

Distribution and isotopic characterization of methane in a confined aquifer in southern Ontario, Canada

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Abstract

Methane is one of the major carbon pools in the groundwater of the confined Alliston Aquifer. Geochemical, geological and hydrological tools were used to evaluate the origin and distribution of this hydrocarbon. The potential sources for methane were migration of thermocatalytic methane from bedrock units and in situ production by bacteria-mediated reactions. The distribution of methane in the aquifer excludes the possibility that methane occurrences were controlled by the nature of the underlying bedrock (limestone vs. shale). ^{13}C and ^2H data in CH_4 from aquifer and bedrock wells indicate that these gases are microbial in origin and they are formed in situ, mainly by CO_2 reduction. Chemical and ^{14}C data in CH_4 and DOC support the hypothesis of the existence of carbon sources for in situ microbial production of CH_4 in the aquifer.

1. Introduction

The predominant carbon pools in groundwater are dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) and a common trace component seems to be methane. However, this hydrocarbon could become a major carbon pool and a potential (explosive) contaminant where present in high concentrations (Coleman, 1976; Barker, 1979; Hughes et al., 1971; Barker and Fritz, 1981; Coleman et al., 1988). This is the case for groundwater in some parts of the Alliston Aquifer, southern Ontario. Many wells that tap this aquifer produce high volumes of methane. As a result, most of the municipal wells have aeration treatment systems. However, the origin and distribution of methane in this aquifer was not well established.

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The presence of methane in groundwater could be associated with in situ production (microbial gas) by bacterial reactions (methanogenesis) or by migration of gases from underlying bedrock reservoirs. The latter type is called thermocatalytic and is formed by decomposition of organic matter at relative high temperature.

Despite the importance of methanogenesis in carbon cycling in groundwater and the potential contribution of groundwater methane to the atmospheric methane pool, few studies have been undertaken regarding the occurrence of methane in groundwater systems. The most extensive studies were carried out in selected aquifers systems in Canada and the United States (Barker and Fritz, 1981; Coleman et al., 1988). These studies show significant methane concentrations in some aquifers associated mainly with microbial degradation of organic matter present in aquifer sediments. A recent study by Simpkins and Parkin (1993) has also documented the occurrence of methane in groundwater in central Iowa. They suggest, based on the Quaternary history and the occurrence of organic sediments, that methane should be also present in groundwater in parts of the midwestern United States. Geochemical studies of the carbon cycle in groundwater have also documented the presence of this hydrocarbon in groundwater. Enriched $\delta^{13}\text{C}$ values and an increase in dissolved inorganic carbon concentration along groundwater flow paths have been attributed to methanogenesis (Chapelle and Knobel, 1985; Chapelle et al., 1988; Grossman et al., 1989).

This paper presents results from a research project having as one of its main objectives the determination of the origin and distribution of methane in the Alliston Aquifer. Two hypotheses were postulated to explain the occurrences of methane in the Alliston Aquifer. One suggested that the occurrence of methane was controlled by the nature of the underlying Paleozoic bedrock (U. Sibul, Ministry of the Environment, MOE, personal communication). Where the underlying bedrock is shaley (Collingwood, Blue Mountains groups), insignificant amounts of gas were found. However, where the bedrock is limestone (Trenton Group), methane is found at high concentration. This implied that the source of methane was leakage or migration from the more permeable limestone bedrock. This hypothesis was supported by the fact that methane is likely present in the Trenton Group. It is well documented that these carbonate rocks are an important reservoir for natural gases in other parts of southern Ontario (Barker and Pollock, 1984).

The second hypothesis, based on carbon isotope analyses of methane from some wells tapping the overburden, suggested that methane was biogenic, produced by bacterial action (Barker and Fritz, 1981). This implied that the methane is produced within the aquifer, since the methane found in the Trenton rocks has an isotopic composition typical of thermocatalytic methane (Barker and Pollock, 1984). Therefore, a bedrock control of the occurrence of methane appeared to be unlikely.

2. Research approach

The research approach includes the use of geochemical, geological and hydrological tools. Among the geochemical tools, stable isotopes (^{13}C , ^2H) were used as

tracers to provide information about the origin of methane. The isotopic composition of CH_4 is a reflection of the processes responsible for the formation of CH_4 . Biogenic methane, excluding the methane generated in landfills, is generally characterized by $\delta^{13}\text{C}$ values less than -60‰ , whereas thermocatalytic methane commonly has values greater than about -45‰ (Coleman, 1976; Barker and Fritz, 1981). In addition, the hydrogen isotope (deuterium) concentration of biogenic methane is related to the deuterium concentration of the associated water. This relationship depends on the type of reactions that are involved in the methane formation (CO_2 reduction vs. acetate dissimilation) (Schoell, 1980; Woltemate et al., 1984).

The occurrence of methane in any type of environment is intimately linked to its carbon precursors. Potential carbon sources for the generation of methane in the Alliston aquifer were recharged dissolved organic carbon (DOC), and organic matter present in the aquifer material and bedrock. The other alternative was migration of methane from the hydrocarbon reservoirs that could exist in the Paleozoic bedrock. Information about the nature of these sources, specifically their age or time of deposition could be useful in linking the methane to its carbon precursor. Carbon-14 was used to evaluate the age of the carbon sources by dating of CH_4 and the DOC carbon pools.

An extensive sampling of groundwater from different areas of the aquifer was carried out to evaluate the distribution of methane. Additional gas analyses included C_2 to C_4 hydrocarbons. The presence of these types of compounds is usually an indication of the thermocatalytic origin of the methane.

Among the geological and hydrogeological activities, a map of the bedrock lithology was constructed to test the hypothesis that the bedrock lithology controlled the distribution of methane in the aquifer, and a map of the groundwater flow regime was updated to evaluate the role of the groundwater as a transport medium for the methane.

3. Study site

This research was carried out in the confined Alliston Aquifer which extends from the vicinity of Aurora to Wasaga beach and includes the area northwest along the Nottawasaga Bay (Fig. 1). The study region is part of the Laurentian Valley which extends from Georgian Bay to Lake Ontario (White and Karrow, 1971). It was expected that the sediments that form the overburden materials at the study site are mainly late Wisconsinan. Early Wisconsinan deposits could exist in the deep part of this buried valley. Evidence of sediments, associated with the Laurentian Valley, are a 50 m sand and clay unit that forms the lower half of the Scarborough Formation at Toronto. Age estimate for this deposit are in the range of 100 ka (Karrow, 1989).

