research sites selected in 1994 by the Canadian
7 Association of Petroleum Producers for investigation of the potential for migration of
8 natural gas to shallow ground water.

9 In May of 1994, a rotary rig (McAllister Water Wells Ltd., Lloydminster) was used
10 for the initial investigation of the shallow subsurface in the vicinity of the production
11 well. A testhole completed in 1994 indicated that there is a major sand and gravel
12 aquifer, apparently an Empress Group unit, that extends from about 25 to 50 m below
13 ground, confined between two aquitards, a marine clay/shale bedrock below (Cretaceous
14 Lea Park Formation) and overlying clayey till. The latter is Quaternary age, and appears
15 to include two or three clayey till units, separated by thin interbeds of sand and silt.

16 Figure 3 provides a plan view of the site and Figure 4 provides a hydrogeologic cross
17 section. Five monitoring wells were installed in the upper portion of this aquifer in 1994,
18 shown as 94-01 to 94-05 on Figure 3. The screens of these wells were completed at
19 approximately 28 to 30 m below ground. In November 1995, three nests of three
20 monitoring wells each (9 total) were completed in the same aquifer within 10 m of the oil
21 production well. These nests are shown as monitoring locations marked 95-06, 95-07 and
22 95-08, near the center of Figure 3. Each nest has 3 monitoring wells, A through C, where
23 A has the shallowest screen (approx. 25 m below ground), and C has the deepest screen

1 (approx. 28 m below ground). These nested wells have screens less than 0.3 m in length
2 to provide a detailed vertical profile for the uppermost portion of the aquifer. Pump
3 testing of the monitoring wells indicated that the hydraulic conductivity of the upper
4 portion of the aquifer is about $6 \cdot 10^{-3}$ cm/s (Van Stempvoort et al. 1996). Given the very
5 low hydraulic gradient at the site (approximately $5 \cdot 10^{-5}$), the lateral flow of ground water
6 in the aquifer is inferred to be southward, at a rate less than 1 m per year.

8 4. Methods

9 In previous investigations, the available monitoring wells were sampled on six
10 occasions: June 1994, October 1994, September 1995, November 1995, and September
11 1996. The sampling was by either bladder pumps (1994) or peristaltic pumps (1995-
12 1996), under low flow conditions (200 mL/min) to minimize turbulence and drawdown,
13 and to promote laminar flow from the aquifer to the pump intake tube. After purging
14 approximately 10 L from each well and discarding this water, samples were collected for
15 the following analyses: major cations (Ca^{2+} , Na^+ , Mg^{2+} , K^+), major anions (sulfate,
16 chloride, bicarbonate), nitrate plus nitrite, and dissolved Fe and Mn. The samples for
17 nitrate plus nitrite analysis were field filtered (0.45 μm) and treated with H_2SO_4 for
18 preservation. Samples for Fe and Mn analysis were also field filtered (0.45 μm), and
19 treated with HNO_3 for preservation. The major cations, Fe and Mn were analyzed by ICP
20 atomic emission spectroscopy. Sulfate was analyzed by turbidimetry, and chloride and
21 nitrate plus nitrite were measured by colorimetry. Bicarbonate was based on alkalinity,

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1 which was determined by potentiometric titration to set pH endpoints, and with laboratory
2 pH values to calculate dissolved bicarbonate.

3 For this study, the wells were resampled in June 2002 as in 1995-1996, except for
4 the three wells in nest 95-06 (A,B, C), which were frozen. The samples were analyzed as
5 above, except that sulfate was determined by ICP.

6 Samples for methane and ethane analyses were collected in 1994-1996 and 2002
7 using in-line airtight, stainless steel samplers, as described by Van Stempvoort and co-
8 workers (Van Stempvoort and Jaworski 1995; Van Stempvoort et al. 1996). For 1995-
9 1996 and 2002 events, each methane sample was collected *in-situ*, at the screen interval
10 of the monitoring well, 25 to 30 m below ground. In-line valves were closed to trap each
11 sample before the sampler was retrieved from the sampling depth and stored on ice in a
12 cooler. Within several days, the dissolved methane and ethane were extracted from the
13 water samples in the laboratory, using degassing (1994) or headspace extraction
14 techniques (1995-1996, 2002) (Van Stempvoort and Jaworski 1995; Van Stempvoort et
15 al. 1996). The respective concentrations were analyzed by gas chromatography (GC).
16 The GC system used was an Agilent 5890 GC, dual packed columns of Porapak N and
17 Molecular Sieve 13X with a flame ionization detector.

18 For the 2002 sampling event, after purging was completed for each well, the pH, Eh
19 and dissolved O₂ in the produced ground water were analyzed in the field, using a YSI
20 556 multi-probe system and flow cell. The flow cell was placed in-line and downgradient
21 of the peristaltic pump, within a few meters of each monitoring well head. Ground water
22 temperatures measured in flow cell ranged from 8.3 to 11°C. Based on other experience
23 with this system, these temperatures were affected by warming, apparently due to friction

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1 during pumping, and exposure of the flow cell to the ambient atmosphere (circa 20-30° C
2 at time of sampling) and sunlight. The estimated in-situ ground water temperature at the
3 well screens is 3 to 7° C, closer the annual average temperature for this region (Table 1).

4 During the 2002 sampling event, 1 L ground water samples were collected for
5 analyses of the isotopic composition of dissolved sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) and total sulfide
6 ($\delta^{34}\text{S}$) (mainly dissolved, some suspended). Ground water was pumped directly into the
7 sample bottles containing 2 mL of concentrated cadmium acetate solution. Ground water
8 contact with air was minimized and hence dissolved sulfide immediately precipitated as
9 cadmium sulfide. For analyses of $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), ground water
10 was transferred to 20 mL glass vacutainers pre-filled with 2 mL of strontium chloride
11 (monobasic) solution. Upon contact with ground water, DIC precipitated as strontium
12 carbonate, which was transported to the laboratory for further analyses.

13 Stable isotope analyses of 2002 samples were conducted in the Isotope Science
14 Laboratory at the University of Calgary. Carbon isotope ratios of DIC were determined
15 on CO_2 obtained via acid treatment of the strontium carbonate precipitates. For sulfur
16 isotope analyses, the CdS precipitate was separated by filtration, converted to Ag_2S ,
17 which was subsequently dried and weighed. Total sulfide contents were estimated
18 gravimetrically. Dissolved sulfate was precipitated as BaSO_4 from the filtered samples
19 by adding 10 mL of a 0.25M BaCl_2 solution. The BaSO_4 precipitate was removed by
20 filtration, dried, and weighed. Sulfur isotope ratios of the Ag_2S and BaSO_4 precipitates
21 were determined on SO_2 generated by combustion in an elemental analyzer coupled to an
22 isotope ratio mass spectrometer in continuous flow mode (Giesemann et al. 1994).

Oxygen isotope ratios of the BaSO₄ precipitates were analyzed on CO generated via pyrolysis in a Finnigan TC/EA reactor at 1450°C coupled to delta plus XL in continuous flow mode. Results are reported in the usual delta (δ) notation in parts per thousand (‰) deviation from the internationally accepted standards Canon Diablo Troilite (V-CDT) for sulfur isotope measurements, Standard Mean Ocean Water (V-SMOW) for oxygen isotope analyses, and V-PDB for carbon isotope ratios.

