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THE GEOCHEMISTRY AND EVOLUTION OF NATURAL ORGANIC SOLUTES IN GROUNDWATER

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ABSTRACT. This paper describes the organic carbon cycle of the recharge environment of a shallow, sandy aquifer, with an emphasis on the origin, flux and geochemical evolution of dissolved organic carbon using liquid chromatography, carbon isotopes and GC-MS techniques. The two components of DOC investigated are hydrophobic acids and C_1–C_{10} hydrophilic compounds. The ^{14}C activity of these components of the DOC was measured using TAMS.

^{14}C analyses of DOC components may provide an additional tool for groundwater dating. The initial ^{14}C activity of DOC in a recharge zone, however, depends mainly on the residence times and cycling of DOC sources in the recharge environment. Using ^{14}C DOC to estimate groundwater residence times between sampling points along a flow path compares well with residence times estimated on the basis of hydraulic parameters and ^{14}C DIC under closed system conditions.

INTRODUCTION

The origin, age, geochemistry and diagenesis of naturally occurring organic solutes (DOC) and their role in the carbon cycle and biogeochemical processes that occur in groundwater flow systems are not well known. Only a few studies have specifically addressed the origin and nature of DOC in groundwater (Leenheer *et al*, 1974; Wallis, 1979; Wallis *et al*, 1981; Barcelona, 1984; Thurman, 1985a,b; Murphy, 1989), primarily due to difficulties in isolating and characterizing the low concentrations of DOC prevalent in most groundwaters (<1mg/L; Leenheer *et al*, 1974).

DOC in groundwater originates from active biological processes in the soil, unsaturated and saturated zones, and may introduce fossil or modern material to the groundwater (*cf* Thurman, 1985b). The potential importance of natural DOC in groundwater has been shown; it may facilitate the transport of metals (McKnight *et al*, 1983; Thurman, 1985a), enhance the solubility of relatively insoluble organic contaminants (Gjessing & Berglin, 1982; Perdue, 1983), and provide a labile carbon source for microbial redox processes (Miller *et al*, 1979; Skogerboe & Wilson, 1981; Starr *et al*, 1987). Also, DOC interferences may cause H^+ determination errors of up to 50% (Herczeg & Hesslein, 1984), as well as contribute to groundwater alkalinity (Willey *et al*, 1975).

The present study is part of a comprehensive investigation of carbon cycling in several groundwater systems of Ontario and Alberta (Wassenaar, ms in preparation). We discuss here the organic carbon cycle of the recharge environment of a shallow, unconfined sand aquifer near Rodney, Ontario and demonstrate the potential use of DOC as a groundwater dating tool.

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STUDY SITE

The study site is a sandy, unconfined aquifer located near Rodney, Ontario (Fig 1). The aquifer is composed of 3–4m of homogenous deltaic sands (Chapman & Putnam, 1984). Topographic relief of the area is low (<1m), resulting in weak hydraulic gradients. Depth to the water table varies from 90 – 110cm. The aquifer underlies agricultural fields that receive annual applications of nitrate fertilizer and herbicides.

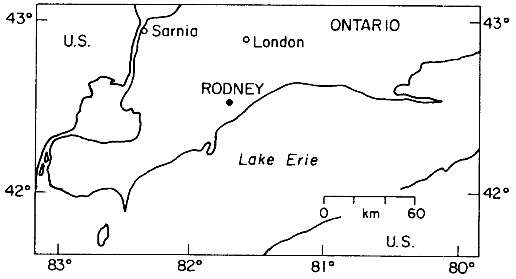

Fig 1. Location of shallow sand aquifer under investigation near Rodney, Ontario

In previous nitrogen studies at the site, Trudell *et al* (1986) and Starr *et al* (1987) demonstrated that the aquifer is anaerobic and high concentrations of nitrate (>50mg/l) are denitrified by bacteria within 100cm below the water table. Starr *et al* (1987) inferred that labile DOC may be a limiting factor for the natural remediation of nitrate contamination at this site.

