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ORGANIC CARBON ISOTOPE GEOCHEMISTRY OF CLAYEY DEPOSITS AND THEIR ASSOCIATED POREWATERS, SOUTHERN ALBERTA

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ABSTRACT

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The organic carbon cycle of slowly permeable, clayey glacial till deposits in the Western Interior Great Plains, southern Alberta, was investigated by examining the relationship between solid organic matter (SOM) in the till sediments and dissolved organic carbon (DOC) in the till porewaters. Geochemically, the tills can be divided into two distinct zones: an upper oxidized (low SOM) till zone, and a lower unoxidized (high SOM) till zone. Till porewaters in both zones are characterized by high DOC contents. Radiocarbon dating and comparison of SOM and DOC fractions suggest DOC in the deep unoxidized zone originated during deglaciation, and is probably representative of groundwater ages in this till zone. In the oxidized zone, DOC originates from variable mixtures of soluble organic matter emplaced during deglaciation, and Cretaceous age coal fragments in this till zone. SOM in the upper till zone was mainly oxidized to CO_2 gas during lowered water table conditions of the Altithermal climatic period. The subsurface production of fossil CO_2 gas has serious implications for using the conventional dissolved inorganic carbon (DIC) ^{14}C groundwater dating method in these clayey till porewaters.

INTRODUCTION

The Western Interior Great Plains region of Canada are overlain by thick, clayey, glacial till deposits up to 60 m in thickness. Intergranular and bulk vertical hydraulic conductivities of unoxidized prairie tills here are estimated to be of the order of $10^{-10} \, \mathrm{m \, s^{-1}}$ or less (Hendry, 1988). Thus, in recent years there has been considerable interest in the hydrogeologic nature of clayey till deposits of this type as potential hazardous waste repositories.

The dynamics of groundwater movement in tills of southern Alberta have been addressed by Hendry (1988), who concluded vertical water movement in unoxidized till to be negligible. However, the ubiquitous presence of an oxidized till zone ranging from 0 to 25 m thick, containing an extensive network

of interconnected fractures, can cause bulk hydraulic conductivities of the till to increase by a factor of $< 10^3$ (Keller et al., 1986; Hendry, 1988). In Alberta, groundwater in the upper 5 m of the oxidized till zone is dominated by fracture flow, with average flow velocities of 3–4 m per 35 years (Hendry, 1988).

The inorganic hydrochemistry of porewater in Alberta prairie tills, particularly regarding the origin of Na^+, SO_4^{2-} and NO_3^- ions, has been thoroughly investigated (Hendry et al., 1984, 1986, 1989). One aspect of prairie tills that has not been investigated, however, is the organic geochemistry of the tills and its relation to the organic geochemistry of till porewaters. In general, till porewaters in the western plains of Alberta are colored, an indicator of high concentrations of dissolved organic carbon, and especially aquatic humic substances (cf. Thurman, 1985a, b).

The significance of natural dissolved organic carbon fractions in groundwater has been demonstrated. Dissolved humic and fulvic acids may facilitate the transport of metals (McKnight et al., 1983; Raspor et al., 1984; Thurman, 1985a), radionuclides (Means et al., 1984), and enhance the solubility of relatively insoluble organic contaminants (Gjessing and Berglind, 1982; Perdue, 1983). Thus, the origin and movement of high DOC and aquatic humic substances in porewaters of low permeability clay deposits are an important consideration in the study of these deposits as potential hazardous waste repositories. Carbon isotopic studies of DOC fractions in groundwater are few (Thurman, 1985b; Wassenaar et al., 1989, 1990; Murphy et al., 1989a, b). Moreover, basic information about dissolved and solid phase organic carbon cycling and movement in groundwater systems is lacking.

This study is an attempt to develop a better understanding of the organic carbon cycle in clayey till deposits of Alberta and their associated porewaters by examining the relationship of solid phase organic carbon in the tills to the dissolved organic carbon in the porewaters. The objective is met by: (1) characterizing the distribution, quantity, and forms of solid phase organic matter (SOM) and dissolved organic carbon (DOC) in the tills using geochemical and liquid chromatographic techniques and, (2) evaluating sources and sinks of SOM and DOC in the tills and porewater using ^{13}C and ^{14}C isotopic analyses of SOM and DOC fractions, and organic carbon mass balance considerations.

