

¹⁴C DATING OF GROUNDWATER CONTAINING MICROBIAL CH₄

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ABSTRACT. Groundwater samples were collected from several different depths in Illinois glacial deposits at a site in east-central Illinois. Dissolved gases were extracted from many of the water samples, measured volumetrically, and analyzed by gas chromatography. The DIC was precipitated as barium carbonate and analyzed for both $\delta^{13}\text{C}$ and ^{14}C . Due to the formation of microbial CH₄, some of the DIC had unusually heavy $\delta^{13}\text{C}$ values of -3 to -1‰. The standard groundwater ^{14}C -age correction models were developed to account for carbonate dissolution as the primary carbon input beneath the soil zone. If the heavy $\delta^{13}\text{C}$ values observed in this study are used in readily available groundwater dating models without accounting for the effects of microbial methane formation, many of the resultant calculated ages are negative (future ages) or mathematically unsolvable. Isotopic and analytical results show a positive correlation ($r^2 = 0.90$) between the $\delta^{13}\text{C}$ of the DIC and the concentration of methane in the groundwater. With this correlation, we were able to correct the $\delta^{13}\text{C}$ values of the DIC which were altered due to microbial CH₄ formation. This adjustment of $\delta^{13}\text{C}$ values, along with estimations of dead carbon input from the redox processes, allowed us to calculate ^{14}C ages using standard groundwater age correction models.

INTRODUCTION

Many aquifers in glacial deposits contain methane formed from microbial decomposition of organic materials within the sediments. Microbial production of methane can significantly affect both the $\delta^{13}\text{C}$ (Barker & Fritz 1981; Grossman *et al.* 1989) and the ^{14}C content of dissolved inorganic carbon (DIC) (Barker, Fritz & Brown 1979) and thus, modify the ^{14}C age of the water. The effects on carbonate chemistry from redox processes make it very difficult to apply most age correction models, especially fixed-model interpretations. This study addresses the problem of ^{14}C dating of groundwater containing microbial methane in Illinois.

Calculating the age of groundwater from ^{14}C analysis of the DIC involves corrections for the water/rock interactions that occur as the water infiltrates the sediments. The total DIC in groundwater is generally a composite of the CO₂ from the soil zone and dissolved carbon from solid carbonates in the sediment through which the water passes. Soil CO₂ that originates primarily from the decomposition of recent organic material and root respiration, generally has a ^{14}C activity similar to that of the modern plants. The solid carbonate in the sediments is usually considered ^{14}C -“dead,” because it generally contains no measurable ^{14}C . Thus, ^{14}C in the DIC of groundwater comes almost entirely from the soil CO₂ that is dissolved in the recharging water. The initial input of ^{14}C from the soil zone is diluted by “dead” carbonate carbon as the groundwater interacts with the sediments. Several age correction models have been developed to account for the dissolution of carbonates (Fontes & Garnier 1979). Because the $\delta^{13}\text{C}$ of soil CO₂ and carbonate carbon are normally very different, the models often estimate the degree of water/rock interactions from the $\delta^{13}\text{C}$ of the DIC in the groundwater. However, when the $\delta^{13}\text{C}$ of the DIC has been altered by the input of an additional source of carbon, such as ^{13}C -enriched CO₂ associated with microbial methane formation, the standard age correction models that utilize $\delta^{13}\text{C}$ of the DIC, are no longer adequate (Barker, Fritz & Brown 1979).

We discuss here the $\delta^{13}\text{C}$ and ^{14}C data and the techniques used to collect water and gas samples from groundwater in glacial deposits located in east-central Illinois. The $\delta^{13}\text{C}$ values of the DIC for many of the groundwater samples are unusually positive. The $\delta^{13}\text{C}$ values of the CH₄ collected from the groundwater samples are quite negative, indicating a microbial origin (Schoell 1980; Whiticar, Faber & Schoell 1986; Coleman, Liu & Riley 1988). The results show a positive correlation ($r^2 = 0.90$) between the concentration of methane and the $\delta^{13}\text{C}$ of the DIC in the ground-

water. It is possible to use this correlation to correct the effect that microbial methane formation has on the $\delta^{13}\text{C}$ and the ¹⁴C activity of the DIC, and obtain more realistic ¹⁴C ages with readily available age correction models. Three age correction models are used in this study: 1) Tamers' (1967) model uses the carbonate chemistry of the water to calculate the contribution of dead carbon; 2) Ingerson and Pearson's (1964) model uses the isotopic composition of the DIC, the soil CO₂ and the solid carbonates to calculate the contribution of dead carbon; and 3) Fontes and Garnier's (1979) model uses both the water carbonate chemistry and isotopic composition of the DIC, soil CO₂ and solid carbonates to calculate the contribution of dead carbon in the total DIC.