Recharge to the Rodney aquifer is rapid, with residence times in the vadose zone of <1–2 yr, based on ^{18}O, ^{2}H, and ^{3}H data. High sulfate concentrations (>100mg/L) are also reduced by microbes within 200cm of the water table as indicated by $\delta^{34}S$ data (Wassenaar *et al*, ms in preparation).

MATERIALS AND METHODS

In October 1986, a six-point stainless steel bundle piezometer was installed in the aquifer near Rodney, each piezometer consisting of 1/8" ID tubing. Sampling ports were screened with 200 mesh stainless steel at 25cm intervals from 125–250cm depth. During installation, cores were taken for stratigraphic and sediment analyses. Water samples from the piezometers were passed through 25 and 0.3μ Balston inorganic microfiber filters. Sampling for the DOC studies took place from October 1986 to April 1988.

Samples for DOC determinations were collected in precleaned glass bottles, acidified and analyzed on a Dohrmann Carbon Analyzer within 24 hr. Sixty to 100L of water were processed from the upper and lower piezometers for carbon isotope and GC-MS analyses of the DOC. These large samples were collected in 20L glass carboys, acidified, stored at 4°C and processed in one week.

The DOC classification scheme of Leenheer and Huffman (1979) was used for DOC component isolation. Briefly, the hydrophobic fraction (A/N/B) is operationally defined by sorption on XAD-8 resin, whereas, the hydrophilic fraction (A/N/B) does not sorb on XAD-8. Since groundwater DOC is dominated by organic acids (Thurman, 1985a), we isolated only the hydrophobic acid component (fulvic and humic acids) by eluting the XAD-8 with base. The C_1–C_{10} component of the hydrophilic fraction was concentrated on Silicalite molecular sieve for geochemical analyses (*cf* Murphy, 1987).

The DOC isolation system consisted of a 1200ml glass and Teflon column containing Amberlite XAD-8 resin to isolate the hydrophobic fraction of the DOC. Hydrophobic acids were eluted from the XAD-8 and freeze-dried (*cf* Thurman & Malcolm, 1981). The XAD-8 column was followed by a glass and Teflon column containing precombusted (800°C) Silicalite molecular sieve to isolate the C_1–C_{10} component of the hydrophilic fraction of the DOC (*cf* Murphy, 1987). Silicalite samples were freeze dried and 20 – 50g were combusted at 800°C under vacuum in the presence of cupric oxide. The CO_2 produced from the combustion of sorbed organics was collected for ^{13}C and ^{14}C determinations. Pyrex capillary tubes containing 0.5 – 1.0g of Silicalite (sample and blank) were thermally desorbed on a Hewlett Packard 5970 GC-MS to 230°C by flushing in a helium stream for organic compound identification. Only the 25 most abundant GC-MS peaks were verified by computer comparison with an internal organic compound library and blank sample.

Teflon tubing and glassware were used in all operations to minimize organic contamination. Details of the DOC isolation methods and classification used can be found in Leenheer and Huffman (1979), Thurman and Malcolm (1981), Thurman (1985a) and Murphy (1987).

Sedimentary organic carbon (humic and fulvic acids combined) was extracted from core material in 0.1 N NaOH (*cf* Schnitzer & Khan, 1972) and analyzed for ^{14}C activity at the Environmental Isotope Laboratory, University of Waterloo, using the benzene technique and liquid scintillation counting. Small DOC samples were analyzed by direct counting of ^{14}C atoms by Tandem Accelerator Mass Spectrometry (TAMS) at the University of Toronto (ISOTRACE Laboratory). The $\delta^{13}C$ content of the DOC and sedimentary humic substances were determined by mass spectrometry at the University of Waterloo, and are reported relative to the PDB standard. All ^{14}C activities are reported in percent modern carbon (pMC) relative to 95% of the activity of oxalic acid standard in 1950 and normalized to a $\delta^{13}C$ of –25‰.