The aquifer is composed of sand and gravel lenses, is confined above by thick glacial clay till, and confined below by Paleozoic bedrock. More detailed information about the overburden materials can be found in Sibul and Choo-Ying (1971). The underlying bedrock is composed by rocks of the Simcoe (Middle Ordovician) and

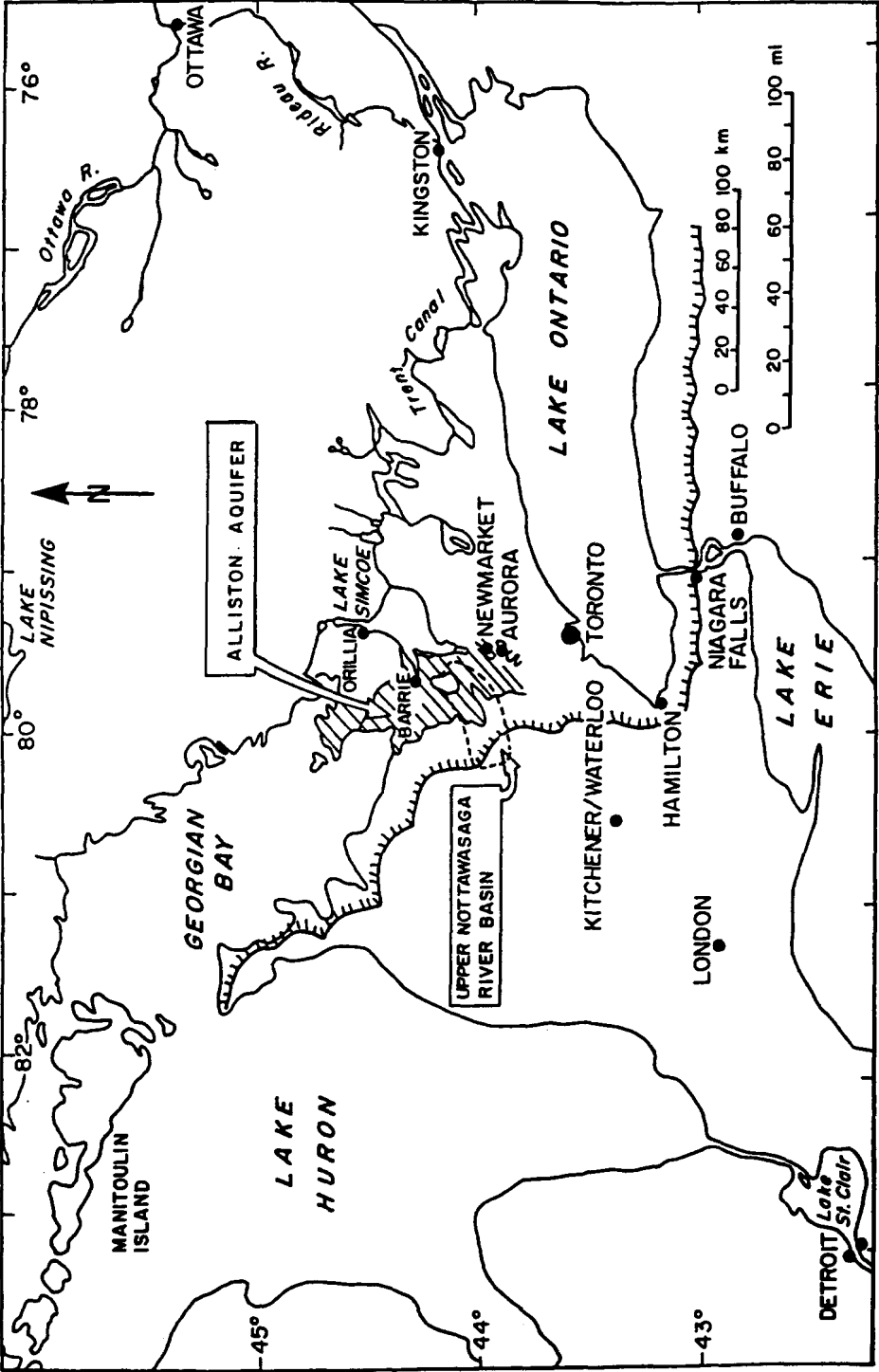


Fig. 1. Study site, Alliston Aquifer.

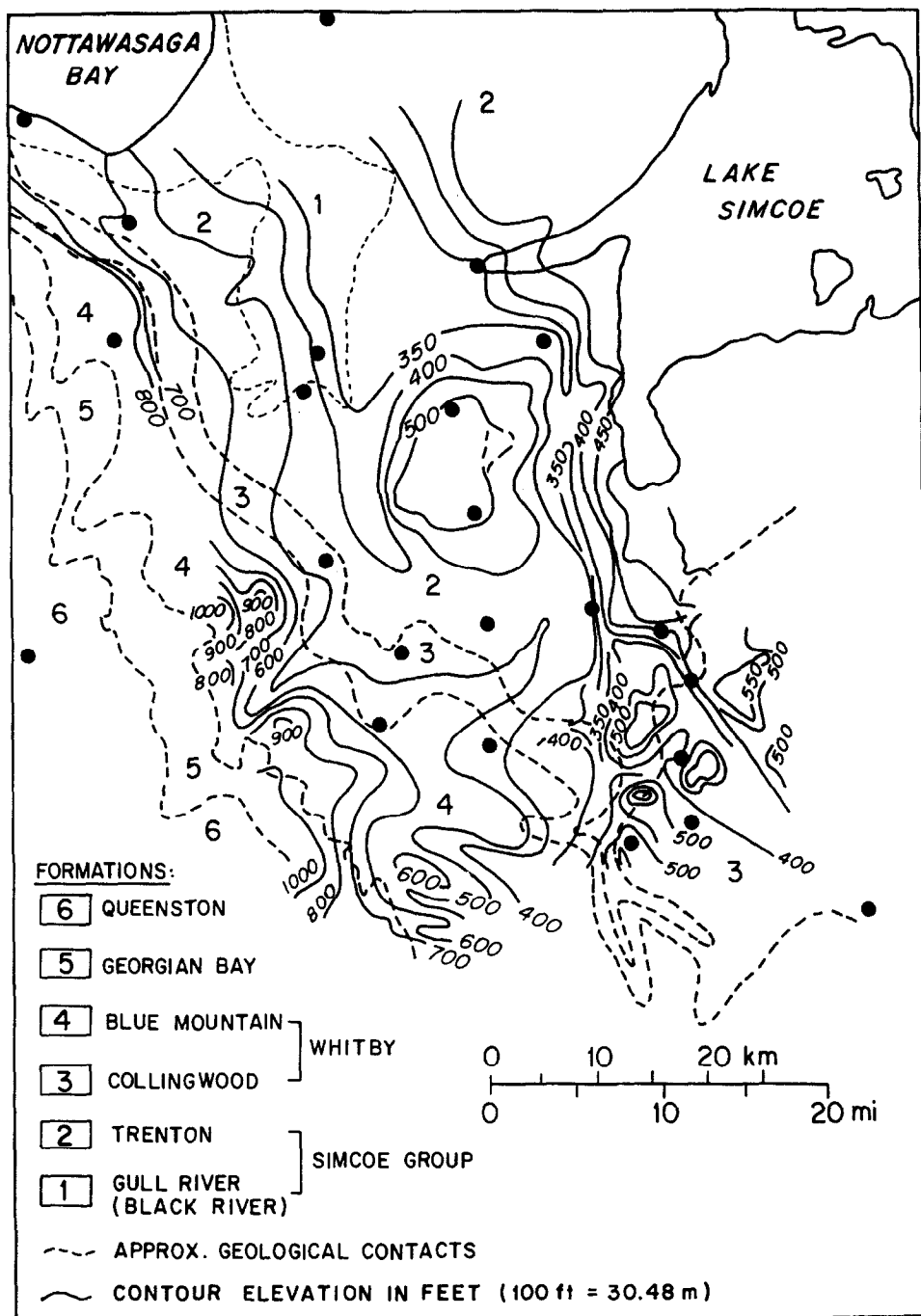


Fig. 2. Plan of the bedrock topography and lithology.