The monitoring wells were also sampled by Alberta Environment in February, 2001. Approximately 250 L was pumped from each well using a Waterra system, directly into a degassing system, which consisted of a heat exchanger and a gas-liquid separator (Geo Five Gas Technologies). Although ideal degassing temperatures (85 to 95 °C) were not achieved, approximately 1000 cc of gas was recovered from each well at temperatures varying from 40 to 70 °C, and this gas was transferred to a Tedlar bag for laboratory analyses. The gas composition was analyzed by gas chromatography (inorganic species and hydrocarbons), and the components were reported on a mole fraction basis. Selected samples were submitted to the University of Alberta for stable isotope analyses of methane and other components (e.g., ethane, propane, butane, CO₂).

The data for degassed samples obtained during the February 2001 sampling event have been reported separately (Rich 2003). The methane data (concentrations, δ¹³C values) are also included in this paper, in order to complement the other methane concentration data obtained during this study.

5. Results and Discussion

5.1 Source of Methane

Sampling at the research site in the mid-1990s indicated elevated levels of methane in the ground water in the close vicinity of the oil production well (Figure 5). Ethane was also present, associated with the elevated concentrations of methane (Figure 6). Typically, the mass ratio of methane/ethane in these samples was between 50 and 500 (Van Stempvoort and Jaworski 1995; Van Stempvoort et al. 1996; Maathuis and Jaworski 1997), which is considered to be diagnostic for a thermogenic source of these hydrocarbons (Taylor et al. 2000). Analyses of the February 2001 Tedlar bag gas samples by Alberta Environment indicated that dissolved propane was also present in most of the wells, at concentrations similar to ethane, as well as traces of other hydrocarbons. Together, these results indicate that thermogenic methane has migrated from the oil production well bore to the adjacent aquifer.

5.2 Lateral Concentration Trends

The concentrations of methane and selected other ground water parameters measured for samples obtained in 2002 are shown in Table 2. Methane concentrations were generally lower in 2002 than during the mid-1990s (Figure 5). In particular, within 10 m of the oil well, the 2002 methane concentrations were approximately an order of magnitude lower than the levels measured in 1995 and 1996. Seasonal fluctuations can be ruled out, given the 25 m thick confining till aquitard above the aquifer at this site. Based on the overall trend from 1996 to 2002, it is likely that one or both of the following had occurred during this time: 1) a reduced rate of leakage of methane from the oil production well to the aquifer between 1996 and 2002, combined with southward, lateral

1 migration and dispersion of the concentrated methane "plume" in the ground water; 2), an
2 increase in the rate of *in-situ* biodegradation of the methane in the aquifer between 1996
3 and 2002, which significantly reduced the dissolved methane concentrations.

4 It is possible that the 1996-2002 methane concentration trend was affected by the
5 withdrawal of approximately 250 L from each well during the 2001 sampling event by
6 Alberta Environment. However, this event removed only a few percent of the total
7 volume of ground water that is present within the upper, screened portion of the aquifer,
8 within 10 m of the oil well. Perhaps the 2001 sampling event resulted in movement of
9 ground water in the vicinity of the well that somehow stimulated the growth of the
10 microorganisms that are degrading the methane in ground water. Alternatively, there may
11 have been an acceleration of the ongoing natural attenuation of the methane during the
12 period 1996 to 2002, unrelated to the 2001 sampling event. We have no conclusive
13 evidence to favour either of these interpretations

14 Dissolved oxygen was generally not detectable (<0.2 mg/L) in the ground water in
15 2002, indicating anaerobic conditions. A low level of dissolved oxygen (0.5 mg/L) was
16 measured by flow cell for one of the "background" monitoring locations, distant from the
17 oil well (94-04). Given that the ground water in this well had dissolved iron and sulfide
18 (Table 2), the single indication of low dissolved oxygen may be spurious, or it may
19 indicate that subzones of oxic and anoxic ground water may occur in the aquifer at this
20 location. Nitrate plus nitrite were not detected in any of the wells in 2002 (< 0.01 to 0.02
21 mg/L as N). Given the lack of oxygen and nitrate, dissolved sulfate with concentrations
22 ranging between 220 and 368 mg/L (Table 2) is apparently the most readily available
23 aqueous phase electron acceptor in the aquifer.

1 In 2002, sulfate concentrations were somewhat lower in samples from monitoring
2 wells within 10 m of the oil well, relative to remote wells (≥ 50 m away) (Table 2, Figure
3 7). This contrasts with the mid-1990s data, which indicated no obvious lateral trend in
4 sulfate concentrations (Figure 7). The 2002 zone of lower sulfate concentrations in
5 ground water near the oil well is associated with elevated bicarbonate and lower Eh
6 values (Table 2). A relatively low Eh value was also measured for remote monitoring
7 well 94-01A, associated with a relatively high concentration of methane (Table 2),
8 suggesting that methane has migrated from the oil well to this monitoring location.

9 The above noted association of somewhat lower sulfate concentrations with elevated
10 bicarbonate concentrations near the oil well, in the same zone where methane has
11 declined over time, suggests that Equation 1 may be an important overall reaction in this
12 zone.

13 Lateral trends in Fe and Mn concentrations in the ground water are not evident
14 (Table 2), suggesting that the reduction of mineral phases containing Fe^{3+} and Mn^{2+}
15 (e.g., oxides) are currently not important as electron accepting processes linked to
16 hydrocarbon degradation in the vicinity of the oil well. It is likely that mineral phase Fe^{3+}
17 and Mn^{2+} are not abundant species in this confined, largely anaerobic aquifer.

18 The 2002 sulfide data (Table 2) do not indicate a lateral trend, related to inferred
19 bacterial sulfate reduction. It is likely that sulfide generated by bacterial sulfate reduction
20 in the vicinity of the oil well is largely precipitated as metal sulfide (e.g., FeS) in the
21 aquifer.

22

23 5.3 Vertical Concentration Trends

1 The three nests of monitoring wells that were installed close to the oil production
2 well (95-06, -07, -08 series) provide useful information on vertical hydrogeochemical
3 trends. Data for ground water samples obtained in 1995 from these wells indicate upward
4 trends of decreasing sulfate concentrations (Figure 8, Table 3) increasing dissolved Fe
5 contents near the top of the aquifer (Table 3), and a weaker trend of increasing methane
6 content in the shallower parts of the aquifer (Figure 9, Table 3). Nitrate was non-
7 detectable throughout the profile (Van Stempvoort et al. 1996). Based on these data, Van
8 Stempvoort et al. (1996) suggested that the methane had migrated from the oil well into
9 the aquifer as a buoyant gas-phase, thus tending to concentrate near the top of the aquifer,
10 below the confining clay till unit. Further they suggested that the methane was being
11 degraded by microorganisms, with Fe^{3+} and sulfate as the electron acceptors, particularly
12 focused in a zone near the top of the aquifer.