RESULTS AND DISCUSSION

Sedimentary Organic Carbon

Trudell (1980) determined the fraction of solid organic carbon (FOC) at the Rodney site (Fig 2). From a high value of 0.5 wt % it decreases

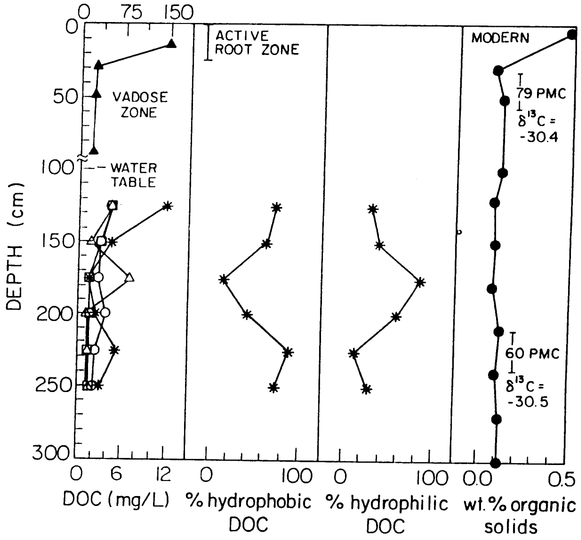

Fig 2. Dissolved organic carbon concentrations, percentage of hydrophobic and hydrophilic fractions of the DOC, weight percent organic solids, and ^{14}C activity and ^{13}C (PDB) isotope data for organic solids from the Rodney sand aquifer. Sampling times are denoted by: ○ – Jan 1987, □ – March 1987, △ – June 1987, * – April 1988. Vadose zone data (▲) from Starr *et al* (1987), and weight % organic solid determinations (●) from Trudell (1980). Note upper scale for vadose zone DOC concentrations.

rapidly to ca 0.08 weight percent below 30cm depth. This FOC consists primarily of finely disseminated particles and occasional fragments of relict rootlets can be found to a depth of at least 300cm. The ^{14}C activity of fulvic and humic acids extracted from core material decreases exponentially (r^2 = 0.95) with depth from assumed modern at the surface to 60 pMC at 210–240cm (Fig 2). These ^{14}C activities probably reflect the mean residence times of a mixture of humic substances of different ages. The dated humic and fulvic acids have $\delta^{13}C$ values of –30.4‰ and –30.5‰ (Fig 2), which is similar to that of C_3 plant derived soil humic substances and sedimentary kerogen (Nissenbaum & Schallinger, 1974; Deines, 1980).

Temporal/Spatial Variations in DOC

The results of DOC analyses are summarized in Figure 2. DOC concentrations in the groundwater at Rodney range from 1–12mg/L with a median of 4.6mg/L. Generally, higher DOC contents (4–12mg/L) occur near the water table and decline with depth (1–1.7mg/L). These DOC concentrations are significantly higher than those observed in major aquifers of the United States, which have a median DOC of 0.7mg/L (Leenheer *et al*, 1974). The higher DOC concentrations in this aquifer are no doubt a result of a lesser degree of attenuation and biodegradation due to rapid recharge through the vadose zone.

DOC concentrations also exhibit temporal variations (Fig 2). Although higher DOC concentrations occur near the water table, DOC peaks also occur below the water table. DOC peaked at 125cm (12mg/L) and 225cm (5mg/L) in April 1988, and at 175cm (4.5mg/L) for March 1987. These peaks could represent the influx of spring or fall recharge, carrying high DOC waters leached from the soil zone. Antweiler and Drever (1983) and Cronan and Aiken (1985) observed that higher concentrations of DOC occur in soils during spring runoff when the soil is saturated. Reardon, Mozeto and Fritz (1980) observed high total organic carbon (TOC) in soil porewaters that were attributed to fall recharge events.

Starr *et al* (1987) measured DOC concentrations in the vadose zone from squeezed core material at this site. Their results are also summarized in Figure 2. The highest vadose/soil zone DOC values occur in the upper soil zone with a maximum value of 150mg/L. From 30–90cm depth, DOC drops to 25–19mg/L and then to <12mg/L below the water table (Fig 2). The sharp drop in porewater DOC concentrations below 5–10cm is a result of adsorption and microbial oxidation in the vadose zone (Dawson *et al*, 1981; Meyer & Tate, 1983; Cronan & Aiken, 1985). Thus, as a result of adsorption, oxidation and microbial biodegradation there is a 10–30 fold decrease in DOC as infiltrating water passes from the soil zone, through the vadose zone to the groundwater.