STUDY SITES

Three sites used in a previous study (Hendry, 1988) were chosen for organic carbon cycle studies of clayey deposits (Sites 1–3; Fig. 1). Sites 1 and 2 are located about 100 km NE of Lethbridge, Alb. (Hendry, 1983; Robertson, 1985). Site 3, located NNE of Lethbridge, was used for SOM determinations only; no DOC studies were performed there. The region is semi-arid, having a mean annual precipitation of 312 mm (Hobbs, 1970). Soils in the study areas are Orthic Brown Chernozems that have a low organic matter content (< 2.0 wt.%). The glacial chronology of southern Alberta is not well defined; however, tills were deposited during the Lethbridge advance of the Late
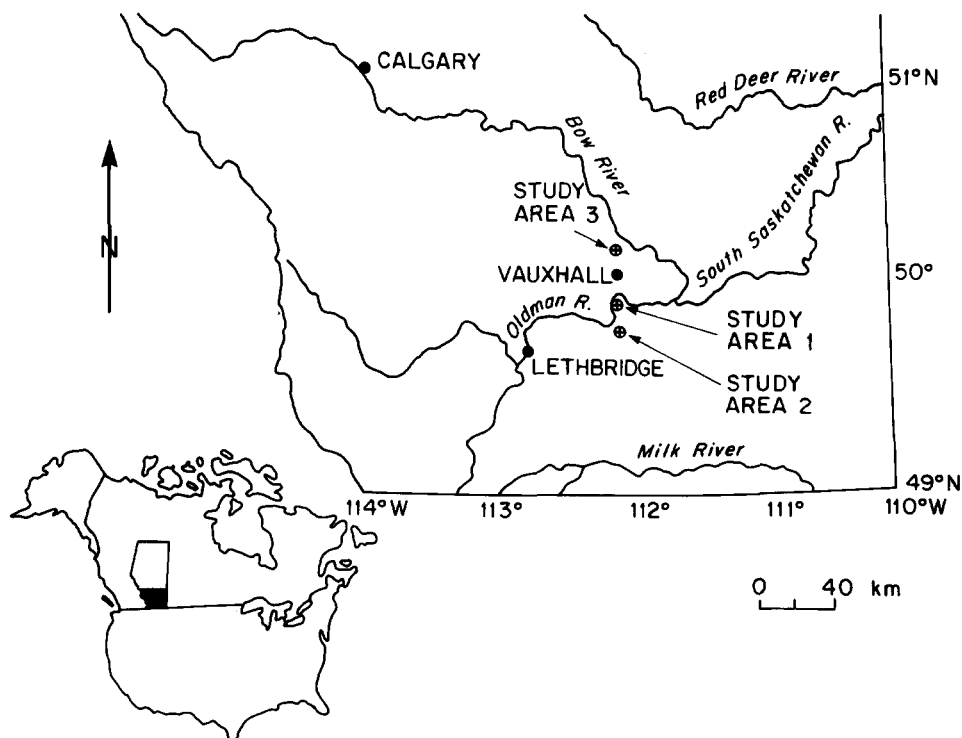
Fig. 1 Location of study sites in southern Alberta, Canada.

Quaternary Lostwood Glaciation between ~22–10 Ka B.P. (Fenton, 1984; Rutter, 1984). The tills are underlain by non-glacial sediments and Upper Cretaceous sandstones and shales of the Judith River Formation (Hendry, 1988).

Piezometer completion details are published in Hendry (1988). Standpipe PVC piezometers (45 mm in diameter) were installed in single augered boreholes. The slotted and screened piezometer intake zones (0.5–1.5 m) were backfilled with silica sand, and bentonite seals (2–30 m) were placed above the sand packs.

Geology and stratigraphy of the tills at Sites 1–3 were determined from cores taken during installation of piezometers. Recognition of oxidized and unoxidized till zones was made on the basis of a distinct color change from brown to grey (Fig. 2). The oxidized and unoxidized till zones do not differ on the basis of grain size, clasts, total N or total S content (Hendry et al., 1986). Visual examination of cores showed that numerous 'coal' fragments occur in the upper oxidized till zone (Fig. 2).

Oxygen-18 values of unoxidized till zone porewaters range between -23.3 and -18.3‰ (SMOW). The $\delta^{18}O$ range for modern precipitation in southern Alberta varies from -22‰ (snow) to -12.5‰ (summer rain). The similarity of
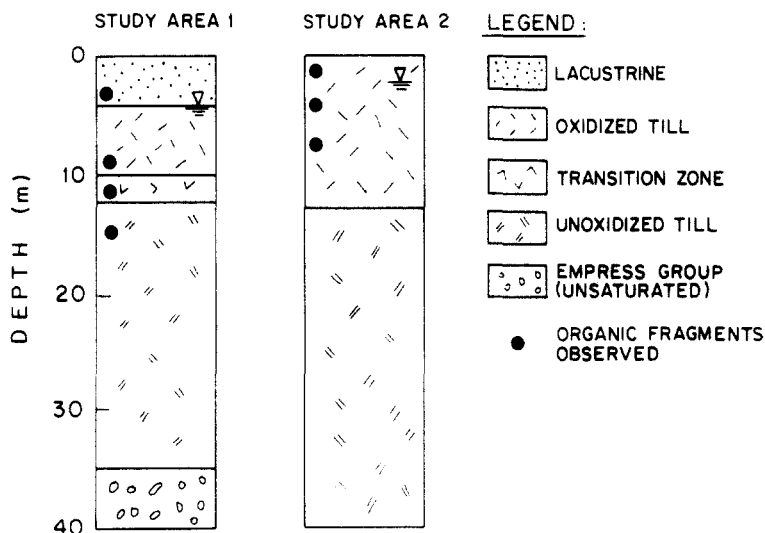
STRATIGRAPHY OF PRAIRIE TILL SITES

Fig. 2. Hydrogeology and stratigraphy of Sites 1–2 determined from cores taken during piezometer installation.

unoxidized till porewater to winter precipitation suggests these porewaters may have originated under cooler climatic conditions than present. Uppermost (< 4–5 m depth) oxidized till zone porewaters are tritiated and show $\delta^{18}O$ and δ^2H isotopic evidence of water loss by evaporation (Hendry, 1988).