SITE LOCATION AND GEOLOGY

Figure 1A shows the location of the site in east-central Illinois. Described in detail by Curry, Berg and Cartwright (1990) and Battelle (1990a), the geology consists of predominantly Illinoian glacial drift overlying Pennsylvanian bedrock (Fig. 1). The bedrock is primarily sandstone and siltstone of the Bond and Modesto Formations; the bedrock topography consists of north-south trending ridges and two buried valleys. The glacial drift is primarily diamicton, silt, sand and gravel deposits, and varies in thickness from 21 to more than 61 m over the bedrock valleys. Figure 1B shows a northeast-southwest trending cross-section of the study site.

Hydrologically, the "upper units" in the cross-section are considered the surficial water-bearing zone. They have highly variable hydraulic characteristics and generally yield low volumes of water. The *mélange* or "fractured" facies of the Vandalia Till Member of the Glasford Formation (Fm.) acts as a transition zone between the upper units and the relatively uniform massive diamicton facies of the Vandalia Till. The uniform Vandalia Till has low-permeability and acts as a confining bed for the water-bearing sand and gravel facies of the Mulberry Grove Member of the Glasford. The Smithboro Till Member and the Petersburg Silt Fm. have low hydraulic conductivities, and together act as a confining bed overlying the Martinsville Sand Fm., which is a confined water-bearing zone in the buried bedrock valleys (Battelle 1990b).

SAMPLING PROCEDURE

This study was part of a larger characterization study of a potential site for a low-level radioactive repository in central Illinois. Many boreholes were drilled in clusters and piezometers installed to different depths for collection of geochemical and hydrological data. Most of the samples of groundwater for ¹⁴C analyses were taken from water-bearing sand and gravel deposits in the upper units and in the Vandalia Till and Mulberry Grove Members of the Glasford Fm., and from the Martinsville Sand Fm. and upper bedrock units.

We collected two types of water samples: a large, 45-liter sample for ¹⁴C dating, and a smaller, 3.8-liter sample under *ca.* 25 psig hydraulic pressure for dissolved gas analysis. To acquire representative samples, we pumped off three times the volume of the well casing before sampling. We installed an on-line filter (0.45 μm) on the water withdrawal line to remove fine clayey sediments suspended in the water. We measured the pH, temperature and alkalinity of the samples in the field and precipitated the DIC and extracted dissolved gas from the samples in the laboratory. Chemical and tritium analyses were done by the Illinois State Water Survey and the University of Miami, respectively, and reported in Battelle (1990b).

We modified the procedures used to precipitate DIC from the water samples for ¹⁴C dating from Geyh and Wagner (1979). The cap of a 50-liter carboy containing the water sample was replaced by a rubber stopper. A CaCl₂-ascarite column was inserted into the rubber stopper to prevent atmo-