Nature of DOC

Characterization of DOC in groundwater is a useful tool for monitoring the diagenesis of DOC caused by sorption, biodegradation and microbial transformations. In groundwater, the hydrophobic fraction of the DOC is primarily composed of high molecular weight humic substances (mainly fulvic acid), whereas the hydrophilic fraction is primarily composed of lower molecular weight (LMW) organic acids (Antweiler & Drever, 1983).

Figure 2 also summarizes results of a total hydrophobic/hydrophilic split of DOC. The total hydrophobic fraction of the DOC varied between 15–88% of the total DOC, and showed significant variations with depth (Fig 2). Similarly, the total hydrophilic fraction also varied with depth from 12–85% of the total DOC.

Thurman (1985b) observed that hydrophobic acids in aquifers are mostly fulvic acid and typically account for <35% of the total DOC, and in surface waters between 50–60% of the DOC. The hydrophobic acid component of DOC isolated from the Rodney aquifer was >95% fulvic acid. Wallis (1979), however, observed that hydrophobic acids accounted for ca 90% of groundwater DOC in a mountain drainage basin. Our data suggest the amount of DOC and its hydrophobic/hydrophilic fractions may be temporally and spatially variable in groundwater. This variability seems to be prevalent in shallow groundwater systems due to seasonal variations associated with recharge events.

Hydrologic transport, however, may account for only part of the variation in the hydrophilic/hydrophobic fractions of DOC in groundwater. The concentration of the total hydrophobic fraction of the DOC shows a strong correlation with total DOC (r^2 = 0.96; Fig 3). However, the total hydrophilic fraction does not correlate as strongly with total concentration of DOC (r^2 = 0.64). Thus, the changes in DOC concentration observed with

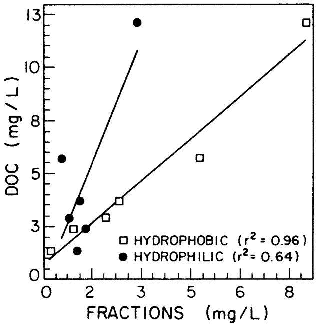

Fig 3. Correlation of the total hydrophobic and total hydrophilic content of the DOC with total DOC concentration. Based on data from the Rodney aquifer in Apr 1988

TABLE 1

GC-MS identified hydrophilic compounds from Rodney sand aquifer. Samples were thermally desorbed from silicalite molecular sieve.

R3-1 - 125cm	R3-6 - 250cm
Dominant compounds	
Methyl acetate	None
Minor compounds	
Toluene	N-hexane
Hydroxylamine	P + m xylenes
Chloroform	Cyclohexane
2-ethyl-1-hexanol	Cyclopentane
P + m xylenes	Stearic acid
Diphosphoric acid, diisooctyl ester	Palmitic acid
1,2-dichloro-benzene	
2-methyl propanate	
2,6-dimethyl-nonane	
Benzene	
Ethyl benzene	
Benzoic acid, methyl ester	

depth are due mainly to variations in the hydrophobic fraction, and to a lesser extent the hydrophilic fraction.

GC-MS and carbon isotopic characterization of the DOC suggest that microbial processes may also be an important control over the hydrophilic fraction of the DOC. Table 1 lists compounds that we were able to identify by GC-MS for the C_1–C_{10} component of the hydrophilic fraction. The GC-MS chromatogram indicated the C_1–C_{10} hydrophilic compounds at 125cm depth are composed mainly (estimated >95%) of very low molecular weight compounds (C_4–C_2), one of which was identified as methyl acetate. The