13 Maathuis and Jaworski (1997) collected samples in September 1996 from the same
14 nested wells, and they also reported upward increasing methane concentrations (Figure 9;
15 Table 3). These data support the earlier interpretation that this hydrocarbon had migrated
16 as a buoyant, gas-phase, and that it had accumulated near the top of the aquifer (Van
17 Stempvoort et al. 1996). There was no obvious vertical trend in dissolved Fe in 1996
18 (Table 3), and the upward decrease of sulfate concentrations in 1996 was not as
19 pronounced as in 1995 (Figure 8; Table 3).

20 Samples collected in June 2002 again indicated a strong trend of decreasing sulfate
21 concentrations near the top of the aquifer (Figure 8; Table 3), while upward trends for
22 methane (Figure 9, Table 3) and Fe (Table 3) in 2002 were not obvious. Similar to the
23 changes in the lateral concentration gradients of methane over the period 1996-2002, the

1 disappearance of an upward increasing methane trend by 2002 (Table 3) could have been
2 influenced by a decreasing rate of methane emission from the production well over time.
3 Alternatively, an increasing rate of *in-situ* biodegradation of methane between 1996 and
4 2002, focused near the top of the aquifer, may have obliterated the upward increasing
5 methane trend by 2002. The 2002 data indicate some upward enrichment of dissolved
6 sulfide in the monitor nests near the oil well (Table 3). This trend supports the
7 interpretation that bacterial sulfate reduction is focused near the top of the aquifer, related
8 to oxidation of methane, which tends to become trapped at the top of the aquifer.
9 However, there are no large increases in sulfide concentrations in ground water in the
10 vicinity of the oil well (Table 2), presumably due to metal sulfide precipitation, as
11 discussed in the previous section

12

13 5.4 Stable Isotope Evidence for Methane Sources, Methane Oxidation, and Bacterial 14 Sulfate Reduction

15 The net decrease of sulfate in ground water near the oil well between 1996 and 2002
16 (Figures 7, 8), concurrent with a reduction in the methane concentrations (Figures 5, 9), is
17 a key finding. This relationship provides direct evidence that bacterial sulfate reduction
18 may have played an important role as a TEAP in a biodegradation process that reduced
19 the concentrations of dissolved methane between 1996 and 2002. In this section, stable
20 isotope data provide further support for this hypothesis.

21 Analyses of the 2001 Tedlar bag gas samples that were degassed from ground water
22 (Alberta Environment) indicate significant lateral trends in the $\delta^{13}\text{C}$ values of methane-C
23 (Figure 10). The dissolved methane near the oil well is relatively ^{13}C -enriched ($\delta^{13}\text{C} = -$

1 62.5 to -52.0 ‰). Although these $\delta^{13}\text{C}$ values are not diagnostic, they fall within the
2 range for low temperature thermogenic methane sampled at depth in the area (Rowe and
3 Meuhlenbachs 1999). This is consistent with the interpretation that this methane has
4 migrated upward along the oil well bore, from a pool of thermogenic gas at depth. At 50
5 m from the oil well (94-01A), a relatively high level of methane (1.5 g/L) had a similar
6 isotopic signature ($\delta^{13}\text{C} = -62.8$ ‰), suggesting that this monitoring location is also
7 impacted by thermogenic methane that has migrated from the oil well. In contrast, the
8 methane at two monitoring locations ≥ 50 m distant from the oil well (94-04, 94-05) have
9 low methane concentrations (0.006 to 0.07 mg/L), with methane $\delta^{13}\text{C}$ values ranging
10 from -71.2 to -82.1 ‰, indicating a dominantly biogenic source of the methane. This
11 "background" methane may be derived from the *in-situ* biodegradation of natural organic
12 matter within the aquifer, or within the underlying "shale" bedrock.

13 Within 10 m of the oil well, there is a marked lateral trend in the methane $\delta^{13}\text{C}$
14 values (2001 data, Figure 10). The methane at monitoring locations within a few meters
15 of the oil well is enriched in ^{13}C by up to 10 per mil compared to the methane at locations
16 8 to 10 m from the oil well (Figure 10). This trend is likely related to methane oxidation
17 (Barker and Fritz 1981a; Grossman et al. 2002). There is no evidence that this trend can
18 be attributed to mixing of methane from two or more isotopically distinct sources.
19 Further, it is unlikely that this trend could be due to a physical isotope fractionation
20 process associated with lateral movement of the methane in the aquifer (Barker and Fritz
21 1981a).

1 It appears that the methane nearest to the oil well has been most strongly affected by
2 methane oxidation, resulting in the most ^{13}C -enriched methane. Similarly, the vertical
3 trend in methane $\delta^{13}\text{C}$ values indicates upwards ^{13}C -enrichment (2001 data, Figure 11),
4 suggesting that the extent of methane oxidation is most pronounced near the top of the
5 aquifer.

6 Based on the lateral and vertical trends of the methane concentrations and methane
7 $\delta^{13}\text{C}$ trends, the zones with highest methane concentrations (nearest to oil well, and
8 nearest to top of aquifer) have also been most strongly affected by methane oxidation.
9 Thus it appears that the zone with the highest methane impact has also been the most
10 favourable to the development of anaerobic, methanotrophic communities.

11 The 2002 data indicate relatively low sulfate concentrations in ground water close to
12 the oil well, coexistent with high concentrations of bicarbonate (DIC), which is relatively
13 ^{13}C -depleted (Table 4). There is a very strong positive correlation between the sulfate
14 concentration and the $\delta^{13}\text{C}$ of the DIC (Table 5; Figure 12), similar to the positive
15 correlation noted for the same parameters in Texas ground water by Zhang et al. (1998).
16 At our research site, there was also a strong negative correlation between the sulfate and
17 bicarbonate concentrations (Table 5; Figure 12). Based on the 2001 data, the methane in
18 monitoring wells close to the oil well (Alberta Environment) had $\delta^{13}\text{C}$ values of -52.0 to
19 -63 ‰ (Figure 10), which is ^{13}C -depleted relative to the DIC (Table 4). Together, these
20 concentration and stable isotope data support an interpretation that the higher
21 concentrations of ^{13}C -depleted bicarbonate near the oil well were produced by the

1 oxidation of ^{13}C -depleted methane to DIC (bicarbonate), linked to bacterial sulfate
2 reduction (depletion) as the main TEAP.
3 Assuming no precipitation of calcite in response to the conversion of methane to
4 DIC, regression of the 2002 values of DIC concentrations versus DIC- $\delta^{13}\text{C}$ values
5 suggests that the DIC added to the ground water in the vicinity of the oil well by methane
6 oxidation had $\delta^{13}\text{C}$ signature of approx. -43 ‰, which is reasonably close to values
7 measured for thermogenic methane at the site (-52.0 to -63 ‰ based on Figure 10). It is
8 likely that associated thermogenic gases (ethane, propane, butane) were also oxidized in
9 the vicinity of the oil well. The 2001 analyses for Tedlar bag samples indicated the
10 following ranges in $\delta^{13}\text{C}$ for these components: -32.4 to -45.6 ‰ for ethane, -24.1 to -32.3
11 ‰ for propane, -22.6 to -34.4 ‰ for butane (Rich 2003). Thus, oxidation of a mixture of
12 methane plus associated heavier hydrocarbons could account for the $\delta^{13}\text{C}$ value of excess
13 DIC as suggested by regression (-43 ‰).