Nottawasaga (Upper Ordovician) groups. The distribution of the various units that form these groups is shown in Fig. 2 and Table 1. The units relevant to this study were the Trenton and Black River limestones and the Collingwood and Blue Mountain shales. The bedrock is not an important source for water supply, and in some areas the water is highly mineralized and not suitable for domestic or stock purposes (Sibul and Choo-Ying, 1971).

The regional groundwater flow pattern suggested that two major flow systems are present, separated by a north–south divide at piezometric elevations greater than 256 m (Aravena and Wassenaar, 1993). One discharged into Nottawasaga Bay (Lake Huron) to the north and the other to Kempenfelt Bay and Cooks Bay (Lake

Table 1
Generalized stratigraphic section of Ordovician bedrock

Liberty (1969)				Sibul and Choo-Ying (1971)		
Group			Formation	Group	Formation	Description
Ordovician	Upper	Nottawasaga	Queenston		Queenston	Red shale
			Georgian Bay		Meaford-Dundas	Shale and limestone; gray, silty with shale interbeds
			Whitby		Blue Mountain	Shale; soft, blue
					Collingwood	Shale; dk brn-gray to black, fissile, bituminous, pyritiferous
						Black shale and lmstn.
	Middle	Simcoe	Lindsay	Trenton	Cobourg	Lmstn; drk brn, dense, argillaceous and very fine-grained
			Verulum		Sherman Falls	Lmst; gray fn-, med-cs-, crystalline with shale interbeds
			Bobcaygeon		Kirfield	Lmstn; gray-brn to drk gray, fn crystalline, fragments, shaley, and carbonaceous
			Gull River	Black River	Coboconk (Sanford, 1961)	Lmstn; lithographic semicrystalline Lmstn; lithographic Lmstn; dolomitic and lithographic

Simcoe) to the northeast. Recharge occurred regionally from the east and west marginal bedrock highs and possibly from the south in the vicinity of Aurora, where there exists an east–west groundwater flow divide. This aquifer is the major water supply for several towns, rural domestic usage and is an essential water resource for an increasing population base in the region.

4. Materials and methods

Domestic and commercial wells completed in the Alliston aquifer and bedrock were used in this study. Bedrock wells are usually screened within the first 6 m of the bedrock units. Detailed information about depth and location of the wells can be found in Figs. 3 and 4. Water and gas samples were collected from these wells for chemical (major gas and inorganic ions) and isotopic analyses (^{18}O , ^2H , ^{13}C , ^{14}C). These samples were taken upstream from on-line pressure tanks, after wells had been pumped for at least 20 min. Water samples for methane concentration analysis were collected in glass syringes. Collection of gases for gas composition and isotopic analyses were carried out using the inverted glass bottle technique (Meents, 1960). Gas analyses were performed by gas chromatography at the Geochemistry Laboratory, University of Waterloo.

For ^{13}C , ^{14}C and ^2H analyses in gas samples, an in-line GC-Combustion-Preparation system was used for the separation and combustion of CH_4 to CO_2 and H_2O . The zinc technique was used to convert the H_2O to H_2 for ^2H analyses (Coleman et al., 1982). The reproducibility and possible contamination in the combustion line for conversion of CH_4 to CO_2 for ^{14}C analysis, were tested by analysis of similar gases at different time during the research, (also a check of sample preservation) and through the analysis of a working standard EIL-8 (commercial CH_4) used in the CH_4 preparation line. These tests show that the analytical reproducibility was better than 0.3 p.m.c. and background in the combustion line was less than 0.2 p.m.c. (Aravena and Wassenaar, 1993).

For DOC determination, samples were filtered through $0.45\ \mu\text{m}$ Ag-membrane filters into 25 ml glass vials and acidified to pH 2 with phosphoric acid. These determinations were done on a Dohrmann Organic Carbon Analyzer at the University of Waterloo. Large groundwater samples (100–120 l) were collected for isolation of aqueous humic substances for isotopic analyses. These samples were filtered through Balston 25 and $0.45\ \mu\text{m}$ inorganic filters into a 20 l glass container and acidified to pH 2 with concentrated HCl.

Stable isotope analyses were performed at the Environmental Isotope Laboratory (EIL), University of Waterloo, on VG Micromass 903 triple-collecting and VG 602D double-collecting mass spectrometers and are expressed in the usual $\delta\text{‰}$ notation. Analytical reproducibility was better than 0.2‰ for ^{13}C , and 3‰ for ^2H .

^{14}C analyses were performed by Tandem Accelerator Mass Spectrometry at IsoTrace, University of Toronto. ^{14}C results are reported in percent modern carbon (p.m.c.), normalized to a $\delta^{13}\text{C}$ of -25‰ (PDB) (Stuiver and Polach, 1977). Precision and reproducibility for ^{14}C determinations was better than 0.5 p.m.c. Radiocarbon