GC-MS used was not able positively to identify smaller organic compounds, such as formate. Acetate, however, is a well-known microbial by-product of anaerobic fermentation of kerogen and perhaps DOC, and is the most common volatile fatty acid found in natural waters (Miller *et al*, 1979; Barcelona, 1980; Thurman 1985a). Interestingly, methyl acetate, as well as many other LMW compounds identified at 125cm (DOC = 12mg/L), are not present downflow at 250cm depth (DOC = 4mg/L; Table 1). We suggest many of these LMW compounds may have been utilized by microbes in the zone of denitrification and sulfate reduction that occurs from 100–200cm depth. LMW organic acids, especially acetate, are well-known substrates for nitrate, sulfate reducing and methanogenic bacteria (*cf* Cappenberg & Prins, 1974). It is possible, however, that seasonal variations in DOC recharge may also affect the types of LMW compounds entering the aquifer.

Virtually all LMW compounds identified in the C_1–C_{10} hydrophilic component of the DOC (Table 1) occur naturally, and are known degradation products of lignins, cellulose and soil organic matter (Thurman, 1985a; Murphy, 1987). The two chlorinated compounds identified, however, may be the result of a reaction of chloride (from chlorinated herbicides) and fulvic acid (*cf* Oliver & Visser, 1980).

It should also be noted that Silicalite appears to adsorb $>C_{10}$ compounds to its surface, such as stearic and palmitic acid (Table 1), which is similar to observations by Murphy (1987). The data also indicate that some Environmental Protection Agency rated priority pollutants (eg, toluene, benzene, xylenes) occur naturally at trace levels in groundwater, since these compounds did not appear in the corresponding blank.

Carbon Isotopes and DOC

Stable and radiogenic carbon isotopes are useful tools for determining the origin, age and diagenesis of organic matter. Only two studies, however, have considered ^{13}C and ^{14}C isotopes in DOC from groundwater (Thurman, 1985b; Murphy, 1987). The results of ^{13}C and ^{14}C TAMS analyses of the hydrophobic acid and C_1–C_{10} hydrophilic components of the DOC from the Rodney aquifer are summarized in Table 2. ^{13}C isotope values measured for both aquatic hydrophobic acid samples were –27.3 and –30.5‰ (PDB; Table 2). These values are similar to soil organic matter and humic substances derived from C_3–type vegetation (Deines, 1980). The $\delta^{13}C$ value of the C_1–C_{10} hydrophilic component at 125cm, however, has an extremely

TABLE 2

Carbon isotopic data for hydrophobic acid and C_1–C_{10} hydrophilic components of DOC in Rodney aquifer

Depth	Hydrophobic acid (fulvic acid)	Hydrophilic (C_1–C_{10})
125cm	92 pmc ($\delta^{13}C = -27.3$)	67 pmc ($\delta^{13}C = -47.0$)
250cm	76 pmc ($\delta^{13}C = -30.5$)	69 pmc ($\delta^{13}C = -24.5$)

depleted value of –47‰ (PDB). If we assume that the C_1–C_{10} hydrophilic component at 125cm is a result of microbial fermentation of particulate organic matter and/or DOC, as suggested by methyl acetate in the sample, then microbial isotope effects may be the cause for ^{12}C enrichment in the sample. This carbon isotopic fractionation process may be analogous to the large isotope effects observed in microbial methane fermentation (*cf* Deines, 1980; Barker & Fritz, 1981).

A loss of ^{12}C enriched LMW acids is evident below the nitrate and sulfate reduction zone. At 250cm depth only larger ($>C_6$) organic compounds were identified and the $\delta^{13}C$ value was –24.0‰, which is similar to that of the precursor C_3 plant matter (Deines, 1980). It is likely that the LMW organic compounds, such as acetate or formate, are preferentially utilized by nitrate and sulfate reducing microbes.

^{14}C data for the hydrophobic acid and C_1–C_{10} hydrophilic components of the DOC are summarized in Table 2. The results indicate significant differences in ^{14}C activity between hydrophobic acid samples collected at 125 and 250cm depth. Substantial differences in ^{14}C activity are also observed between the hydrophobic acid and C_1–C_{10} hydrophilic components. The hydrophobic acid component at 125cm has a ^{14}C activity of 92 pMC but has only 76 pMC at 250cm (Table 2). Clearly, the hydrophobic acid component at 125cm (92 pMC) must originate from the upper soil profile when compared to the ^{14}C activity of humic substances extracted from the core, which are only 79 pMC at a depth of 30cm (Fig 2).