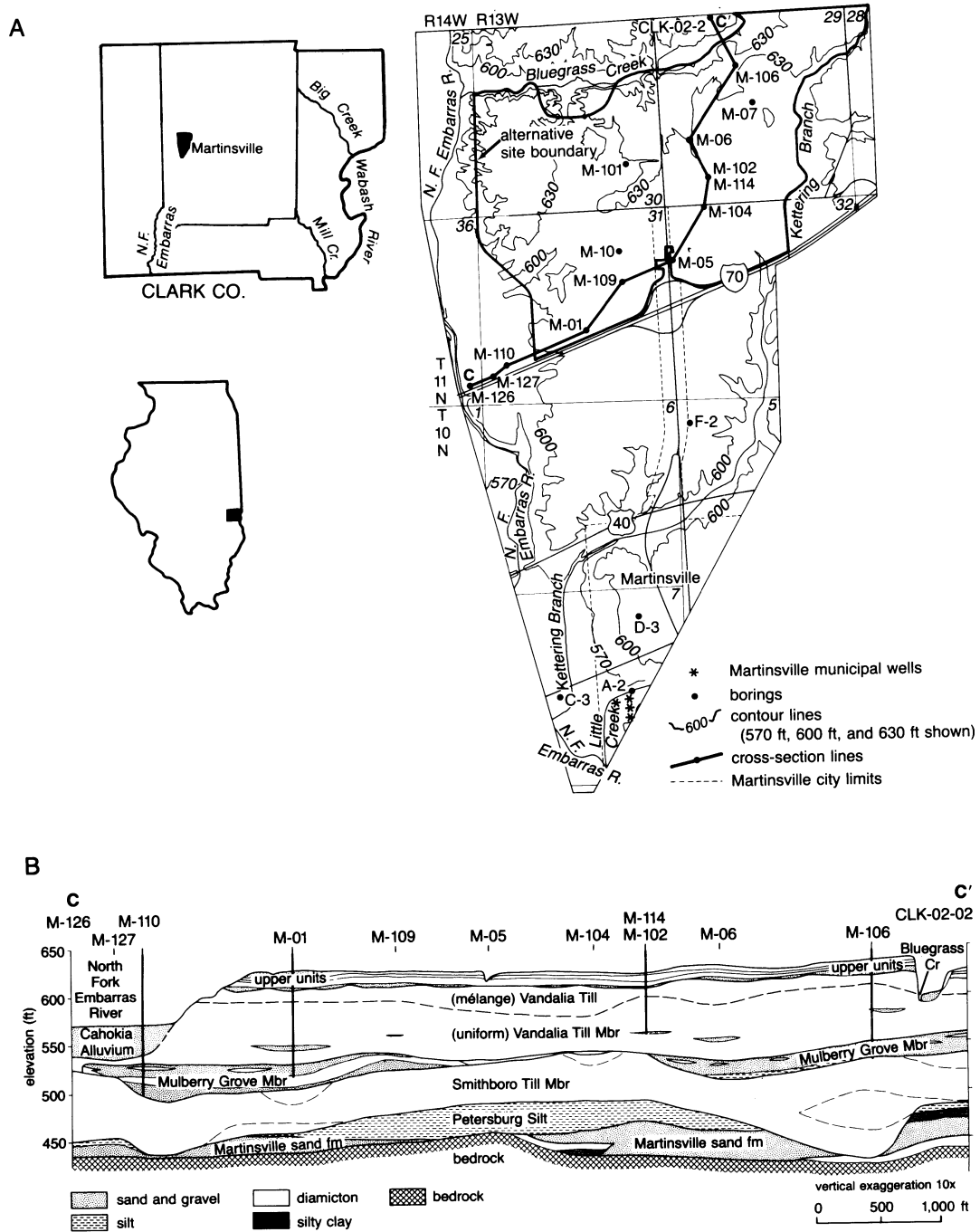


Fig. 1. Location (A) and cross-section (B) of the study site

spheric CO₂ from entering the carboy during the precipitation process. We added 2 liters of 0.5 M BaCl₂ and 2 liters of 0.5 N NaOH solutions to the sample through the spigot and mixed them thoroughly with the sample by shaking the carboy vigorously. Although BaCO₃ precipitates immediately upon adding BaCl₂ and NaOH solutions, we allowed the precipitate to settle overnight. After the settling, the top solution was drained off through the spigot. The precipitate was then rinsed repeatedly by CO₂-free, deionized water in the carboy until the pH approached neutrality. The sample slurry was then siphoned into a 4-liter vacuum flask and filtered through a buchner funnel filtration apparatus. The BaCO₃ was converted first into CO₂ and ultimately into benzene on a vacuum system. The benzene was collected, weighed and counted in a liquid scintillation counter for its ¹⁴C activity. A split of the CO₂ was taken from the ¹⁴C vacuum system and sealed in pyrex tubing for δ¹³C determination. The δ¹³C was determined on a Finnigan Delta-E isotope ratio mass spectrometer with a reproducibility of ±0.1‰ between replicates. We report the δ¹³C values relative to PDB.

Figure 2 shows the apparatus designed to collect the pressurized water samples for dissolved gas analysis. It consists of a brass sample container, a pressurized expansion tank and a flow manifold. The pressure expansion tank was used to dampen the pulsations caused by the pump (piston or bladder type). By adjusting the flow bypass valve on the manifold, we maintained the pressure in the tank at *ca.* 25 psig. After the pressure was stabilized in the expansion tank, we opened the pre-evacuated brass sample container to the manifold. We adjusted the rate of sample filling so that the pressure in the manifold did not drop much below 20 psig. The sample container was closed off and disconnected from the system after the pressure of the system reached 25 psig.