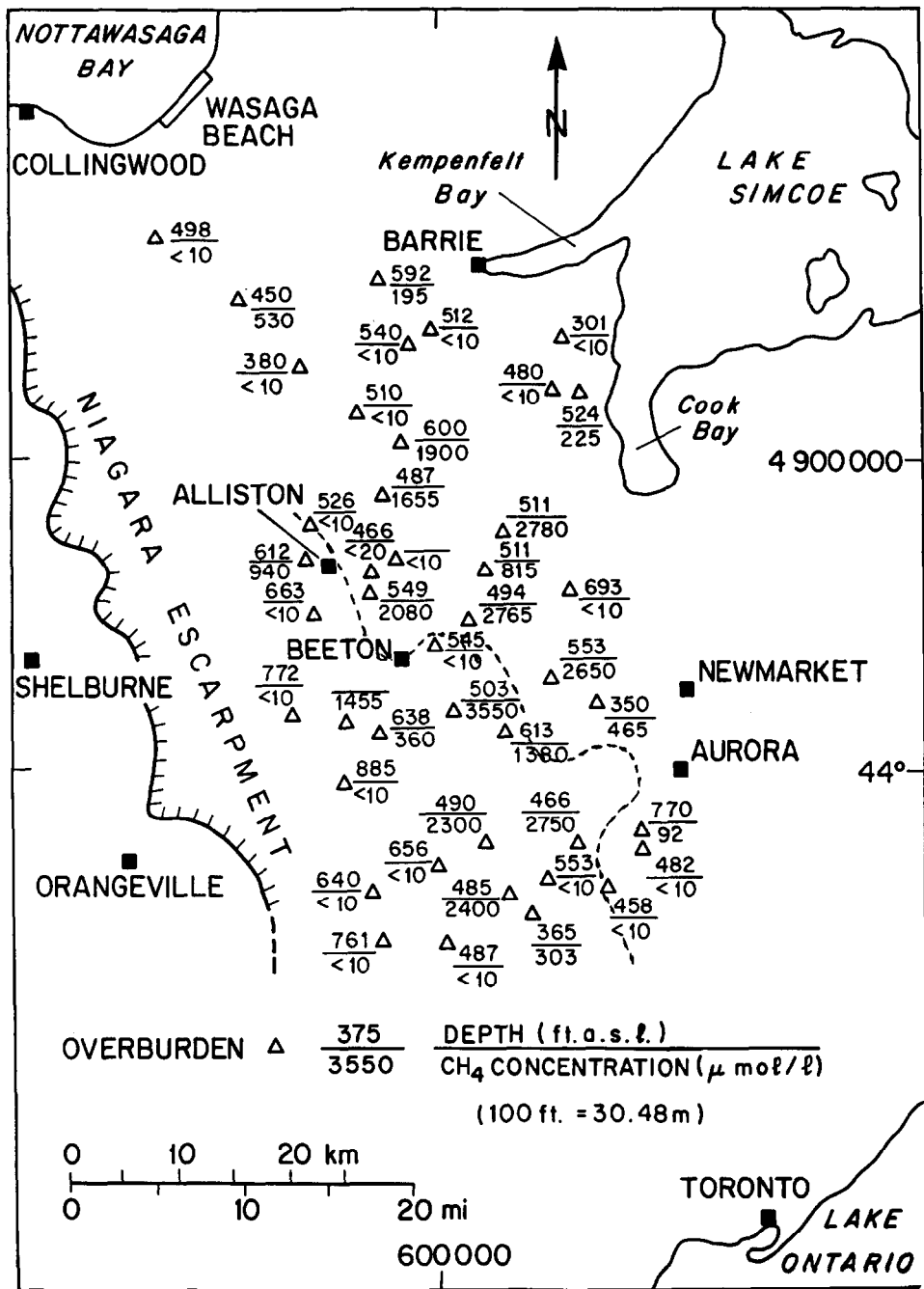


Fig. 3. Sampling locations and methane concentration in overburden wells, Alliston Aquifer. Dotted lines mark the boundary between the limestone and the shale bedrock units.

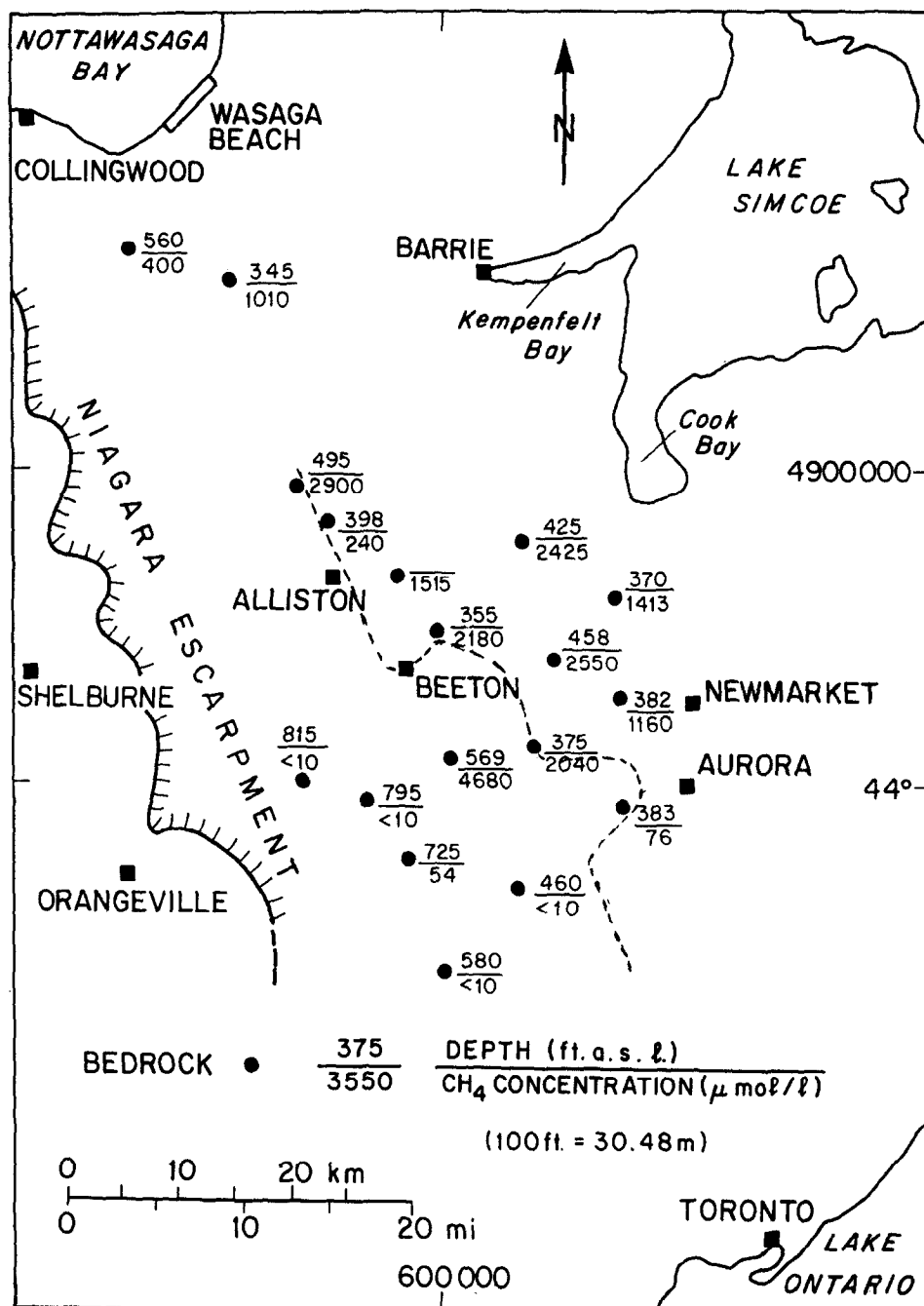


Fig. 4. Sampling locations and methane concentration in bedrock wells, Alliston Aquifer. Dotted lines mark the boundary between the limestone and the shale bedrock units.

ages are calculated using the decay equation defined as

$$A_s = A_0 \exp(-\lambda t)$$

where λ is $\ln 2/T$, A_s is the measured ^{14}C activity of the sample normalized to a $\delta^{13}\text{C}$ of -25‰ , A_0 is the initial ^{14}C at $t = 0$ (100 p.m.c.), T is the ^{14}C half-life and t is the age of the sample.