The present day water table is found at depths of between 2 and 4 m at Sites 1–3, well above the lower boundary of the oxidized till zone at about 12–15 m depth (Fig. 2). Hendry et al. (1986) concluded that lower water table conditions existed during the warmer, drier climatic conditions of the Altithermal period (~ 8–6 Ka B.P.), allowing for aerobic oxidation of reduced sulfur to account for the present SO_4^{2-} concentrations in the oxidized till zone porewaters.

MATERIALS AND METHODS

Solid organic carbon

Thirty-three samples of till taken from cores at Sites 1–3 were analyzed for their solid organic matter (SOM) content. One large organic fragment (~ 5 cm in diameter) was carefully removed from a core at 7 m depth at Site 1 for measurement of ^{13}C and ^{14}C contents. Samples were oven dried at 100°C for 48 h and powdered using a mortar and pestle. Aliquots of samples were then taken for SOM and $\delta^{13}C$ analyses.

Approximately 10 g of till sediment were used for SOM analyses. Samples

were pre-weighed into glass test tubes, and acidified with 1 N HCl until inorganic carbonate (TIC) dissolution was complete. Samples were then repeatedly centrifuged, decanted and rinsed until neutral pH was attained. The test tubes and samples were oven dried (100°C) for 24 h and reweighed. Weight difference due to carbonate removal yielded the TIC. A further pre-weighed aliquot of this carbonate-free core material was combusted at 800°C in a pure O_2 atmosphere. The CO_2 produced from the combustion of organic carbon was measured on a LECO carbon analyzer/integrator and converted to weight percent SOM. SOM reproducibility was better than ± 15% (r.s.d). Eleven samples of SOM CO_2 gas were retained for analysis of stable carbon isotope content.

Dissolved organic carbon

Piezometers from Sites and 1 and 2 were bailed and allowed to recover for two weeks prior to sampling to ensure the collection of fresh formation water. Samples for total DOC determinations were collected by filtering porewater samples through 0.45 µg Ag-membrane filters into 25-ml pre-cleaned glass bottles. Samples were acidified to pH 2 by dropwise addition of concentrated phosphoric acid, and were subsequently analyzed on a Dohrmann Carbon Analyzer using standard techniques within 48 h of returning to the laboratory. Sample and standard reproducibility was better than ± 10% (r.s.d.).

A high molecular weight (HMW) and low molecular weight (LMW) fraction of the DOC were isolated from large groundwater samples for ^{14}C and ^{13}C analyses. The operational DOC fractionation/extraction techniques used are described in detail by Thurman and Malcolm (1981) and Murphy et al., (1989a, b). A HMW aquatic fulvic acid fraction (~ 500–5000 mol. wt.) of the DOC was isolated from groundwater samples using XAD-8 chromatography (Thurman and Malcolm, 1981). A LMW DOC fraction ($\lesssim$ 100 mol. wt.) was isolated by adsorption into a Silicalite molecular sieve (Murphy et al., 1989b). These extraction methods allowed for recovery and carbon isotopic analyses of 60–80% of the total DOC load in the till porewaters. The remaining 20–40% of the DOC is of intermediate molecular weight (~ 100–500), and could not be suitably extracted for isotopic analyses.

Groundwater samples for DOC fractionation/extraction were obtained by bailing the piezometers into pre-cleaned 20 l glass carboys. Ten to 20 l of sample were immediately returned to the laboratory, filtered through 25 and 0.45 µm Balston® microfibre filters, and acidified to pH 2 with concentrated hydro-chloric acid. The DOC isolation system consisted of a 1.2-l and 75-ml capacity glass and Teflon chromatography column containing extensively pre-cleaned Amberlite XAD-8® resin to isolate and concentrate the HMW fraction of the DOC. HMW DOC, composed of aquatic fulvic acids, were eluted from the XAD-8 with dilute NaOH and hydrogen saturated by passing the sample through a strong H$^+$ cation exchange resin (BioRad AG MP-50). HMW DOC samples were then freeze-dried and stored in sealed glass vials (Thurman and

Malcolm, 1981). The smaller XAD-8 column was used both for concentration of the HMW DOC, and for hydrophobic/hydrophilic fractionation of the DOC (Thurman, 1985b).