Considering the hydrology of the aquifer, the reduction in ^{14}C activity of the hydrophobic acid component cannot represent the advective residence time between 125 and 250cm. Two hypotheses can account for this lower ^{14}C activity. One possibility is that the hydrophobic acid component of the DOC is a mixture of young carbon from the soil zone and older components from the sediments, the latter being more significant at depth. This mixing of young and older humic substances may be seasonally variable. However, we can also argue that perhaps a "young" (and more labile?) component of the hydrophobic acid component of the DOC is being preferentially consumed by microbes. It is generally believed that humic substances and aquifer kerogen, due to their refractory nature, are not a readily available carbon source for microbes. If this is true, the addition of large mol wt humic substances from aquifer organic material would not account for the observations. On the other hand, humic substances are complex macromolecules (Schnitzer & Khan, 1972). Thurman (1985b) has observed that aquatic humic substances isolated from groundwater contain less oxygen than surficial aquatic humic substances. This loss of oxygen was attributed to possible microbial action on the humic substances. Thus, it is possible that a "younger," labile portion of the hydrophobic acids are being consumed by microbes in the zone of denitrification and sulfate reduction.

A second possibility is that the ^{14}C activity differences of the hydrophobic acid component in the aquifer as a whole simply reflect temporal differences in the ^{14}C activity of DOC entering the aquifer from the vadose zone (*ie,* spring DOC flux *vs* fall recharge). In this respect, it is interesting to note that the lower ^{14}C-DOC activity at 250cm depth is paralleled by a $\delta^{18}O$ value of the water near –11‰ reflecting winter/spring recharge, whereas the sample collected at 125cm has a $\delta^{18}O$ value near –8‰ reflecting summer/fall recharge.

The ^{14}C activities of the C_1–C_{10} hydrophilic component are significantly lower than the hydrophobic acid component and are similar for both samples (67–69 pMC; Table 2). This indicates that a significant input of old carbon is added to the C_1–C_{10} hydrophilic component of the DOC.

We have identified a large component of LMW organic acids for the sample at 125cm (Table 1). The presence of methyl acetate, and possibly the ^{12}C enrichment, indicate this component of the DOC may contain a significant amount of organic solutes derived from microbial fermentation of FOC and/or DOC. Moreover, the total hydrophilic fraction does not correlate strongly with total amount of DOC (Fig 3), which varies seasonally, and is generally present in concentrations of <2mg/L. The similarity of the ^{14}C content of the C_1–C_{10} hydrophilic component of the DOC and the carbon in the solid phase (Table 2; Fig 2) seems to suggest a direct link between the two.

DOC as a Potential Groundwater Dating Tool

The geochemistry and geology of the Milk River Aquifer in southern Alberta is well known (Meyboom, 1960; Schwartz & Muhlenbachs, 1979; Phillips *et al* 1986; Murphy 1989; Hendry & Schwartz, in press). Murphy (1989) has presented complete DOC characterization for the Milk River aquifer from samples collected at a great distance from the recharge zone. We present additional DOC and DIC ^{14}C data obtained near the aquifer recharge zone, along a clearly defined flow path of the eastern part of the aquifer under closed-system conditions (flow path 1 of Hendry & Schwartz, in press).

^{14}C determinations were made for the hydrophobic acid and C_1–C_{10} hydrophilic component of the DOC, and for the DIC (Hendry, pers commun, 1988), from wells MR-85 (DOC = 2mg/L) and MR-52 (DOC = 1.8mg/L) near the recharge zone, 12km apart. Figure 4 shows results of ^{14}C data and the generalized stratigraphy.