5. Results and discussion

5.1. Gas composition and CH_4 concentration

Gas composition data for overburden and bedrock wells are presented in Table 2. These data may not necessarily represent the actual gas composition that is dissolved at aquifer pressure since different components may come out of solution at different rates when the pressure is released during pumping. These analyses indicated that the main components of these gases extracted from groundwater were methane and nitrogen. The average percentage of these two gases were 80% and 15%, respectively. However, in some groundwaters N_2 gas was the main component. No traces of C_2 to C_4 hydrocarbons were found in these samples.

Table 2
Chemical composition of gases in ground water, Alliston Aquifer

Well	CH_4 (%)	N_2 (%)	O_2 (%)	CO_2 (%)	AR (%)
OV17	71.9	27.4	0.5	0.85	
OV10	52.9	38.9	0.17	0.15	0.36
OV15	79.8	17.8	0.45	1.13	
OV16	76.1	21.9	< 0.02	2.59	0.63
OV17	44.3	45.8	0.15	0.30	0.94
OV19	74.4	23.8	< 0.02	0.06	0.15
OV21	71.0	29.1	0.55	0.36	
OV23	79.4	17.0	0.25	0.58	0.34
OV32	75.0	26.3	< 0.02	0.91	< 0.01
OV34	32.5	66.1	< 0.02	0.35	0.14
OV43	64.2	34.8	< 0.02	0.96	0.72
OV49	70.2	23.4	1.08	0.10	0.18
BR3	87.8	8.3	0.14	0.91	
BR4	83.2	13.8	0.3	1.15	
BR5	61.3	34.2	3.4	0.17	
BR6	49.3	49.2	< 0.02	0.79	0.48
BR7	64.5	35.5	0.8	0.44	
BR8	44.2	45.8	7.6	0.37	
BR11	31.7	58.7	0.41	0.10	0.64
BR12	6.0	92.7	< 0.02	0.10	0.75
BR14	66.1	35.6	< 0.02	0.25	0.75

OV, overburden; BR, bedrock.

Table 3
Geochemical data for methane, dissolved organic carbon and groundwater, Alliston Aquifer

Well	Elevation/Depth (m.a.s.l./m)	CH ₄ ($\mu\text{mol l}^{-1}$)	H ₂ O $\delta^2\text{H}$				DOC			
			$\delta^2\text{H}$ (‰ SMOW)	$\delta^{13}\text{C}$ (‰ PDB)	^{14}C (p.m.c.)	Age (years BP)	(mg l ⁻¹)	$\delta^{13}\text{C}$ (‰ PDB)	^{14}C (p.m.c.)	Age (years BP)
OV2	239 (59)	<10					2.0	-26.3	80.6	1800
OV6	312 (47)	<10					2.2	-26.5	77.1	2150
OV9	244 (54)	360					2.7	-26.2	16.9	14700
OV19	246 (98)	2780		-73	2.8	29600	6.4	-26.1	12.2	17400
OV10	226 (74)	1655	-274	-81	4.4	25800	6.8	-28.0	10.0	19000
OV7	229 (59)	2080	-258	-77	3.3	28200	7.4	-26.9	9.3	19600
OV34	207 (88)	943	-281	-89	2.7	29900	8.0	-27.6	4.5	25600
OV16	235 (71)	2765	-240	-72			8.7			
OV15	268 (125)	3550	-264	-77	2.3	31200	18.0	-27.0	3.8	27000
OV21	230 (63)	2650	-260	-79	0.6	42300 ^a	9.6	-27.0	2.0	32300
OV23	302 (175)	2750	-264	-80	1.5	34700 ^a	15.0	-27.4	1.2	36600 ^a
OV17	259 (111)	1391	-278	-84	16.7	14800	9.0	-26.1	8.6	20300
OV49	226 (112)	2040	-266	-74	11.0	18200	7.0	-27.2	8.2	20700
OV43	284 (147)	2400	-271	-82	13.2	16700	9.0	-26.3	5.0	24800
OV32	290 (153)	2300	-270	-77	10.9	18300	11.4			
BR18	274 (47)	400					4.7	-27.0	38.7	7800
BR12	270 (160)	2400	-268	-89	1.6	34200	0.9	-26.9	9.4	19500
BR14	247 (96)	2900	-280	-81	1.8	33200	1.7	-27.3	7.1	21900
BR6	290 (108)	2425	-279	-83	0.5	43800 ^a	6.0	-27.4	3.6	27500
BR3	291 (129)	4680	-270	-70	1.4	35300 ^a	9.4	-27.5	1.9	32700
BR2	305 (66)	<10					1.4	-26.7	1.2	36600 ^a
BR4	205 (75)	2180	-243	-74			8.2			
BR5	na	2425	-262	-77			7.1			
BR7	236 (93)	2550	-269	-81			5.2			
BR8	na	1515	-228	-69			12.6			
BR11	221 (104)	1160	-259	-80			2.0			

OV, overburden; BR, bedrock.

^a Values close to the ^{14}C detection limit.

Water samples for determination of methane concentration were collected in glass syringes. For some samples supersaturated with methane (saturation at 25°C is 1310 $\mu\text{mol l}^{-1}$), degassing during sampling may have caused some errors in the determination of methane concentration. However, these possible errors should not have any significant implications in the overall distribution of methane concentration in the aquifer. Methane concentration data are plotted in Fig. 3 for overburden groundwater and Fig. 4 for bedrock groundwater. The broken line represents the boundary between the Trenton and Gull River limestones and the Collingwood and Blue Mountain shale bedrock (Fig. 2, Table 1). It appeared that the area southeast of Alliston towards Beeton had the highest concentration of methane, in both bedrock and overburden wells. A trend toward decreasing methane concentration was observed in the areas north and northeast of Alliston. No methane was found in overburden and bedrock wells sampled along the west side of the aquifer.

A comparison of the regional distribution of methane with the areal distribution of the underlying Ordovician bedrock indicated that the lithology of the bedrock does not influence the distribution of methane in the aquifer. High concentrations of methane were observed in overburden and bedrock wells underlain either by limestone or shale.