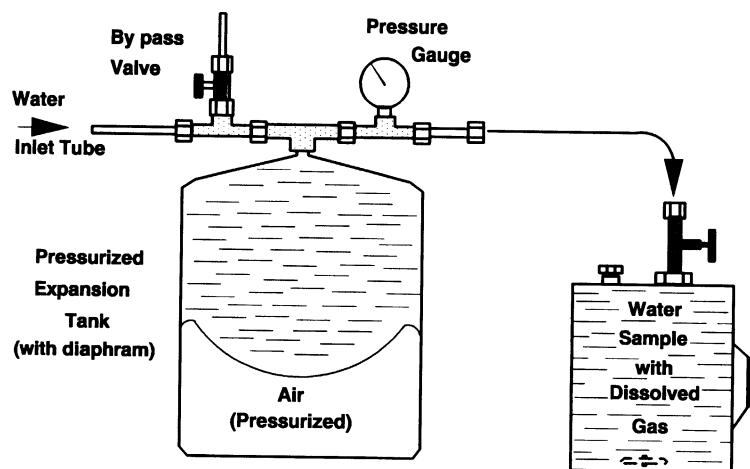


Fig. 2. Pressurized water sampling apparatus

Figure 3 shows the system used for the extraction of dissolved gases from the pressurized water samples. Prior to the extraction of the gases, the tubing connecting the gas buret to the sample container was evacuated by a direct drive vacuum pump in conjunction with the peristaltic pump. The two-way valve on top of the buret was then switched to connect the buret and the peristaltic pump. We then opened the valve on top of the sample container, and the gases released from the water sample were transferred *via* the peristaltic pump to the gas buret, which was previously filled with saturated Na₂SO₄ solution. As the gas was transferred into the buret, the solution was displaced to a reservoir open to the atmosphere. The water sample was heated to *ca.* 60°C and stirred continuously throughout the extraction process. We allowed 2 h for gas extraction. After the extraction was completed, the reservoir solution was brought down to the same level as the solution in

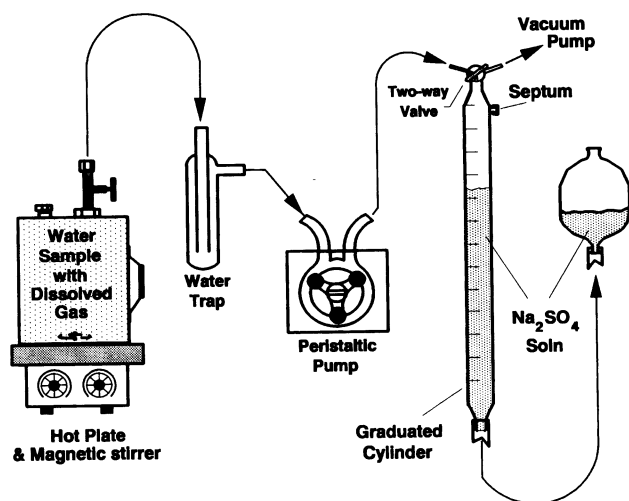


Fig. 3. Dissolved gas extraction apparatus

the buret, and the volume of gas extracted was read directly off the graduated buret. The extracted gas was then transferred through the septum on the buret into a preevacuated serum bottle and analyzed for its chemical composition by gas chromatography.

The system used to prepare CH_4 , extracted from the water samples, for $\delta^{13}\text{C}$ determination consists of a GC column, a GC detector and a combustion/collection flow unit. A gas sample, 2–50 ml, depending on the concentration of CH_4 in the sample, was injected into the system and carried by helium flow through a GC column. The methane was separated from other gases by the column and flowed into a quartz combustion tube filled with cupric oxide (CuO) preheated to 850°C . The methane was oxidized to form CO_2 , which was collected in a liquid-nitrogen-cooled trap on the vacuum line. The CO_2 was purified, volumetrically measured, sealed in pyrex tubing and analyzed on the isotope ratio mass spectrometer.

RESULTS AND DISCUSSION

Our discussion focuses on the isotopic and methane data from groundwater samples taken from deposits in the Glasford Fm., particularly the Mulberry Grove Member. Table 1 shows the pH, alkalinity, $\delta^{13}\text{C}$ of the DIC, ^{14}C of DIC, and tritium contents of the samples used in this study. Table 1 also shows the quantity of CH_4 measured and the $\delta^{13}\text{C}$ of the CH_4 for several groundwater samples taken from the sand and gravel facies of the Mulberry Grove unit.

The very negative $\delta^{13}\text{C}$ values of the CH_4 are indicative of CH_4 that formed by methanogenic reduction of CO_2 (Whiticar, Faber & Schoell 1986; Coleman, Liu & Riley 1988). Two metabolic pathways are primarily recognized in the literature for the formation of microbial methane, fermentation and CO_2 reduction, represented by the following box diagram:

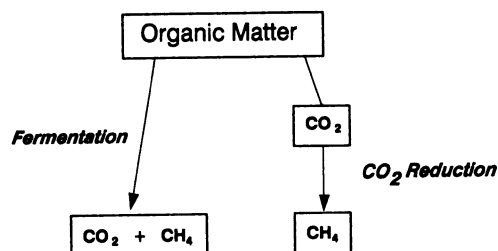


TABLE 1. pH, Alkalinity, Methane and Isotopic Data for Groundwater in Illinois

Stratigraphic unit	Well no.	pH	Alkalinity (meq liter ⁻¹)	δ ¹³ C (‰)	¹⁴ C (pMC)	Tritium (TU)*	CH ₄ (mmol liter ⁻¹)	δ ¹³ C (‰)
<i>Upper units</i>								
Cahokia Alv.	A-3	6.72	6.89	-15.4	98.7	11.1	na**	na
Pearl Fm.	M-106	7.48	4.60	-14.0	84.4	23.9	0.00	na
Pearl Fm.	M-01	6.80	6.34	-13.7	75.3	17.2	na	na
<i>Glasford Fm.</i>								
Vandalia fra.	D-4	6.65	6.94	-15.5	91.8	14.5	na	na
Vandalia fra.	M-101	7.45	6.25	-14.4	58.3	na	na	na
Vandalia uni.	C-5	6.81	6.19	-11.1	77.7	22.7	na	na
Mulberry Grv.	C-4	7.37	6.19	-13.0	60.4	22.9	na	na
Mulberry Grv.	M-110	7.51	6.23	-12.3	43.2	29.8	0.00	na
Mulberry Grv.	A-2	7.21	9.01	-13.4	42.2	6.3	na	na
Mulberry Grv.	M-106	7.41	9.60	-7.5	25.6	na	0.95	na
Mulberry Grv.	M-07	7.41	7.95	-10.6	25.3	0.47	0.73	na
Mulberry Grv.	D-3	7.46	7.67	-11.1	22.2	0.01	0.73	-87.6
Mulberry Grv.	M-10	7.35	10.80	-3.2	15.6	na	na	na
Vandalia uni.	M-114	7.84	10.20	-2.0	13.7	0.09	na	na
Mulberry Grv.	C-3	7.29	10.68	-1.3	11.4	0.25	3.53	-76.3
Mulberry Grv.	M-01	7.31	11.36	-2.4	10.0	0.15	2.37	-77.3
Mulberry Grv.	F-2	7.68	7.84	-5.9	5.4	na	2.35	-83.2

*Tritium data from Battelle (1990b)

**na = not analyzed

During microbial formation of CH₄ by the CO₂ reduction pathway, CH₄ becomes enriched in ¹²C, while the CO₂ becomes enriched in ¹³C. Thus, as CH₄ is produced, the continuous input of ¹³C-enriched CO₂ to the groundwater will result in unusually positive δ¹³C values for the DIC, as observed in many of the samples at this site.

Figure 4 shows the correlation between the concentration of CH₄ and the δ¹³C of the DIC in the groundwater. Samples with higher CH₄ concentrations also have more positive δ¹³C values for the DIC. Using this positive correlation between CH₄ concentration and δ¹³C of the DIC, one can estimate what the δ¹³C of the DIC would be without the input of isotopically heavy CO₂ into the aquifer. For the Mulberry Grove unit, the y-intercept (zero concentration of CH₄) gives a δ¹³C for the DIC of ca. -12.3‰. This is more positive than the δ¹³C of water sampled from the upper units (Table 1), and probably reflects further dissolution of carbonate carbon (which has a δ¹³C value close to zero) as the water passed through additional sediments.

If we apply a value of -12.3‰ for the δ¹³C of the DIC in the age correction models using δ¹³C, such as those of Ingerson and Pearson (1964) and Fontes and Garnier (1979), the resulting ages for the groundwater from the Glasford Fm. are more reasonable than if the DIC δ¹³C values are used without correction. If the measured DIC δ¹³C values are directly used in these models, many of the resultant ages are negative, or else mathematically unsolvable. For comparison, Table 2A shows the calculated ages for the groundwater in the Glasford Fm. using: 1) no water/rock correction for the ¹⁴C analyses; 2) Tamers' model (which does not rely on δ¹³C values and assumes 50% of the alkalinity is from carbonate dissolution); 3) Ingerson and Pearson's model with and without correcting the δ¹³C values due to the influence of methane formation; and 4) Fontes and Garnier's model with and without correcting the δ¹³C values due to the influence of methane formation.