14 Other than methane and associated thermogenic gases such as ethane, there is no
15 known organic carbon source in the aquifer that would have such ^{13}C depleted signatures.
16 Detailed modeling of the shifts in $\delta^{13}\text{C}_{\text{DIC}}$ values and the mass balance of the carbon pool
17 associated with the conversion of methane to DIC for this site are not available. Such
18 modeling would take into account the amounts of methane and other hydrocarbons
19 oxidized, the associated kinetic isotope fractionation factors during oxidation, the
20 equilibrium mass exchange between various DIC components, the precipitation of
21 carbonate, and isotopic fractionation associated with CO_2 /bicarbonate/carbonate
22 equilibria.

1 For 2002 ground water samples, the $\delta^{34}\text{S}$ value of sulfide-S is depleted by
2 approximately 30 to 50 ‰, compared to the $\delta^{34}\text{S}$ value of the sulfate (Table 4). This is
3 strong evidence that in-situ bacterial reduction of sulfate to sulfide has occurred. This
4 process is known to produce ^{34}S -depleted sulfide (more negative $\delta^{34}\text{S}$ values), relative to
5 residual sulfate (e.g., Harrison and Thode 1958).

6 The lateral distribution of the $\delta^{34}\text{S}$ values of sulfate-S (2002) provide strong
7 supporting evidence that bacterial sulfate reduction has been focused near the oil well.
8 The wells within 10 m of the oil well have lower concentrations of sulfate that is ^{34}S -
9 enriched (more positive $\delta^{34}\text{S}$ values), compared to the "background" sulfate in wells at
10 wells 50 or more m from the oil well (Table 4). Overall, there is a very strong negative
11 correlation between the sulfate concentrations and the $\delta^{34}\text{S}$ values for the sulfate-S (Table
12 5).

13 Figure 13 is a plot of $\delta^{34}\text{S}_{\text{sulfate}}$ versus $\delta^{18}\text{O}_{\text{sulfate}}$ values for the 2002 samples. The
14 data plot along a trend from lower left to upper right, with the remote well samples
15 having typically low values. This trend also provides strong evidence in support of the
16 interpretation that bacterial sulfate reduction is taking place at monitor locations close to
17 the oil well, linked to methane oxidation. Microbial reduction of sulfate will tend to
18 enrich residual sulfate in both ^{34}S and ^{18}O , thus driving the values toward the upper right
19 area in Figure 13.

20

21 5.5 Discussion

1 This study demonstrates the value of using stable isotope analyses of sulfur, oxygen
2 and carbon species to support the investigation of natural attenuation of natural gas in
3 ground water. Based on the results of this study, bacterial sulfate reduction appears to
4 have the potential to play a major role in the bioattenuation of fugitive natural gas
5 emissions to the ground water environment in western Canada. Other ground water
6 chemistry data obtained in the mid-1990s suggest that this process is also occurring at the
7 three other production well sites in the Lloydminster area that were selected for research
8 (Van Stempvoort and Jaworski 1995; Van Stempvoort et al. 1996). Thus, this inferred
9 natural process may play an important role in attenuating this greenhouse gas and limiting
10 its impact on the atmosphere.

11 Further study should be conducted to see whether it may be possible to enhance this
12 process in soils and ground water in order to mitigate the migration of this greenhouse gas
13 from the subsurface to the atmosphere, at oil and gas producing sites, and at other
14 methane-rich sites, such as landfills.

15 The results of this study also have important implications for the current practice of
16 monitored natural attenuation (MNA) as a management approach at sites with
17 hydrocarbon-contaminated ground water. In particular, the apparent direct link between
18 bacterial sulfate reduction and methane oxidation has important implications for the
19 current practice of delineating redox zones in aquifers at these sites. Applications of
20 MNA typically subdivide the contaminated aquifers into zones where various TEAPs
21 dominate or play exclusive roles in degradation of contaminants. Often, separate zones
22 where bacterial sulfate reduction, methanogenesis other other TEAPs dominate are
23 defined. Based on the results of this study, such an approach appears to be incomplete, at

1 least for cases where some of the methane may migrate laterally in the aquifer and then be
2 consumed in a sulfate reducing zone. In such cases, the conceptual model of
3 biodegradation processes should consider methanogenesis, at least in part, as an
4 intermediate electron accepting process rather than a terminal electron accepting process.

5 For MNA sites where methane produced by methanogenic bacteria has migrated
6 from a contaminant source area to peripheral zones where sulfate is present, an estimate
7 should be obtained of the amount of methane that has been degraded by microorganisms,
8 with bacterial sulfate reduction as the TEAP. Otherwise, the role played by methanogens
9 in the overall degradation of petroleum hydrocarbons or other organic contaminants in
10 ground water may be underestimated.

11 Further, Hansen et al. (2001) and others have shown that bacterial sulfate reduction
12 and methanogenesis can sometimes occur in the same zone. Radiolabelling experiments
13 (e.g., Hansen et al. 2001) might be useful to indicate the rates of both methane production
14 and methane oxidation.

15 16 Acknowledgements

17 Funding was provided by the Program for Energy Research and Development and the
18 Lloydminster Area Operators Gas Migration Team. Earlier studies at the research site by
19 the Saskatchewan Research Council were funded by the Canadian Association of
20 Petroleum Producers, the Lloydminster Area Operators Gas Migration Team, and the
21 federal Panel for Energy Research and Development. From 1994-2002, access to the site
22 was provided by Amoco Canada, Elan Energy and Canadian Natural Resources Limited.
23 The 2001 Tedlar gas samples were collected and analyzed by Maxxam Analytics Inc. of

Edmonton, Alberta. Stable isotope analyses of hydrocarbons in 2001 Tedlar bag samples were conducted by K. Muehlenbachs at the University of Alberta, Edmonton.

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Table 1. Climate normals, 1971-2000 for Elk Point, Alberta, which is approximately 20 km north of the research site (Environment Canada data).

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1

Mean daily temperature, July (°C)	Mean daily temperature, January (°C)	Mean daily temperature, Annual (°C)	Mean Annual Precipitation (mm)
16.2	-16.7	1.2	442.3

Table 2. Selected dissolved species, bicarbonate and Eh values in monitoring wells (June 3, 2002). Oxygen and nitrate were generally not detectable (see text). Given the range in field pH (7.02 - 7.36), the dissolved Fe and Mn are mainly Fe²⁺ and Mn²⁺, respectively.

	Methane mg/L	sulfate mg/L	sulfide * mg/L	Fe mg/L	Mn mg/L	bicarbonate mg/L	Eh mV
Remote monitoring wells (≥ 50 m from oil well)							
94-01A	1.5	368	0.6	2.9	0.25	575	-110.6
94-04	0.006	357	3	4.3	0.34	570	-65.7
94-05	0.07	355	17	4.1	0.67	582	-67
Average	0.52	360	7	3.8	0.42	576	-81.1
Proximal Monitoring wells (within 10 m of oil well)							
94-02	0.92	322	2	6.8	0.74	616	-107.2
94-03	0.05	358	0.9	4.6	0.35	601	-85.6
95-07A	0.2	349	3	6.5	0.4	606	-92.4
95-07B	1.9	348	8	7.4	0.39	606	-103.4
95-07C	2.4	220	7	1.5	0.48	720	-127.1
95-08A	2.5	313	4	1.2	0.36	644	-115.1
95-08B	0.56	254	8	3	0.42	699	-113
95-08C	0.13	236	13	4.8	0.35	647	-139.3
Average	1.08	300	6	4.5	0.44	642	-110.4

*obtained relatively pure CdS precipitates in all samples, suspended sulfide minimized by slow pumping rate.