The ^{14}C activities of the DIC are 9.2 and 1.7 pMC for wells MR-85 and MR-52, respectively. The $\delta^{13}C$ of the DIC are –12.5 and –12.4‰ (PDB). Since the groundwater is at carbonate saturation and the $\delta^{13}C$ of the DIC essentially does not change between the wells, we assume that no dissolution of ^{14}C-"dead" carbonate minerals is taking place as groundwater flows between the wells. Then, the reduction in ^{14}C activity of the DIC from wells MR-85 to MR-52 represents ^{14}C decay only and can be used to estimate groundwater residence times between the wells (Fig 4).

The hydrophobic acid component of the DOC changes in ^{14}C activity from 30.6 to 6.5 pMC, whereas the ^{14}C activity of the C_1–C_{10} hydrophilic component changes from 46.8 to 7.4 pMC between wells MR-85 and MR-52 (Fig 4). Variable ^{14}C ages between the two components at each well may be due to differences in residence times in the vadose zone or microbial processes in the aquifer. However, it is important to note that the uncorrected *age differences* (Fig 4) for all organic *and* inorganic components between the wells are remarkably similar – between 12,460 and 14,760 yr (Fig 4). This suggests that both the DOC and DIC in the groundwater behave conserva-

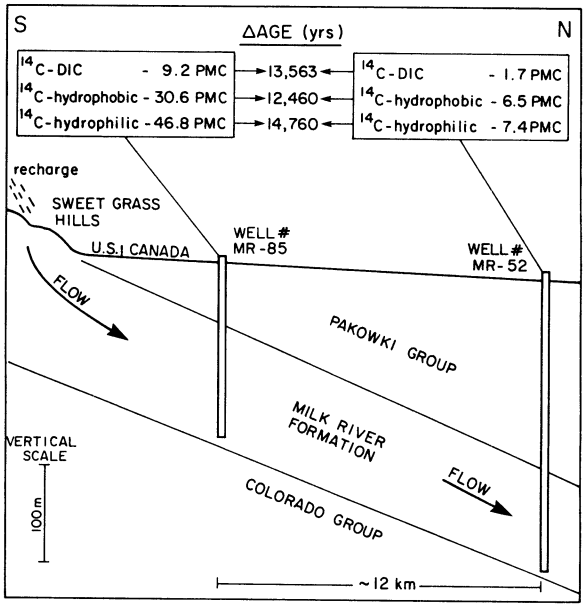

Fig 4. Example of the use of ^{14}C-DOC (hydrophobic acid and C_1–C_{10} hydrophilic components) compared with ^{14}C-DIC as a groundwater dating tool near the recharge environment of the Cretaceous age Milk River aquifer, southeastern Alberta, Canada. Note uncorrected age *differences* for both dissolved organic components and dissolved inorganic carbon between wells MR-85 and MR-52 are remarkably similar, and are believed to reflect advective residence times. Simplified stratigraphy based on data from Hendry and Schwartz (in press).

tively between the two wells, and are a suitable reflection of advective transport along the flow path. Moreover, the uncorrected age differences for both the DIC and the DOC components translate to an average groundwater velocity of 2.5 to 3.0 × 10^{-8} m/s. This agrees very well with groundwater velocities estimated by Hendry and Schwartz (in press) of 1 × 10^{-8} m/s based on hydraulic parameters.

We conclude that ^{14}C dating of DOC may indeed be a potential and alternate groundwater dating tool. However, in light of the Rodney shallow aquifer DOC data, we suggest that, to use DOC–^{14}C as a groundwater dating tool, the residence times and cycling of DOC in the recharge zone of the flow system should be carefully evaluated. Also, information may be needed concerning the addition of "dead" or variable age DOC to the system by microbial fermentation processes on aquifer kerogen. Groundwater flow systems containing high amounts of organic matter, such as buried peat or petroleum deposits, would probably not be suitable candidates for ^{14}C-DOC dating. In any case, under suitable conditions the ^{14}C activity of DOC between sampling points along the flow path may be more relevant for determining groundwater residence times than using individual ^{14}C-DOC data.

With respect to the Milk River aquifer, we could argue that geochemical corrections will diminish the ^{14}C-DIC age differences and, as a consequence, lead to the conclusion that "dead" organic carbon is being added to the DOC pool. This aspect is presently under study and will be discussed in a series of forthcoming papers.

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