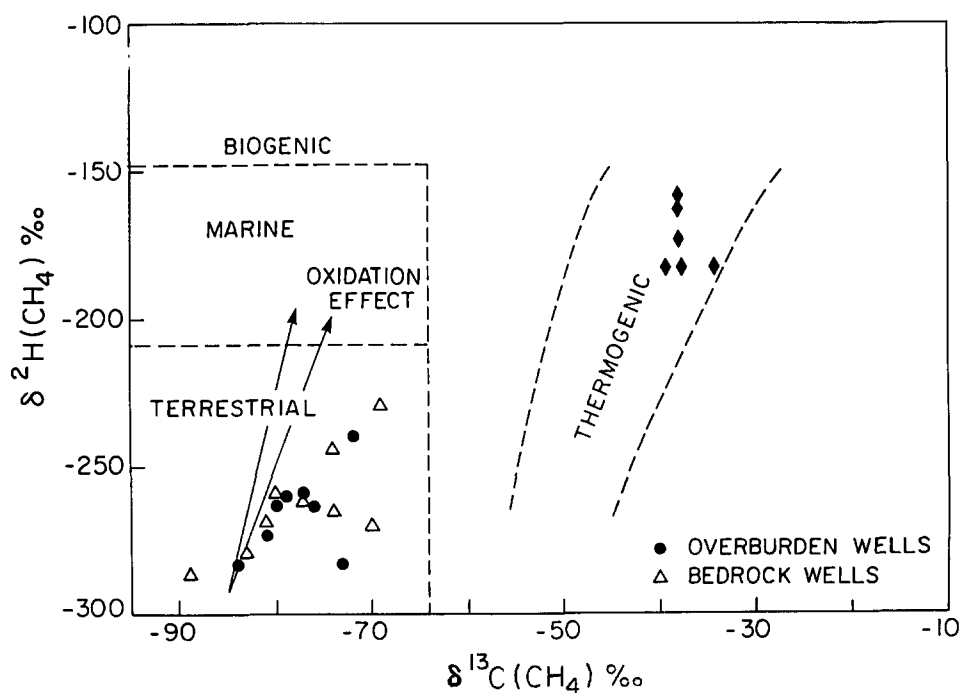


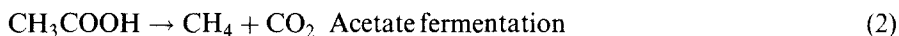
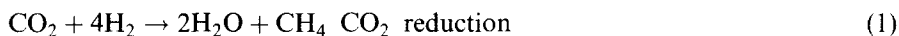
Fig. 5. Relationship between isotopic composition and genesis of methane. (♦) From Barker and Pollock (1984).

5.2. ^{13}C and deuterium data

$\delta^{13}\text{C}$ values of methane samples ranged from -69 to -89‰ , with a mean value of -79‰ (Table 3). A similar isotopic range is observed in methane from overburden and bedrock wells. The wide range in $\delta^{13}\text{C}$ values observed in the methane samples can be related to a combination of isotopic effects occurring during methane production, (reservoir effect; Coleman et al., 1988) and maybe differences in carbon pathways. The $\delta^{13}\text{C}$ data are similar to those reported from some overburden wells from the same aquifer by Barker and Fritz (1981). Fig. 5 shows the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ distribution of methane gases of different origin (Schoell, 1980). All methane results from the Alliston groundwaters plot in the field of biogenic methane. These results eliminated the possibility that the source of methane was the Paleozoic bedrock. The methane present in these types of rocks in Southern Ontario has a ^{13}C composition range of between -37.4 and -40.3‰ , which is typical of thermogenic gases (Barker and Pollock, 1984).

The trend toward enriched (more positive) isotopic values observed in Fig. 5 could be a result of methane oxidation. This process appeared to be occurring in artesian wells (BR8 and BR4), where groundwater is contaminated with air at the outflow. Oxidation of methane is the only process that enriches the residual methane in ^{13}C and ^2H and can shift their isotopic composition to the field of thermogenic methane (Coleman et al., 1981).

The methane isotope data are also plotted in a graph $\delta^2\text{H}$ (CH_4) vs. $\delta^2\text{H}$ (H_2O) (Fig. 6). The lines plotted in this graph represent the contribution of the reaction pathways that can be involved in the formation of methane. These pathways are represented by the following reactions



The lines 0:100 and 80:20 represent 100% CO_2 reduction and 80% acetate fermentation, respectively. The data plotted on and above the 100% CO_2 lines, clearly show the effect of oxidation in the $\delta^2\text{H}$ content of some methane samples (BR4, BR8 and OV16). Fig. 6 indicates that CO_2 reduction seems to be the main reaction pathway for the formation of methane in the Alliston aquifer. This is in agreement with the interpretation by Coleman et al. (1988) that indicated that CO_2 reduction is the predominant pathway in groundwater systems. Earlier research based on limited data suggested that CO_2 reduction occurs mainly in marine sediments (Whiticar et al., 1986), however CO_2 reduction is also reported to occur in wetland sediments (Lansdown et al., 1992).

5.3. Relationship between chemical and ^{13}C composition of the gas

Information about methane geochemistry could also be inferred from the chemical composition of the groundwater gas. CH_4 was the predominant component of the gas, however some gas samples showed a predominance of N_2 over CH_4 . It seems that

gases characterized by high N_2 levels and low CH_4 content were associated with ^{13}C depleted CH_4 (Fig. 7). A similar relationship was observed by Coleman et al. (1988) in gases from Illinois groundwater. This pattern was explained by a varying admixture of CH_4 to groundwater having a fixed N_2 content. The addition of a small amount of CH_4 would result in a high N_2/CH_4 ratio, whereas a large addition would generate low N_2/CH_4 ratios. High N_2/CH_4 could be explained by a combination of a short groundwater residence time in the zone of methanogenesis compared with methane production rate or vice versa in the case of lower N_2/CH_4 ratios.

The inverse relation between N_2/CH_4 and ^{13}C content of the CH_4 seems to agree with this hypothesis. This discussion will consider a closed system and CO_2 reduction as the main pathway for methane formation. Owing to isotope effects occurring during methanogenesis, methane will be depleted in ^{13}C compared with CO_2 , but