The XAD-8 column was set up in tandem with a 300-ml glass and Teflon chromatrography column containing pre-cleaned (by combustion at 800°C in a muffle furnace) Union Carbide Silicalite® molecular sieve to isolate a LMW fraction of the DOC (Murphy et al., 1989b). Silicalite is composed of an inert, porous hydrophobic silica framework that effectively sorbs small organic molecules less than ~ 10 Å in diameter from water (Shultz-Sibbel et al., 1982). Desorption of LMW DOC samples from Silicalite for isotopic analyses is described below. Groundwater samples were pumped sequentially through the XAD-8 and Silicalite columns with a small peristaltic pump (Thurman and Malcolm, 1981; Murphy et al., 1989b). Teflon® or Viton® tubing and glassware were used in all operations to minimize contamination.

Carbon isotopic analyses

Samples of freeze-dried HMW DOC (fulvic acid) were combusted in pure O_2 atmosphere, and the resulting CO_2 gas was cryogenically trapped for $\delta^{13}C$ and ^{14}C determinations. Fifty to 100 g of Silicalite containing sorbed LMW DOC samples were lyophilized to eliminate excess water, and combusted at 800°C under vacuum in the presence of cupric oxide. The CO_2 produced from the combustion of sorbed LMW organics was cryogenically isolated and purified for $\delta^{13}C$ and ^{14}C determinations.

The ^{13}C content of the HMW and LMW DOC, and SOM were determined on a VG Micromass 903 triple collecting mass-spectrometer at the Environmental Isotope Laboratory, University of Waterloo, and are reported relative to the PDB standard in the usual δ notation:

$$\delta_{sample} = [(R_{sample} - 1)/(R_{std})] * 1000 \tag{1}$$

where R is the ratio of $^{13}C/^{12}C$ in the sample and international standard (PDB).

Samples of HMW and LMW DOC, and SOM were analyzed for their ^{14}C content by direct counting of ^{14}C atoms by Tandem Accelerator Mass Spectrometry (TAMS) at the University of Toronto (Isotrace Laboratory). Radiocarbon results are reported in percent of modern carbon (PMC) relative to 95% of the activity of oxalic acid standard in 1950, and normalized to a $\delta^{13}C$ of $-25‰$ (PDB). Finite radiocarbon ages are calculated using the equation for ^{14}C decay:

$$Age = -(t_{1/2}/\ln 2) \ln a^{14}/a_0^{14} \tag{2}$$

where: a^{14} is the measured ^{14}C activity of the sample; a_0^{14} is the initial ^{14}C activity at $t = 0$ (100 PMC); $t_{1/2}$ is the ^{14}C isotope half-life (5730 $\pm$ 40). Analytical reproducibility for ^{14}C determinations by TAMS was better than ± 0.8 PMC (r.s.d.).

RESULTS AND DISCUSSION

SOM determinations

Results of SOM determinations on core material from Sites 1–3 are summarized in Table 1 and are plotted vs. depth in Fig. 3. In the oxidized till zone SOM content ranges from 0.04 to 0.75 wt.% with a mean of 0.39 wt.% (Table 1). The SOM content of tills in the unoxidized zone range between 0.24 and 1.28 wt.% with a mean of 0.66 wt.% (Table 1). The SOM content of the tills are high for detrital sediments (Blatt et al., 1980), and are probably a reflection of a coaliferous, Cretaceous bedrock provenance. The mean SOM content of the unoxidized till zone is higher than in the oxidized till zone (Fig. 3): an unpaired Students t-test confirmed a statistically significant difference ($p < 0.05$) in SOM content between the oxidized and unoxidized till zones at the 95% confidence level.

DOC determinations

The results of DOC contents of porewaters at Sites 1 and 2 are summarized in Table 2 and plotted vs. depth in Fig. 4. DOC concentrations in the tills are high compared with average DOC concentrations of ~ 1.0 mg C l^{-1} in major U.S.A. aquifers (Leenheer et al., 1974). In the oxidized till zone DOC concentrations range from 14.0 to 48.7 mg C l^{-1} with a mean DOC of 24.1 mg C l^{-1} (Table 2). The unoxidized till zone DOC concentrations range from 7.5 to 36.0 mg C l^{-1} with a mean DOC of 17.0 mg C l^{-1}. The DOC contents of oxidized till zone porewaters are slightly higher than porewaters in the unoxidized till zone. An unpaired Students t-test verified the existence of a significant difference ($p < 0.05$) between oxidized and unoxidized zone DOC concentrations at the 95% confidence level. The DOC trend observed in the oxidized and unoxidized till zones is opposite to the SOM differences observed in the till. Higher average DOC contents occur in oxidized till zone porewaters where the average SOM content of the till is low. Conversely, lower average DOC concentrations occur in porewaters of the unoxidized till zone where SOM content is higher. Several replicate DOC analyses from the piezometers sampled over one year are shown in Table 2. Reproducibility of DOC appears variable – in some wells DOC concentrations decrease over time as the piezometers are routinely bailed (e.g. well 1812E-5N), while in other piezometers the DOC concentrations remain static (e.g. well 5-C-84). It is not known why these DOC variations occur.