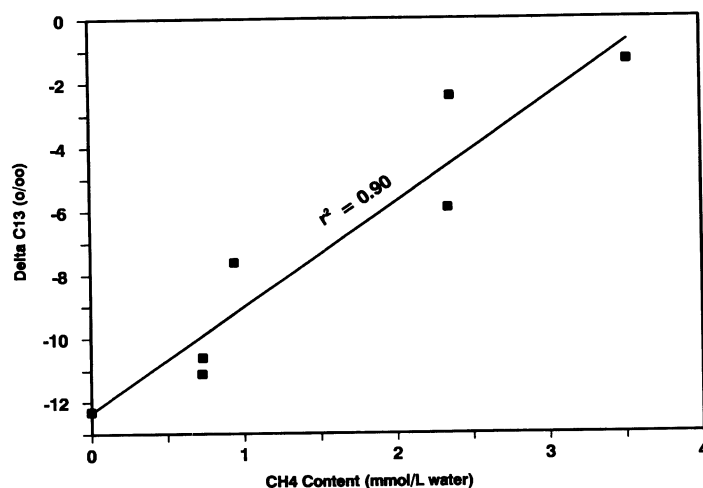


Fig. 4. Correlation of CH_4 content and $\delta^{13}\text{C}$ of DIC (Glasford Fm.)

TABLE 2. Age of DIC (in ^{14}C yr BP) calculated using three different models and effects of correcting for methane formation

A. Comparison of ^{14}C yr BP* using measured and adjusted (-12.3%) DIC $\delta^{13}\text{C}$ values

Well no.	Analytical (uncorrected)	Tamers' model**	Ingerson and Pearson Corrections		Fontes and Garnier Corrections	
			No methane	Methane	No methane	Methane
M-106	11,300	6300	1800	6400	-17,800	6500
M-07	11,400	6400	5100	6500	3200	6600
D-3	12,400	7400	6600	7600	5600	7800
M-10	15,400	10,500	-3000	10,500	†	10,500
M-114	16,400	10,900	-8600	11,500	†	12,100
C-3	17,900	13,100	-17,000	13,000	†	13,000
M-01	19,000	14,200	-3100	14,200	†	14,000
F-2	24,100	18,800	12,300	19,200	†	19,700

B. Q-factor corrections "dead" carbon input from decomposition of organic material due to microbial methane formation

Well no.	Q factor	Tamers' model	Ingerson and Pearson	Fontes and Garnier
M-106	$0.88 \pm .05^\ddagger$	5300	5400	5500
M-07	$0.89 \pm .04$	5500	5500	5600
D-3	$0.89 \pm .04$	6400	6600	6800
M-10	$0.70 \pm .11$	7600	7600	7600
M-114	$0.62 \pm .15$	6900	7500	8100
C-3	$0.62 \pm .15$	9200	9100	9000
M-01	$0.76 \pm .09$	12,000	11,900	11,800
F-2	$0.63 \pm .14$	15,000	15,400	15,900

*Age equation: $T = 8270 \cdot \ln[A_0/A]$; **This model does not use an isotopic correction

†Age cannot be calculated, $A_0 < 0$; ‡The error for Q is based on the variation for estimating the amount of dead carbon input using the Rayleigh model and the variation of ^{14}C concentration for CH_4 .

The footnote of Table 2 shows the equation used to convert the ¹⁴C percent modern carbon (pMC) values into an age (¹⁴C yr BP). In the age equation, *A₀* is the calculated initial ¹⁴C activity derived from the age correction models, and *A* is the measured ¹⁴C activity obtained for each sample. For the two correction models that use δ¹³C values to estimate the contributions of soil CO₂ and the solid carbonate in the DIC, we used -21.4‰ and -1‰, respectively. A value of -21.4‰ was measured for the soil CO₂ with a pCO₂ of 2.6%. This is similar to δ¹³C values observed for soil CO₂ in Ontario by Fritz, Mozeto and Reardon (1985). A δ¹³C value of -1‰ was measured for solid carbonate in samples of the Glasford and Smithboro Fms. at this site.

The results in Table 2A show that once the influence of methane formation on the isotopic data of DIC is adjusted, the age correction models utilizing the δ¹³C values give reasonable results. However, when considering the ¹⁴C activity input to the groundwater, one must take into account that the CH₄ formation at this site occurs in Illinoian glacial deposits. Thus, all the CO₂ influx associated with the CH₄ formation is radioactively “dead.” Besides the dissolution of carbonate in these groundwaters, additional dead carbon is introduced from the CO₂ produced during anaerobic degradation of Illinoian-age organic material. The estimation of total dead carbon in the DIC as about one-half the alkalinity (Tamers 1967, 1975; Fontes & Garnier 1979) is not correct when there has been significant input of dead CO₂ associated with microbial CH₄ formation.