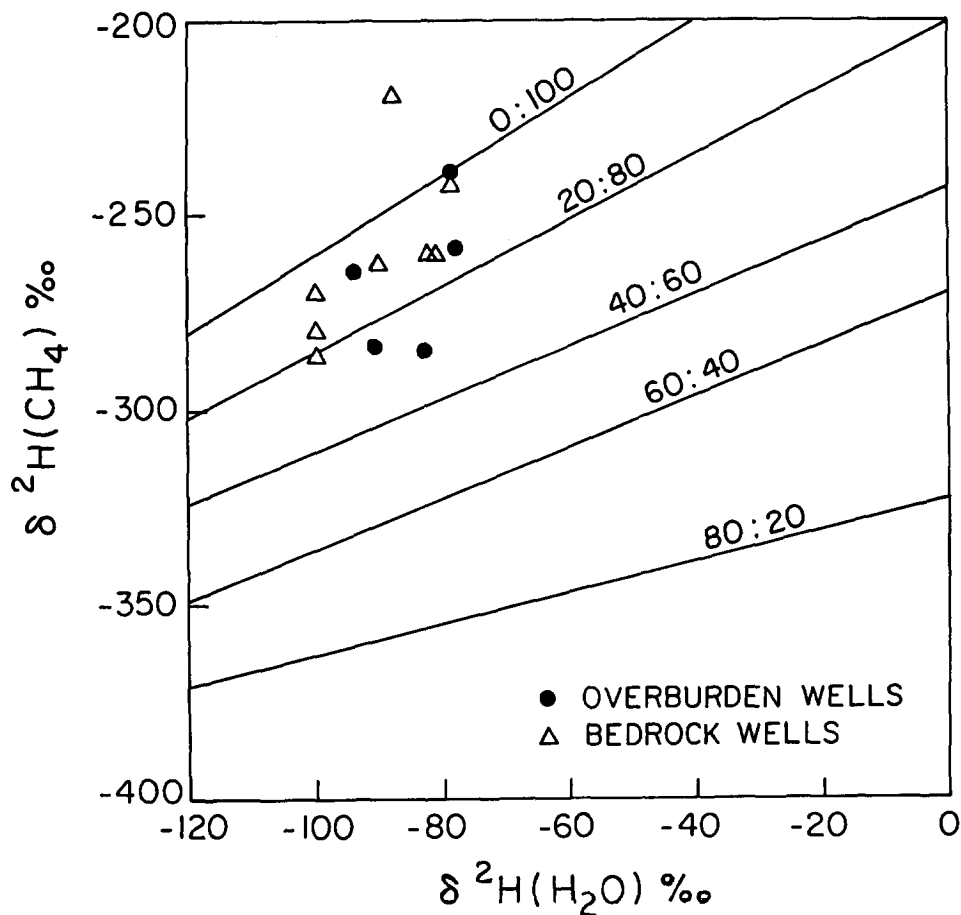


Fig. 6. Deuterium composition of methane and ground water, Alliston Aquifer. The lines 0:100 and 80:20 represent 100% CO_2 reduction and 80% acetate fermentation, respectively.

as the reaction proceeds the remaining methane and its associated CO_2 will become enriched in ^{13}C compared with the initial values (Balabane et al., 1987). This is called the reservoir effect. Therefore, if the reactant (CO_2) and the product (CH_4) are removed rather quickly from the area of methanogenesis, the reservoir effect will be minimal and isotopically depleted CH_4 will be present in the groundwater. This model is compatible with short groundwater residence times in the methanogenic zone compared with methane production rate. It is possible that the main cause of ^{13}C variations observed in methane from the aquifer could be related to a variable extent of the reservoir effect.

The $\delta^{13}\text{C}$ pattern of DIC also seems to be consistent with mixing and reservoir effects. The trend of lower N_2/CH_4 ratios associated with enriched $\delta^{13}\text{C}$ CH_4 values observed in Fig. 7 was also correlated with a trend toward enriched $\delta^{13}\text{C}$ DIC values. This implied that the CO_2 involved in methanogenesis, which was incorporated in the DIC pool, becomes isotopically enriched in ^{13}C as the reaction proceeds, generating CH_4 richer in ^{13}C .

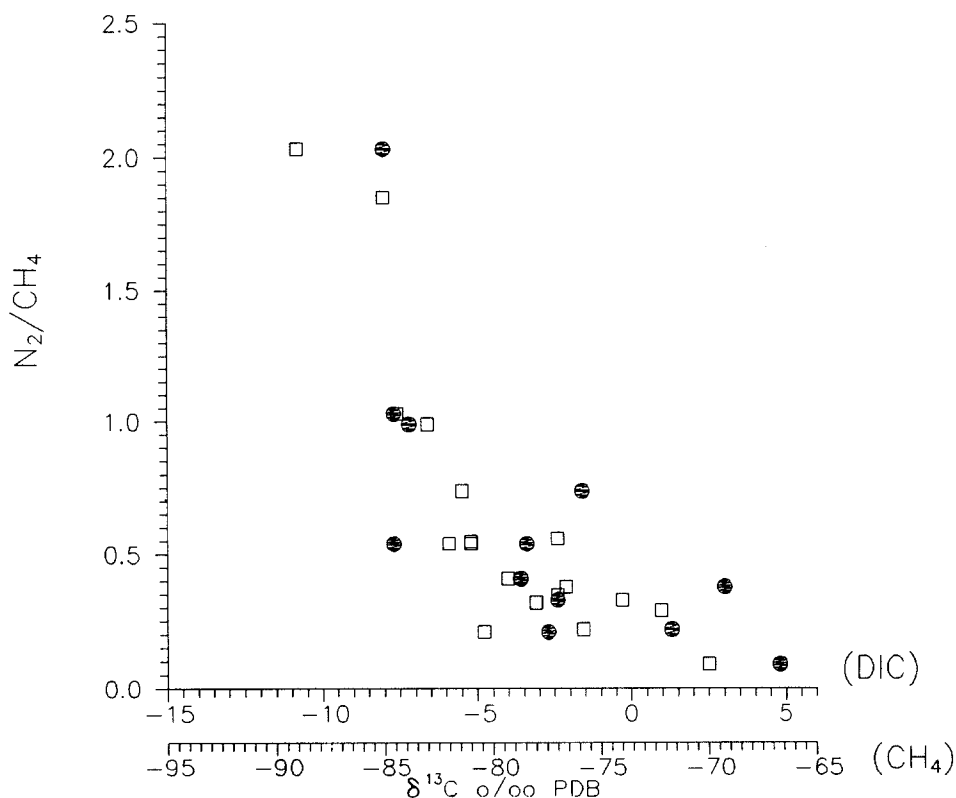


Fig. 7. N_2/CH_4 ratios vs. $\delta^{13}\text{C}$ composition of CH_4 and DIC. (●, DIC; □, CH_4).

5.4. Carbon sources for methane

Evaluation of potential carbon sources for CH_4 , with the expectation of establishing age boundaries regarding organic carbon sources for CH_4 was explored through chemical and carbon isotope analyses (^{14}C , ^{13}C). Potential sources in the confined aquifer were (1) DOC recharged in the groundwater, (2) organic sediments buried in the aquifer matrix and/or (3) kerogen in the underlying Paleozoic bedrock.

5.5. DOC

Since DOC was one of the potential carbon sources for CH_4 and could provide direct information about organic sources, an extensive chemical and isotopic characterization of this carbon pool was carried out in the aquifer. These data showed a range of DOC concentrations between 1 and 17 mg l^{-1} (Table 2). Typical DOC concentrations are less than 1 mg l^{-1} in deep groundwater (Thurman, 1985) and less than 5 mg l^{-1} in unconfined aquifers in the Alliston area (Wassenaar, 1990). The high DOC concentrations found in the Alliston Aquifer suggested that the groundwater was moving through aquifer materials that are rich in organic matter. A significant linear correlation between DOC and CH_4 concentration (Aravena and Wassenaar, 1993) suggested that both carbon pools are related to a common carbon source present in some part of the aquifer.