Results of a hydrophobic/hydrophilic fractionation of the DOC are shown in Table 3. The hydrophobic DOC fraction ranges between 42 and 82% of the total DOC with an average of 62%. This differs from modern surface waters and most groundwaters. Surface waters are typically 50% hydrophobic (Stuber and Leenheer, 1978), and groundwaters are typically < 35% hydrophobic (Malcolm et al., 1977). This has been attributed to adsorption or transformation of hydro-

TABLE 1

Distribution of carbon forms in Alberta prairie tills determined from core material

Depth (m)	Zone	SOM (wt.%)	TIC (wt.%)	TC (wt.%)
Site #1				
4.5	O	0.23	1.4	1.63
6.0	O	0.04	1.0	1.04
6.3	O	0.40	2.7	3.10
7.5	O	0.34	1.3	1.64
10.5	O	0.55	0.8	1.35
12.0	O	0.45	1.3	1.75
19.0	U	0.33	1.4	1.73
22.0	U	0.46	0.7	1.16
23.0	U	0.56	2.4	2.96
Site #2				
3.0	O	0.51	0.63	1.14
4.5	O	0.39	0.63	1.02
6.0	O	0.23	1.50	1.73
7.5	O	0.12	0.13	0.25
9.0	O	0.75	0.88	1.63
10.5	U	0.38	0.92	1.30
12.0	U	0.24	0.95	1.19
13.5	U	0.48	0.78	1.26
15.0	U	0.58	0.96	1.54
16.5	U	1.28	0.43	1.71
18.0	U	0.71	0.87	1.58
19.5	U	0.57	0.73	1.30
21.0	U	0.58	1.08	1.66
22.5	U	0.78	0.88	1.36
24.0	U	0.65	1.10	1.75
Site #3				
4.9	O	0.52	0.30	0.82
5.2	O	0.47	0.29	0.76
5.5	O	0.46	0.25	0.71
5.8	O	0.35	0.21	0.56
6.1	O	0.43	0.26	0.69
14.6	U	0.96	0.40	1.36
14.9	U	1.05	0.40	1.45
15.2	U	0.84	0.48	1.32
15.8	U	0.81	0.43	1.24
Oxidized zone				
Mean		0.39	0.84	1.24
S.D.		0.17	0.66	0.66
Unoxidized zone				
Mean		0.66	0.88	1.52
S.D.		0.26	0.47	0.41

SOM, solid organic carbon; TIC, total inorganic carbon; TC = SOM + TIC; O, oxidized zone; U, unoxidized zone.
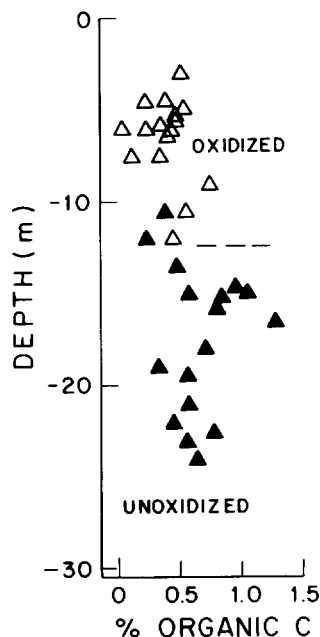
Fig. 3. SOM vs. depth at Sites 1–3 expressed as wt.%. Open triangles,, oxidized zone samples; closed triangles, unoxidized zone samples.

phobic compounds into simpler hydrophilic acids in groundwater (Thurman, 1985a, b). In the case of the till porewaters, the higher percentage of hydrophobic materials may also be a result of the association of porewater with hydrophobic materials present in the tills, such as coal fragments.

Stable Carbon Isotopes — SOM and DOC

Stable carbon isotope results of SOM are summarized in Table 4. The $\sigma^{13}C$ values of SOM in the oxidized and unoxidized till zones range from -26.7 to $-25.5‰$ with a mean of $-26.0‰$ (PDB). The $\sigma^{13}C$ of HMW DOC (Table 4) ranges from -29.5 to $-24.8‰$ with a mean value of $-26.6‰$. These values are typical of terrestrial Calvin Cycle (C_3) plants (Smith and Epstein, 1971; Deines, 1980) and terrestrial soil humic substances (Nissenbaum, 1974).

The $\sigma^{13}C$ values of LMW DOC are variable and range from -10 to -45. Three samples have unusually light $\sigma^{13}C$ values of about -45. A similar range of depleted $\sigma^{13}C$ values for LMW DOC were observed by Murphy et al. (1989b) in a study of DOC fractions in the Milk River aquifer. The data indicate that the depleted $\sigma^{13}C$ of LMW DOC also contain the lowest ^{14}C activities (Fig. 5). This suggests that $\sigma^{13}C$ depleted LMW organic compounds may be partly derived from bacterial activity on coal fragments in the tills, with an accompanying ^{13}C fractionation.