Given the good correlation between the CH₄ concentration and the δ¹³C of the DIC, the amount of dead carbon input due to redox processes is probably related to the characteristics of the CH₄ in the system. Using the Rayleigh (1896) distillation model, one can estimate how much CO₂ was consumed to form CH₄ of a certain isotopic composition (Gautier, Kharaka & Surdam 1985). Based on the accumulation of data by Whitticar, Faber and Schoell (1986), a fractionation factor, α_{CO₂-CH₄} (isotopic fractionation of ¹³C between CO₂ and CH₄), of 1.075 was used for CH₄ formation by the CO₂ reduction pathway. The δ¹³C of the CO₂ from the degradation of organic matter is assumed to be -25‰. According to the Rayleigh model, only up to *ca.* 40% of the CO₂ is consumed to form CH₄ with δ¹³C values similar to those found at this site (Hackley & Liu, *ms.*). This implies that the amount of CH₄ measured is significantly less than the amount of dead CO₂ input into the DIC of the water system. However, this may not be the case, considering that the ¹⁴C activity of the CH₄ is significantly lower than that of the associated DIC.

If we assume that the dead CO₂ equilibrated with the DIC prior to reduction to CH₄, the ¹⁴C activity of the CH₄ and DIC should be the same. According to the ¹⁴C activity of four samples (1 from the Mulberry Grove, 2 from the Martinsville Sand and 1 from the bedrock aquifer), the CH₄ has, on average, only *ca.* 44% of the ¹⁴C activity observed in the DIC. Assuming there is no significant contribution of CH₄ from the fermentation pathway (supported by the isotopic data: δ¹³C values of -76 to -87‰ and δD values of -223 to -242‰ (Hackley & Liu, *ms.*)), then the lower ¹⁴C activity for the CH₄ indicates that a significant fraction of the dead CO₂ was directly converted to CH₄ prior to equilibrating with the DIC. This information alone implies that the amount of dead CO₂ input into the DIC is significantly less than the amount of CH₄ present. However, by combining this ¹⁴C information with the Rayleigh distillation prediction for the amount of CO₂ consumed to form CH₄ (a mean value of *ca.* 35%), the amount of dead CO₂ input to the DIC is estimated at 44%/35% (*ca.* 1.3 ± 0.5 times the amount of CH₄ present).

For the wells where CH₄ was not measured, the relationship between δ¹³C of DIC and CH₄ concentration in Figure 4 is used to estimate the amount of CH₄ present. The CH₄ concentration is then multiplied by 1.3 to estimate the amount of dead CO₂ input for each sample. Once the moles of dead CO₂ input are estimated, an additional correction factor, which we refer to as *Q*, can

be applied to the age equation to account for this extra dead carbon input, when calculating the ^{14}C age of the water. Using Q , the age equation then becomes

$$T = 8270 \cdot \ln(Q \cdot A_o / A). \quad (1)$$

Q is determined by subtracting the estimated amount of dead CO_2 , added to the system as a result of degradation of organic matter, from the total DIC and then dividing by the total DIC. For example, if the total DIC is equal to $10 \text{ mmol liter}^{-1}$, and the amount of dead CO_2 is determined to be *ca.* $1.5 \text{ mmol liter}^{-1}$, then $Q = 0.85$.

Table 2B shows the calculated values for Q as well as the resultant ages using the Q values with previously determined A_o values for the three age correction models listed in Table 2A. The application of the Q factor changes the calculated ^{14}C ages up to *ca.* 3.5 ka. The comparison of ages in Tables 2A and 2B shows the importance of determining whether microbial CH_4 is present in groundwater and correcting for its influence when calculating ^{14}C ages of the groundwater. The effect of microbial methane on the $\delta^{13}\text{C}$ of DIC may vary, depending on the extent of CH_4 production, the chemistry of the water and the lithology of the sediments. Thus, it is important to determine the concentration of CH_4 in groundwater samples and the $\delta^{13}\text{C}$ of the CH_4 to be sure the CH_4 is of microbial origin.

The variation of ^{14}C ages observed among the samples in the Glasford Fm. (Table 2) can be explained by hydrological and geochemical data, which indicate that older groundwater from the Martinsville sand and bedrock units mixes with Glasford groundwater in a southwest direction across the study site (Battelle 1990b). The Mulberry Grove Member samples listed in Table 1 with significant tritium values are located in the vicinity of the Embarras River valley where the confining uniform facies of the Vandalia Till Member is very thin (*e.g.*, M-110 in Fig. 1B). Younger water from the alluvium deposits in the river valley mixes with the older water of the Mulberry Grove Member (Battelle 1990b).