Table 3. Correlation coefficients for various parameters (mg/L) versus depth (m) below the top of the aquifer, monitor nests -06, -07, -08. Positive correlation indicates diminishing concentrations upward; negative correlation indicates increasing concentrations upward. Maximum possible correlation is value of either 1 or -1. NA indicates not available.

	1995	1996	2002
Methane	-0.318	-0.671	0.024
Fe	-0.893	-0.172	0.144
Sulfate	0.763	0.420	0.818
Sulfide	NA	NA	-0.787

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Table 4. Hydrochemical parameters for groundwater sampled in 2002.

SAMPLE NAME	sulfate mg/L	$\delta^{34}\text{S}_{\text{sulfate}}$	$\delta^{18}\text{O}_{\text{sulfate}}$	$\delta^{34}\text{S}_{\text{sulfide}}$	bicarbonate mg/L	$\delta^{13}\text{C}_{\text{DIC}}$
Remote monitoring wells (≥ 50 m from oil well)						
94-01A	368	-10.2		-54.1	575	-14.2
94-04	357	-9.7		-40.5	570	-13.8
94-05	355	-9.7		-42.0	582	-13.9
Proximal Monitoring wells (within 10 m of oil well)						
94-02	322	-5.0		-48.8	616	-15.4
94-03	358	-8.7		-47.9	601	-14.2
95-07A	349	-8.0		-45.7	606	-14.4
95-07B	348	-7.9		-39.5	606	-14.4
95-07C	220	-14.5		-40.7	720	-18.8
95-08A	313	-0.2		-53.7	644	-16.7
95-08B	254	-11.2		-47.5	699	-19.3
95-08C	236	6.4		-40.9	647	-19.7

Table 5. Correlation coefficients for various parameters for all wells sampled in 2002 (cf. Tables 2, 4).

	$\delta^{34}\text{S}$ -sulfate	$\delta^{34}\text{S}$ - sulfide	$\delta^{13}\text{C}$ -DIC	bicarbonate
Sulfate	-0.977	-0.252	0.970	-0.917

Figure Captions:

Figure 1. Schematic of upward natural gas migration along the borehole of an oil or gas well to surface, and also to an aquifer in the shallow subsurface.

Figure 2. Graph showing relationship between sulfate and methane concentrations in ground water, Lloydminster area. These analyses were based on samples collected from private water wells in 1996 in research funded by the Canadian Association of Petroleum Producers (Maathuis and Jaworksi, 1997).

Figure 3. Plan view of the research site showing locations of former oil production well and monitoring wells. Monitoring locations 95-06, 95-07 and 95-08 are nests of 3 monitoring wells each. See text for further details, and refer to Figure 4 for a cross section of this site.

Figure 4. Schematic cross section of the research site (location on Figure 3).

Geophysical logs are shown for the test hole on left: Sp is self potential, R is resistivity.

Figure 5a. Lateral trend of methane concentrations in November 1995, September 1996 and June 2002, relative to location of oil well. 1994 data are not shown because only five monitoring wells were available.

Figure 5b. Lateral trend of methane, as mole fraction of sample degassed from ground water, relative to location of oil well (2001 data). In contrast, Figure 5a shows methane concentrations in mg/L.

Figure 6. Data for ground water samples collected in 1995 and 1996 indicating relationship between methane and ethane concentrations.

Figure 7. Lateral trend in sulfate concentrations in ground water, relative to the location of the oil well.

Figure 8. Vertical trends of sulfate concentrations in ground water, including data from 3 profiles near the oil well (monitoring wells -06, -07 and -08).

Figure 9. Vertical distribution of methane concentrations for the three monitoring wells nests close to the oil well.

Figure 10. Lateral trend in methane $\delta^{13}\text{C}$ in 2001, relative to location of oil well.

Figure 11. Vertical trend in methane $\delta^{13}\text{C}$ in 2001, relative to top of the aquifer.

Figure 12. Graphs showing relationships between the concentrations of sulfate in 2002 ground water samples, and bicarbonate concentrations (top), $\delta^{13}\text{C}_{\text{DIC}}$ in ground water (bottom).

Figure 13. Plot of $\delta^{34}\text{S}_{\text{sulfate}}$ versus $\delta^{18}\text{O}_{\text{sulfate}}$ for ground water in 2002.