TABLE 2

Dissolved organic carbon data for Alberta prairie till sites. Collected September 1987

Depth (m)	Zone[1]	Well No.	DOC (mg C l^{-1})		
Site #1					
5.1	O	1812E-1N	14.0[3]		
8.0	O	1812E-2N	18.6[4]		
9.4	O	1812E-5O	25.9		
15.4	U	1812E-6N	19.3	36.0[3]	
16.2	U	1812E-3N	25.0[3],	7.5[4]	
21.1	U	1812E-4N	9.6[4]		
25.8	U	1812E-5N	20.5	11.0[3],	7.5[4]
35.0	U	1812E-8N	25.0[3]		
Site #2					
W.T.[2]	O	13-C-84	21.9		
4.3	O	5-C-84	19.5		
5.3	O	3-C-84	48.7		
9.4	O	2-C-84	30.2		
9.4	O	13-C-84	14.3		
12.5	U	5-C-84	20.6[3]		
13.4	U	13-C-84	10.7,	9.9[4]	
14.0	U	3-C-84	14.2		
28.0	U	13-C-84	23.2,	22.0[3],	11.2[4]
30.2	U	5-C-84	15.0,	17.0[3]	
30.2	U	2-C-84	14.0,	12.0[3]	
30.4	U	1-C-84	23.0		
30.5	U	3-C-84	20.9		
30.6	U	8-C-84	16.0		
Oxidized zone					
Mean			24.1		
S.D.			11.3		
Unoxidized zone					
Mean			17.0		
S.D.			7.0		

[1]O, oxidized zone; U, unoxidized zone.
[2]Water table well.
[3]Collected in June, 1987.
[4]Collected in August, 1988.

Solid Organic Carbon Sources

SOM in the tills may consist of a mixture of organic matter derived from Cretaceous age coal fragments (no ^{14}C) emplaced with the till, and organic matter formed at the time the tills were deposited ($\sim$ 22–10 Ka B.P.; Fenton, 1984). Results of two ^{14}C determinations on SOM from the tills are reported in Table 4. SOM humic substances extracted in 0.1 N BaOH (cf. Schnitzer and
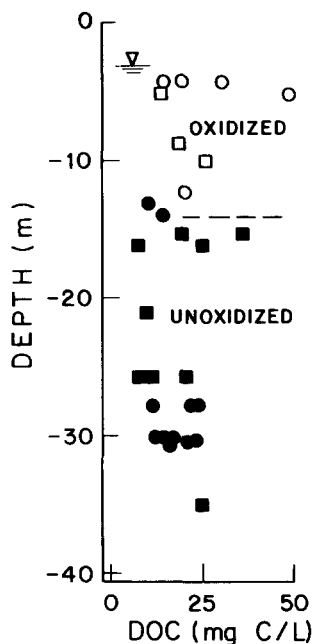
Fig. 4. Concentrations of DOC in porewaters vs. depth. Squares, Site 1; circles, Site 2. Open symbols, oxidized zone; closed symbols, unoxidized zone.

TABLE 3

Total hydrophobic/hydrophilic fractionation for DOC from prairie tills of Alberta

Depth (m)	% hydrophobic	% hydrophilic	Zone[1]
Site #1			
8.0	58.8	41.2	O
9.4	82.6	17.4	O
16.2	42.2	57.8	U
21.1	56.9	43.1	U
25.8	66.7	33.3	U
Site #2			
9.4	62.8	37.2	O
13.2	61.8	38.2	U
27.9	65.7	34.3	U

[1]O, oxidized; U, unoxidized.

Khan, 1972) from oxidized zone till at 11–12 m depth at Site 1 yielded a ^{14}C activity of 8.8 PMC ($\sim$ 20 Ka B.P.). Although this humic SOM ^{14}C activity could represent a mixture of reworked older and younger sedimentary organic carbon sources, it lies within the estimated age range of till deposition (22–10 Ka B.P.).

The large organic fragment removed from core stratigraphically higher

TABLE 4

Carbon isotope data for HMW and LMW DOC fractions and SOM from Alberta till sites

Depth (m)	¹⁴C-LMW (PMC)	δ¹³C (PDB)	¹⁴C-HMW (PMC)	δ¹³C, ‰ (PDB)	Zone[1]
Dissolved Organic Carbon					
Site #1					
8.0	33.4	− 17.3	6.7	− 24.8	O
9.4	10.2	− 13.2	11.4	− 29.5	O
15.4	35.1	− 11.9	9.5	− 29.5	U
16.2	14.2	− 10.0	9.7	− 25.1	U
21.1	1.9	− 45.0	19.0	− 25.4	U
25.8	18.8	− 15.1	16.6	− 27.0	U
Site #2					
9.4	4.6	− 45.5	36.8	− 25.6	O
13.4	2.9	− 46.0	19.8	− 26.0	U
28.0	25.5	− 28.4	22.8	− 27.2	U
Solid Organic Carbon					
Site #1					
2–3		− 26.7			O
4–5		− 25.9, − 25.5			O
6–7		− 25.9			O
8–9		− 25.8			O
11–12	8.8	− 25.8			O
12–13		− 25.8			O
16.8–17.2		− 26.2			U
17.2–17.7		− 26.1			U
"Coal fragment"					
7.5	1.1	− 25.5			O

[1] O, oxidized; U, unoxidized.