CONCLUSIONS

In groundwater containing microbial methane, the influence of methane formation must be determined before applying most age correction models using $\delta^{13}\text{C}$ values. The glacial deposits in east-central Illinois show a positive correlation between the CH_4 concentration and the $\delta^{13}\text{C}$ of the DIC in the groundwater samples from one formation. The above correlation was used to modify the $\delta^{13}\text{C}$ of the DIC in the system, correcting for the input of isotopically heavy CO_2 due to microbial CH_4 formation. Since methane occurred only in samples from sediments of Illinoian age, we assumed that all the CO_2 input from the redox processes contained no ^{14}C . Using the Rayleigh distillation model, along with ^{14}C data on CH_4 , we can reasonably estimate how much biogenic dead CO_2 contributed to the DIC. Both the adjustment of $\delta^{13}\text{C}$ of DIC and the estimates of dead carbon input from redox processes enabled us to calculate realistic ages using readily available age correction models.

ACKNOWLEDGMENTS

This research was supported by Battelle Memorial Institute through a contract with the ISGS. Hanson Engineers, Inc. assisted in the collection of groundwater samples. We wish to acknowledge J. Q. Cao, H. H. Hwang and E. M. McMillion for their assistance in the field and isotope laboratory at the ISGS.

REFERENCES

- Barker, J. F. and Fritz, P. 1981 The occurrence and origin of methane in some groundwater flow systems. *Canadian Journal of Earth Sciences* 18: 1802–1816.
- Barker, J. F., Fritz, P. and Brown, R. M. 1979 Carbon-14 measurements in aquifers with methane. *Isotope Hydrology 1978, Proceedings of a Symposium IAEA-SM-228/33*. IAEA: 661–678.
- Battelle 1990a Geological and geotechnical investigations. In *Alternative Site Investigation Studies Clark County, Illinois*, Vol. II. Battelle Memorial Institute and Hanson Engineers, Inc., Springfield, Illinois.
- _____ 1990b Hydrological Investigations. In *Alternative Site Investigation Studies Clark County, Illinois*, Vol. III. Battelle Memorial Institute and Hanson Engineers, Inc., Springfield, Illinois.
- Coleman, D. D., Liu, C. L. and Riley, K. M. 1988 Microbial methane in the shallow paleozoic sediments and glacial deposits of Illinois, USA. *Chemical Geology* 71: 23–40.
- Curry, B. B., Berg, R. C. and Cartwright, M. R. T. 1990 Quaternary geology of the Martinsville Alternative Site, Clark County, Illinois. *Illinois State Geological Survey Open File Report*.
- Fontes, J. C. and Garnier, J. M. 1979 Determination of the initial ¹⁴C activity of the total dissolved carbon: A review of the existing models and a new approach. *Water Resources Research* 15(2): 399–413.
- Fritz, P., Mozeto, A. A. and Reardon, E. J. 1985 Practical considerations on carbon isotope studies on soil carbon dioxide. *Chemical Geology (Isotope Geoscience Section)* 58: 89–95.
- Gautier, D. L., Kharaka, Y. K. and Surdam, R. C. 1985 Relationship of organic matter and mineral diagenesis. SEPM Short Course No. 17: 56–58.
- Geyh, M. A. and Wagner, R. H. (ms.) 1979 Guideline for groundwater sampling for isotope analyses. Unpublished laboratory notes, ¹⁴C and ³H-Laboratory, Niedersächsische Landesamt für Bodenforschung, Hannover, Germany.
- Grossman, E. L., Coffman, K. B., Fritz, S. J. and Wada, H. 1989 Bacterial production of methane and its influence on groundwater chemistry in east-central Texas aquifers. *Geology* 17: 495–499.
- Hackley, K. C. and Liu, C. L. (ms.) Influence of microbial methane formation on δ¹³C and radiocarbon age of dissolved inorganic carbon (DIC) in groundwater. Unpublished manuscript.
- Ingerson, E. and Pearson, F. J. 1964 Estimation of age and rate of motion of groundwater by the ¹⁴C-method. In *Recent Research in the Fields of Hydrosphere, Atmosphere and Nuclear Geochemistry*. Tokyo, Maruzen: 263–283.
- Rayleigh, J. W. S. 1896 Theoretical considerations respecting the separation of gases by diffusion and similar processes. *Philosophical Magazine* 42: 493–498.
- Schoell, M. 1980 The hydrogen and carbon isotopic composition of methane from natural gases of various origin. *Geochimica et Cosmochimica Acta* 44: 649–661.
- Tamers, M. A. 1967 Surface-water infiltration and groundwater movement in arid zones of Venezuela. In *Isotopes in Hydrology*. IAEA, Vienna: 339–351.
- _____ 1975 Validity of radiocarbon dates on groundwater. *Geophysical Survey* 2: 217–239.
- Whiticar, M. J., Faber, E. and Schoell, M. 1986 Biogenic methane formation in marine and freshwater environments: CO₂ reduction vs. acetate formation – Isotope evidence. *Geochimica et Cosmochimica Acta* 50: 693–709.