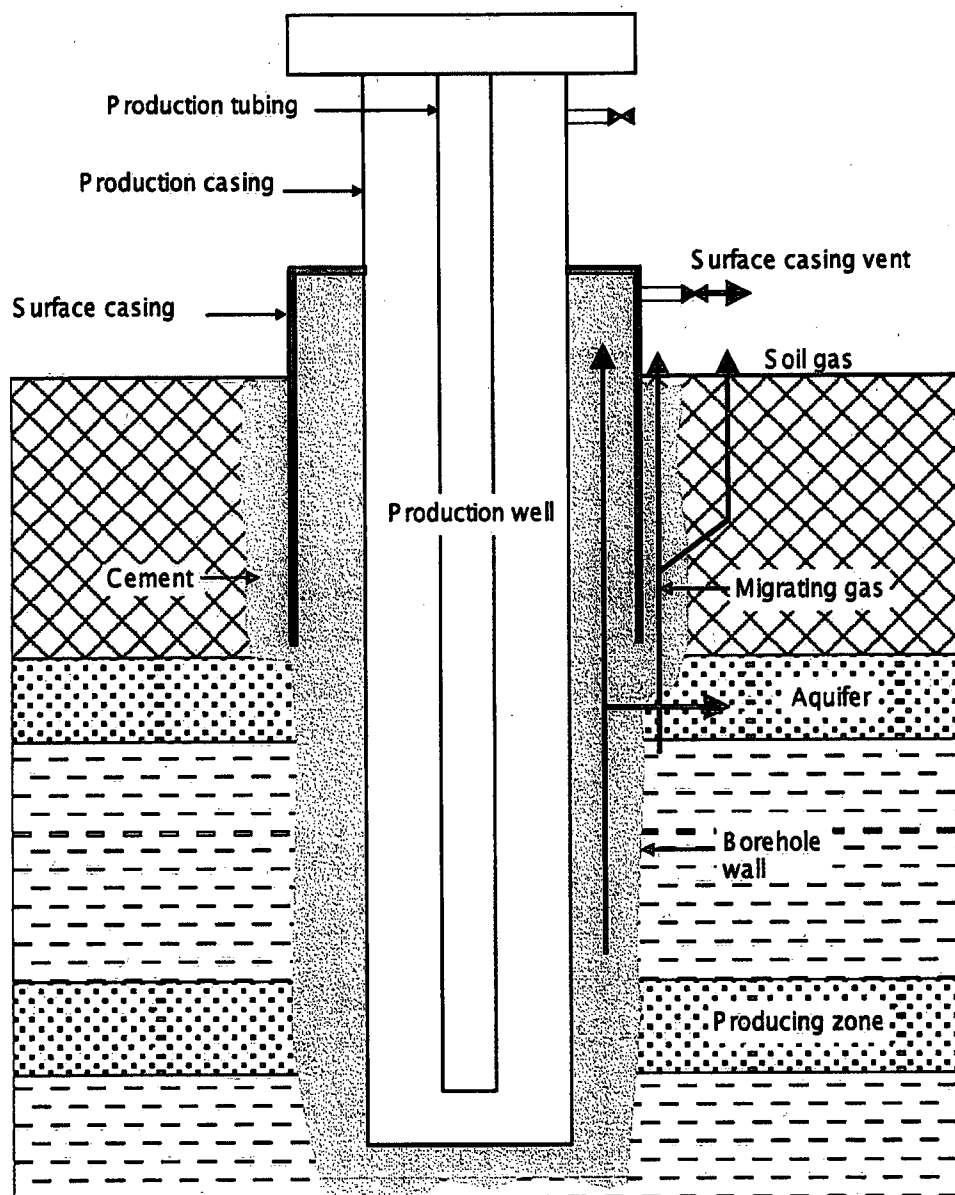


fig 1

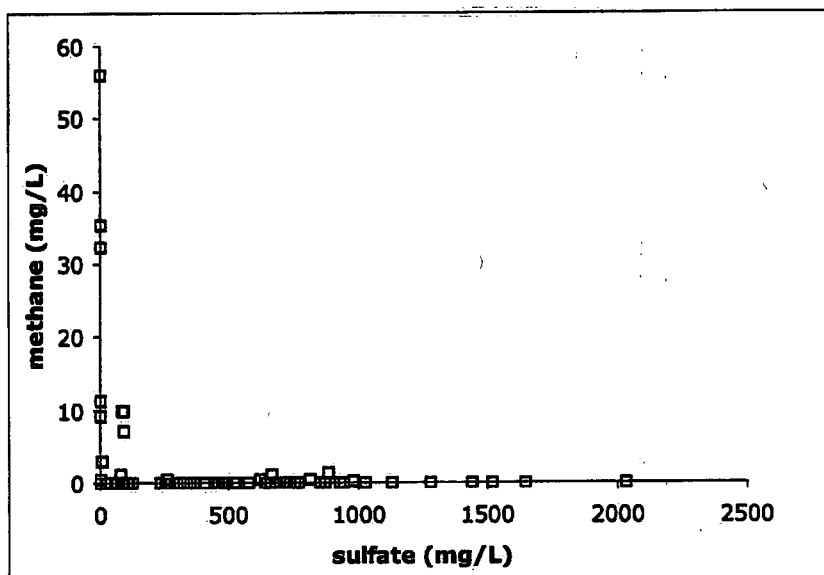


fig 2

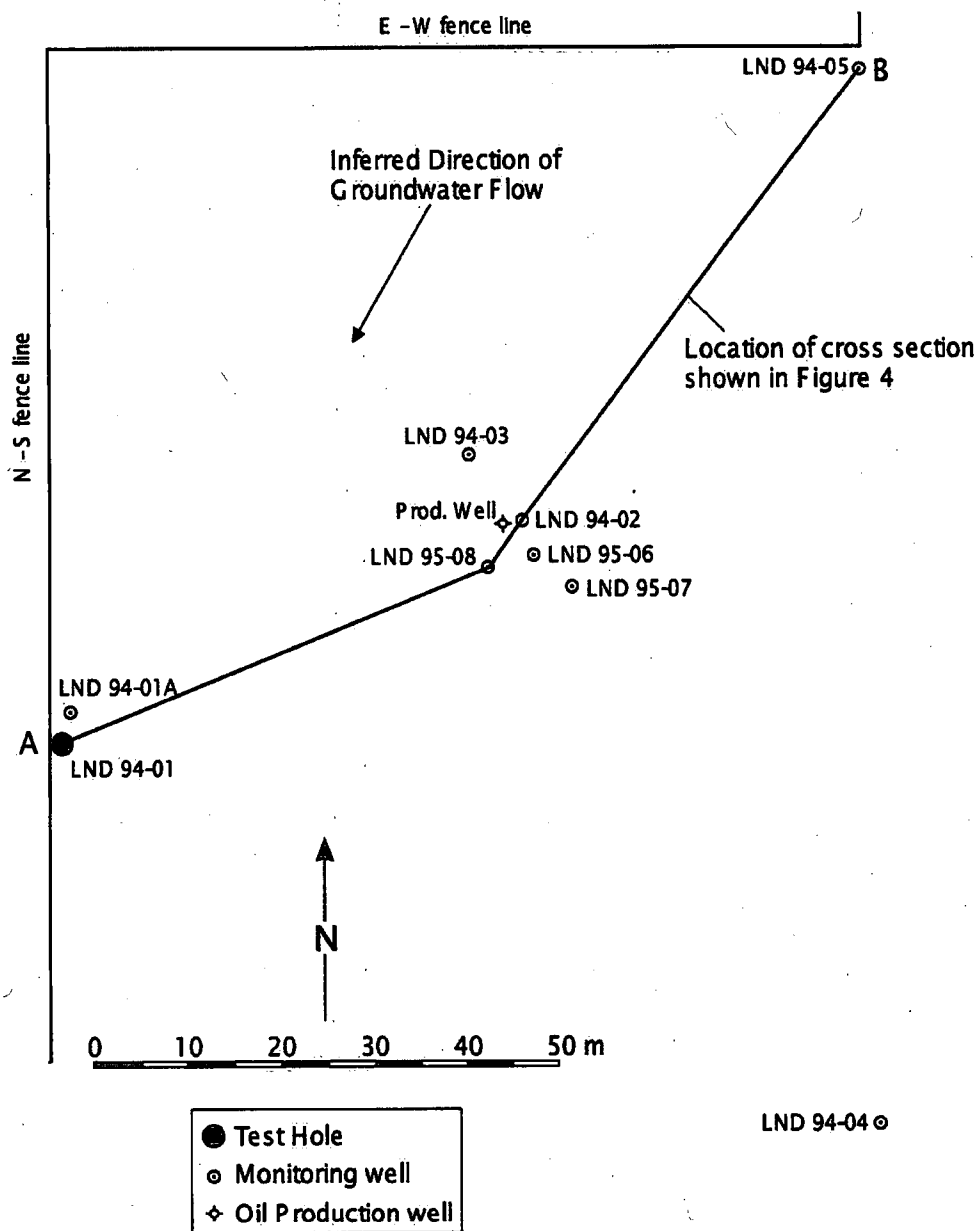


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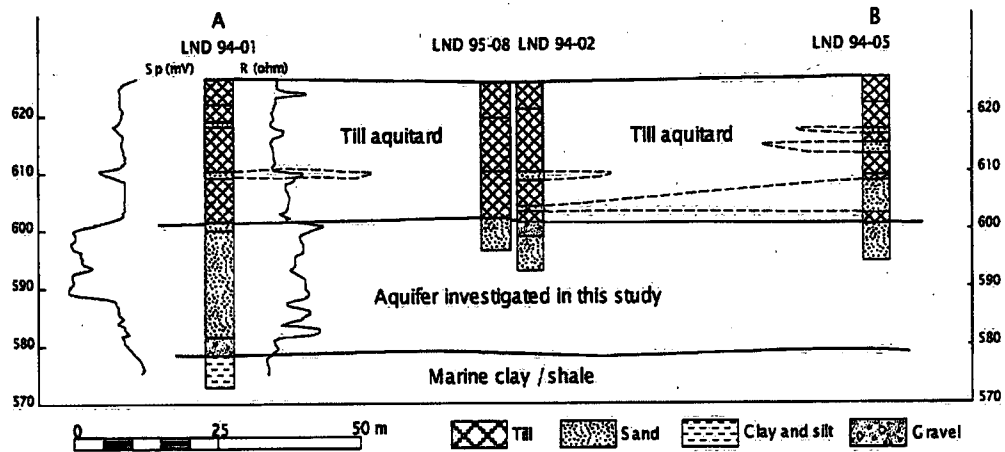