(7.5 m depth) at Site 1 contained about 1 PMC ¹⁴C. A few previously published radiocarbon dates reported for 'wood' in the tills of this region, yielded similar ¹⁴C activities to the organic fragment (Jackson and Pawson, 1984). The question arises whether the large organic fragments observed in the till are Quaternary wood, or Cretaceous coal fragments. A geochemical elemental analysis of the organic fragment yielded a similar composition to coal (C, 67%; H, 1.9%; O, 6.2%), supporting the hypothesis that large organic fragments observed in the tills are coal derived from Cretaceous bedrock, not Quaternary age wood. Moreover, the fact that SOM humic material at greater depth contains a significantly higher ¹⁴C activity also supports this hypothesis. It is possible that previous workers interpreted coal fragments (slightly contaminated with ¹⁴C) as Quaternary age wood, resulting in overestimation of till ages. The low, but measureable, ¹⁴C activity suggests that Cretaceous coal fragments incorporated in the tills may be contaminated by a younger source of organic carbon (cf. Geyh et al., 1983), possibly by adsorption of DOC that contains ¹⁴C.
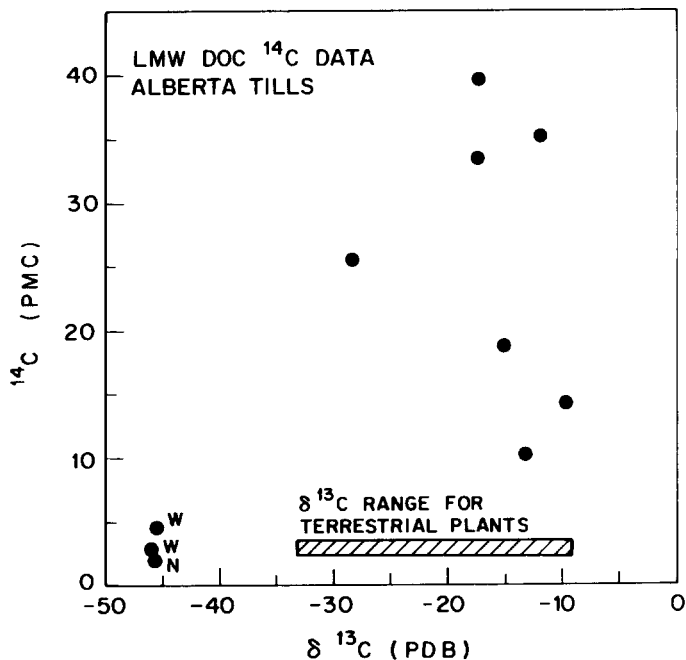
Fig. 5. δ^{13}C vs. ^{14}C activity of LMW DOC fraction from porewaters.

Dissolved organic carbon sources

The ^{14}C activities of SOM aid in providing constraints on sources of DOC in the porewaters. DOC in the porewaters could be derived from three possible sources: (1) coal fragments (no ^{14}C); (2) organic matter emplaced at the time the tills were deposited (~ 7–30 PMC, ~ 22–10 Ka B.P.); or (3) post-glacial derived organic matter (> 30 PMC, < 10 Ka B.P.). Because there is no apparent groundwater movement in the unoxidized till zone, only two sources can be applied to DOC in the unoxidized zone — Cretaceous coal fragments, and organic matter deposited during till emplacement. In the upper 5 m of the oxidized till zone, one may expect post-glacial soil derived DOC where a piezometer intersects fractures.

Results of ^{14}C analyses of HMW and LMW DOC fractions from Site 1 are summarized in Table 4 and plotted vs. depth in Fig. 6a. Radiocarbon activities of the LMW DOC fraction range from 1.9 to 35.1 PMC (33–8.6 Ka B.P.), whereas ^{14}C in the HMW DOC fraction ranges from 6.7 to 19.8 PMC (22–10 Ka B.P.). The HMW DOC fraction shows a 'younging' trend with increasing depth in the till, whereas the LMW DOC fraction varies widely with depth (Fig. 6a).

At Site 2 (Fig. 6b; Table 4) radiocarbon activities of the LMW DOC fraction range from 2.9 to 25.5 PMC (29–11.3 Ka B.P.). Radiocarbon activities of the HMW DOC fraction range from 19.8 to 36.8 PMC (13.4–8.3 Ka B.P.). The HMW
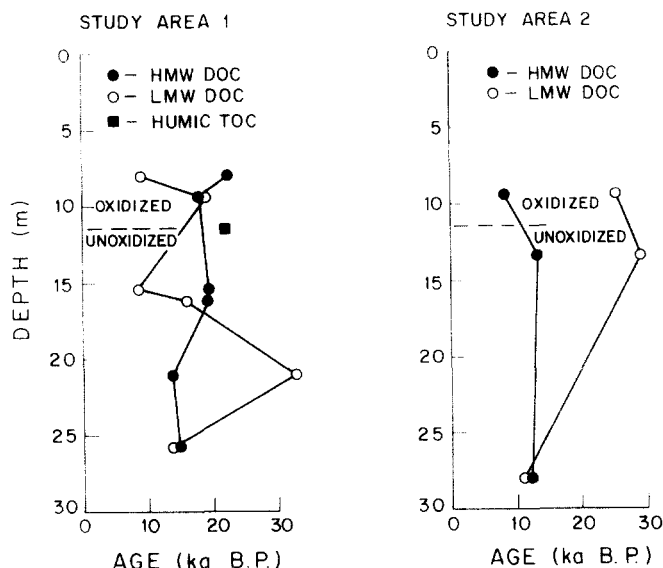
Fig. 6. Results of ^{14}C data of HMW and LMW DOC fractions plotted as radiocarbon age vs. depth at Sites 1 and 2. One sample of humic SOM is shown at Site. 1

DOC fraction is significantly younger than LMW DOC in the oxidized zone, whereas the ^{14}C activities of the two DOC fractions are of similar depth in the unoxidized zone (Fig. 6b).