5.6. ^{14}C content of CH_4

^{14}C analyses of CH_4 samples are reported in Table 2 and plotted in Fig. 8. Radiocarbon ages for the groundwater methane samples range from about 15 000 to 44 000 years BP. The older group (< 1.5 p.m.c.) should be viewed with caution, since they are subject to a large uncertainty. The ^{14}C activities are close to the detection limit of the radiocarbon technique. The ^{14}C data obtained in this study were in agreement with radiocarbon ages reported by Barker et al. (1979) on overburden methane. These ages provided only an estimate of the age of the carbon sources for methane and did not provide information about the residence time of the groundwater. Measurable ^{14}C and the $\delta^{13}\text{C}$ values were direct evidence that the bulk of the methane cannot be derived from bedrock thermocatalytic methane, and must be generated from organic carbon sources within the aquifer. Potential for production of biogenic methane in the bedrock units likely exists in the organic-rich Collingwood shale located in the western and southern part of the study area (Russel and Telford, 1983). However, no ^{14}C differences are observed in methane present in either the limestone or shales units. Furthermore, most of the radiocarbon dates on methane samples correlated well with regionally dated organic peat and wood samples that represent interglacial periods in the study region (Aravena and Wassenaar, 1993). Thus, the ^{14}C and $\delta^{13}\text{C}$ data supported the hypothesis that buried mid-Wisconsinan organic-rich sediments were the carbon sources for methane gas in the Alliston aquifer, and that advective transport of dissolved CH_4 into adjacent Paleozoic bedrock formations occurred.

A common carbon source for CH_4 and DOC inferred from the chemical data is

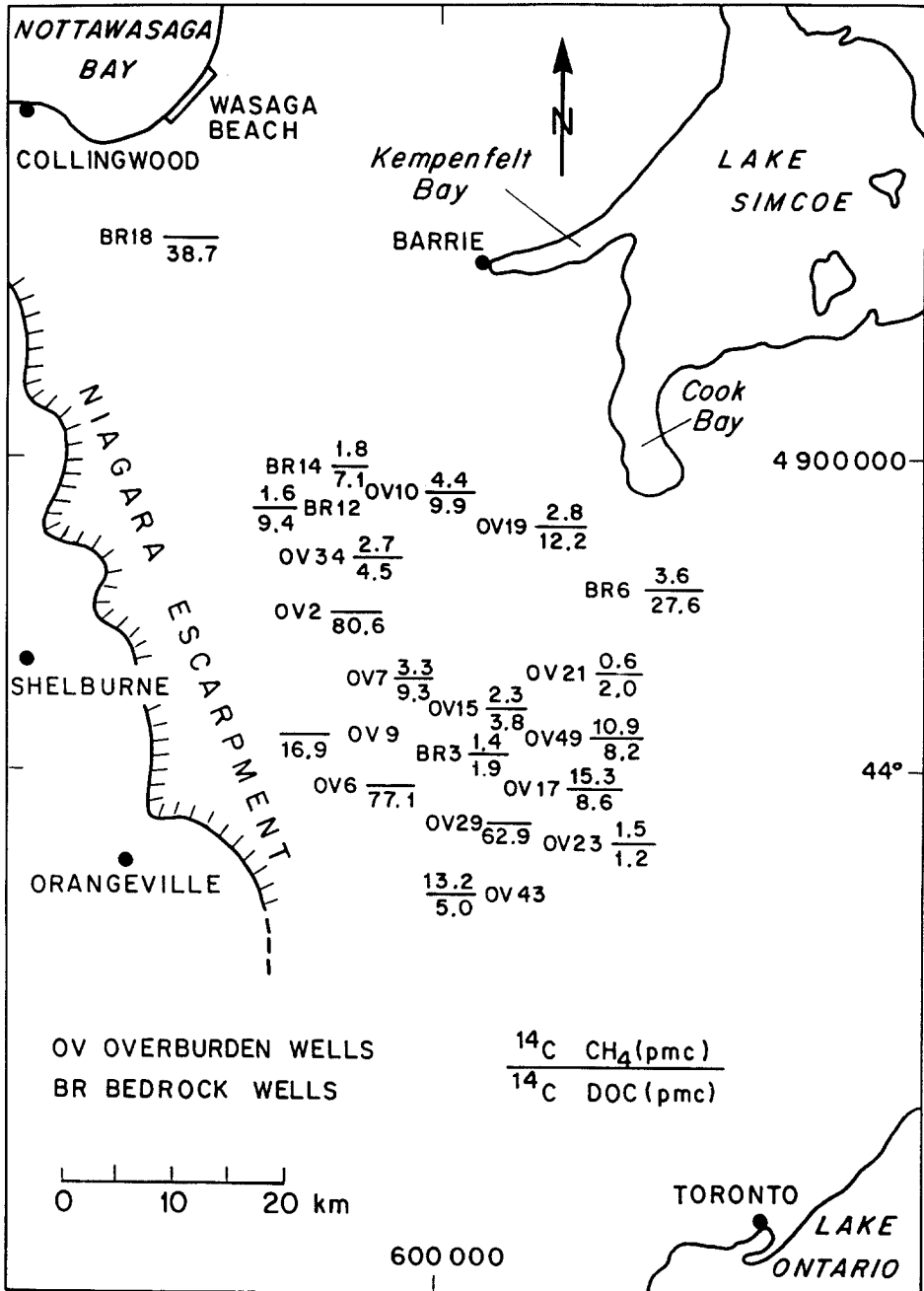


Fig. 8. ^{14}C distribution of CH₄ and DOC samples in overburden and bedrock groundwater.

supported by an intercomparison of ^{14}C data between CH_4 and DOC (Fig. 8). These data show similar ^{14}C activity in some parts of the aquifer for both carbon pools. However, in other parts of the aquifer, DOC radiocarbon ages are younger or older than methane radiocarbon ages. This pattern is related to a combination of the groundwater flow regime, input of younger soil zone carbon for DOC in recharge areas and different ages of carbon sources for CH_4 in the aquifer (Aravena and Wassenaar, 1993). The measurable radiocarbon activities for CH_4 and DOC eliminate the possibility of a significant Paleozoic bedrock carbon source for both carbon pools in the Alliston groundwater. $\delta^{13}\text{C}$ and ^{13}C -NMR data on DOC samples (Aravena, 1993) support this idea. These data indicated that the source of the DOC in the aquifer is terrestrial in origin, discarding the marine carbon in the shale bedrock as a source of carbon to the groundwater.

6. Conclusions

CH_4 is one of the major carbon pools in the groundwater of the confined Alliston Aquifer. No relationship was observed between CH_4 distribution and the underlying bedrock lithology, which argues against the hypothesis that the distribution of CH_4 was controlled by the lithology of the bedrock (limestone vs. shale). ^{13}C and ^2H data in CH_4 from overburden and bedrock wells show no indication of input of thermocatalytic CH_4 expected from the bedrock units. These data indicate that these gases are microbial in origin and that they are formed mainly by the CO_2 reduction pathway. Radiocarbon data in CH_4 and DOC and $\delta^{13}\text{C}$ and ^{13}C -NMR data on DOC samples eliminate the possibility of a significant Paleozoic bedrock carbon source for both carbon pools in the Alliston groundwater and support the hypothesis of the existence of organic-rich sediment sources in the Alliston Aquifer matrix.

This study and research in USA aquifers suggest that biogenic methane is more likely to be present in North American aquifers, located in areas affected by glaciations during the Quaternary. The occurrences of methane in groundwater deserves much more attention regarding its potential as a contributing source to the atmospheric methane pool, via groundwater discharge to rivers and lakes and through water supply facilities.

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