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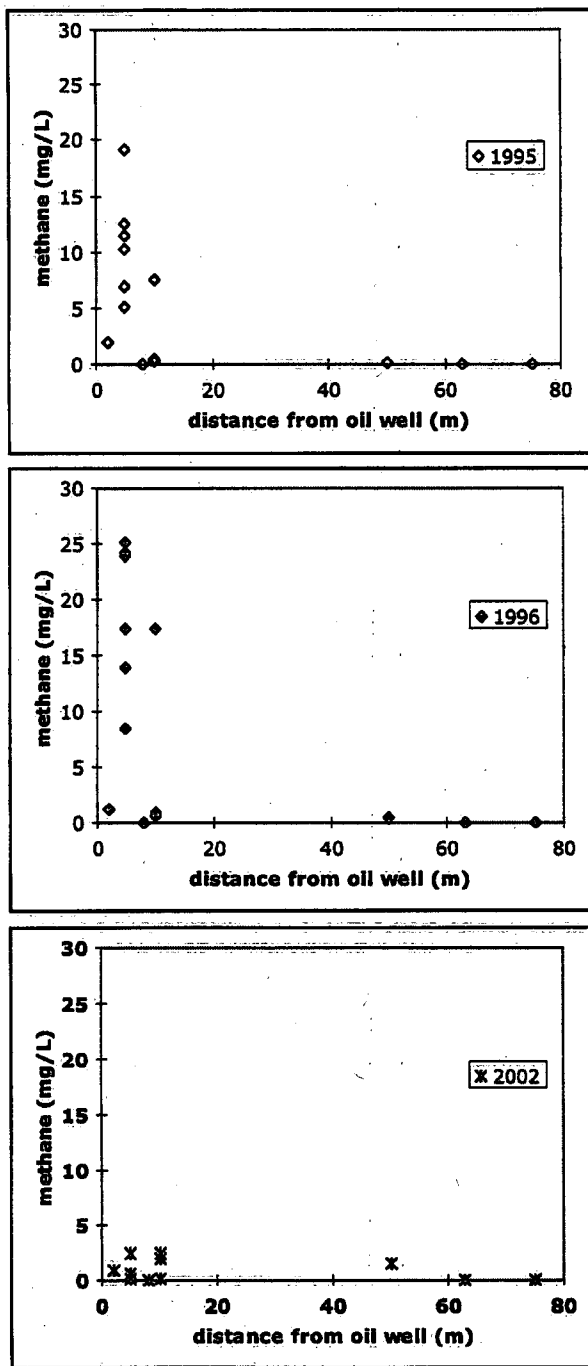


fig 5 a

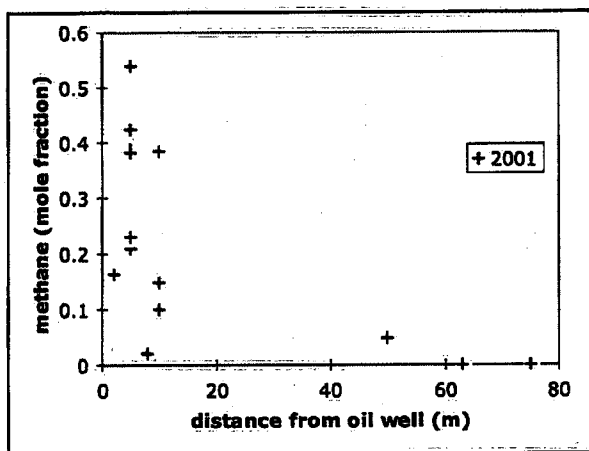


fig 5b

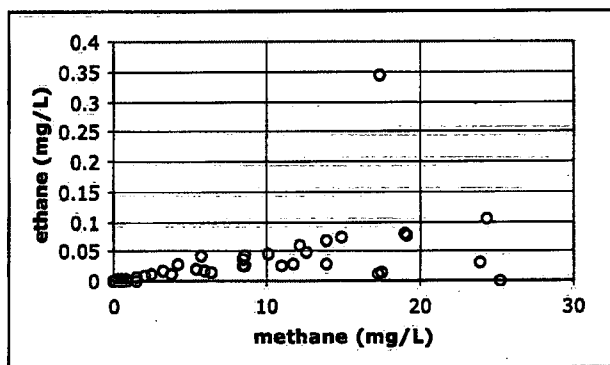


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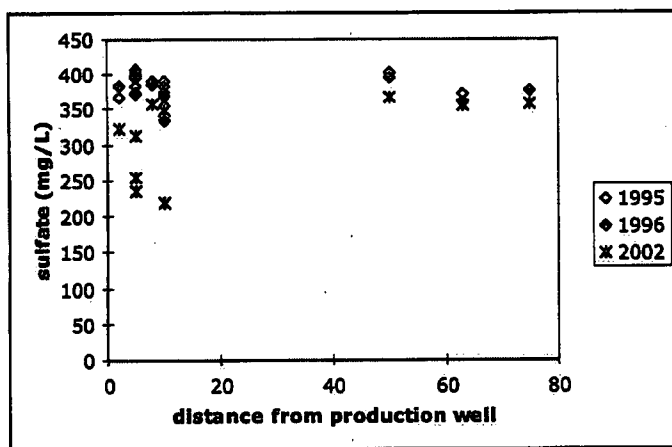


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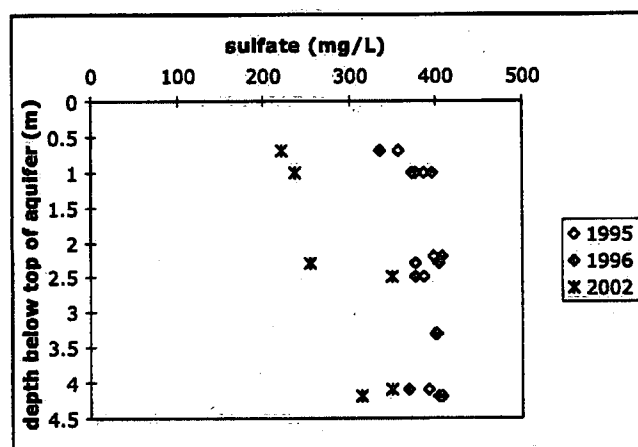


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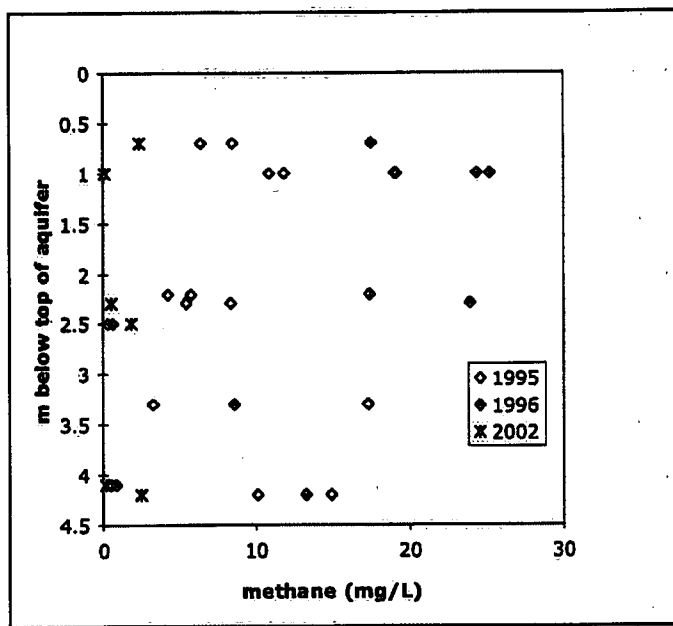


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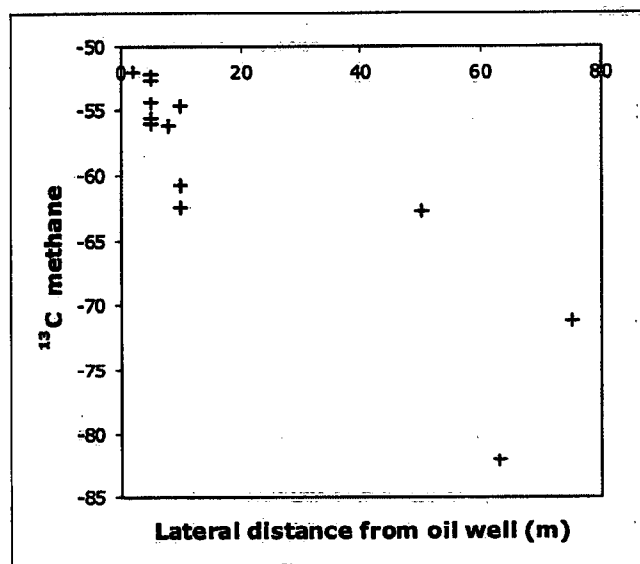


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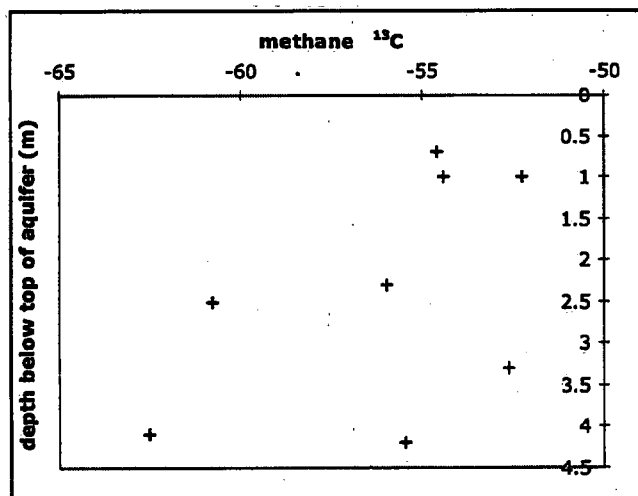


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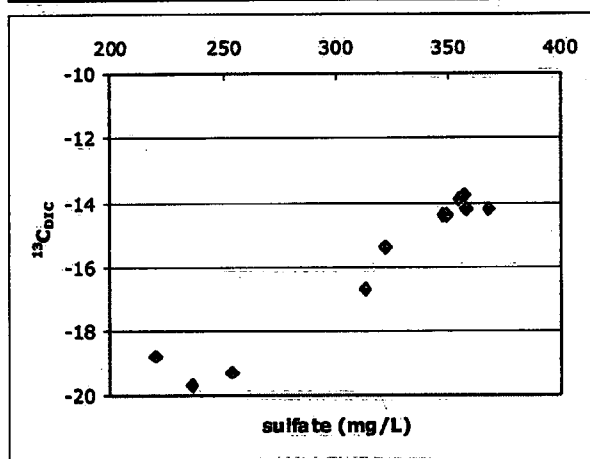
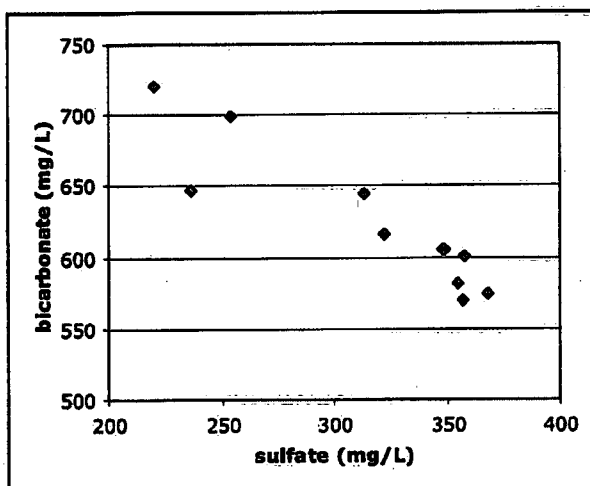


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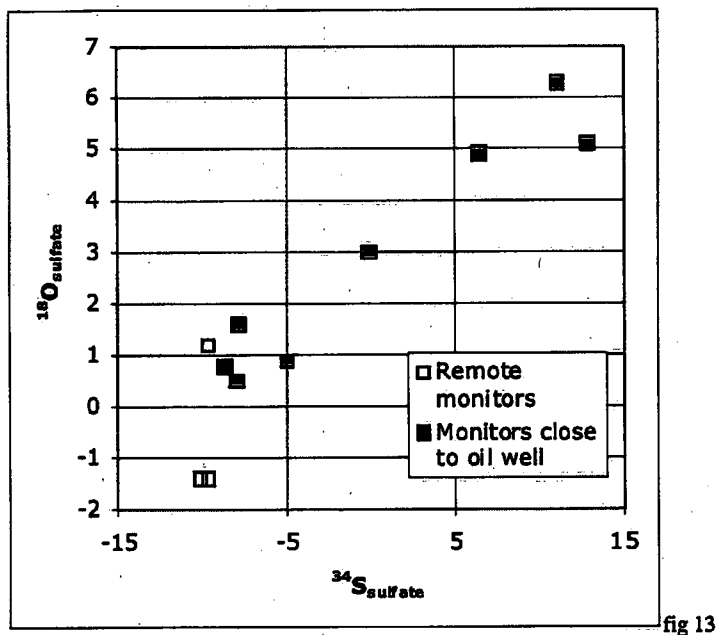


fig 13

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