A number of interpretations can be made from all the ^{14}C DOC data. If Cretaceous coal fragments were the only source of DOC in the till porewaters, no measureable ^{14}C activity in any DOC fraction would be expected. Because the overall DOC ^{14}C range is 1.9–36.8 PMC, a 100% Cretaceous coal fragment origin for DOC in the tills is not possible. If DOC originated only during emplacement of the tills, a ^{14}C range of 7–30 PMC (22–10 Ka B.P.; Fenton, 1984) would be expected. On the other hand, DOC fractions with ^{14}C activities greater than ~30 PMC could have originated subsequently to deglaciation. Overall, three of eighteen DOC radicarbon dates are younger than the Lostwood Glaciation (>30 PMC), twelve lie within the age range of the Lostwood Glaciation ($\approx$ 7–30 PMC), and three samples are significantly older than the age of the Lostwood Glaciation (<5 PMC).

It should be noted that HMW and LMW DOC ^{14}C ages from the deepest piezometers in the unoxidized till zone at both sites range between 14.8 and 11.3 Ka B.P. (Fig. 6a,b), a range that is correlative with the estimated time of glacial retreat deposition in this region (Clayton and Moran, 1982; Rutter, 1984). This suggests that DOC in the unoxidized till zone originated during deglaciation and deposition of the till and porewaters. Because no coal fragments were observed in the deeper unoxidized till, it is possible that DOC in this zone is not contaminated with old carbon from coal fragments. In this

case, because groundwater movement in the unoxidized till zone is neglibile, the ^{14}C ages of the DOC fractions would then be representative of the age of porewaters in the deep unoxidized till zone. However, since even minimum contamination cannot be entirely dismissed, the ^{14}C ages of DOC fractions in the deeper unoxidized till porewaters can only be used to infer a maximuma age of about 14–11 Ka B.P. to the groundwaters. A late glacial origin is also supported by depleted σ^{18}O values of porewater in the unoxidized till zone that are similar to present winter precipitation.

From the principle of superposition and measured downward hydraulic gradients, it is clear that DOC ^{14}C ages in the overlying oxidized till porewaters cannot be older than the age range defined by DOC deep in the unoxidized till (Fig. 6a, b). Thus, older observed HMW and LMW DOC ages in the overlying porewaters must be affected to varying degrees by 'dead' organic carbon from the coal fragments observed in this zone. Dilution of HMW DOC with old organic carbon is most evident at Site 1 where a trend of HWM DOC ages becoming younger with depth is observed (Fig. 6a). For example, a simple ^{14}C isotopic mass balance for HMW DOC using the youngest age (19.0 PMC at 21.1 m depth) and the oldest age (6.7 PMC at 8.0 m depth) at Site 1 suggests that HMW DOC may be diluted by up to 65% with 'dead' carbon from coal fragments around the uppermost piezometer. It was observed earlier that three LMW DOC samples with usually light σ^{13}C values have ^{14}C activities < 5 PMC (Fig. 5), suggesting some LMW DOC may be produced by bacterial activity associated with the coal fragments (cf. Atlas and Bartha, 1987). Isolated enclaves of microbial activity associated with coal fragments were observed by Fujikawa and Hendry (1990).

Loss of solid organic carbon

It has been established that the mean SOM content of the thick oxidized till zone is significantly lower than the mean SOM content of the unoxidized zone (10.5 and 17.8 g organic C l^{-1} till, respectively; using a porosity of 0.4 and particle mass density of 2.7 kg l^{-1}). Assuming the oxidized till zone was initially unoxidized after deglaciation (Hendry et al., 1986), then a loss of 7.3 g of organic C l^{-1} till must be accounted for in the oxidized zone. Two sinks are considered to account for the depletion of SOM in the oxidized zone. These are aerobic oxidation of SOM, and the conversion of SOM to DOC.

Aerobic oxidation of SOM could occur under closed or open system conditions (Stumm and Morgan, 1981). The closed system environment requires an excess and steady supply of dissolved oxygen using the following stoichiometry;

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \tag{4}$$

Hendry et al. (1986) considered this mechanism for the oxidation of reduced sulfur in the oxidized zone and concluded that this process cannot apply to the

tills, as it would require an unrealistically high flux of oxygen saturated recharge.

Open system oxidation of SOM requires the stoichiometry of eqn. (4) and a steady supply of gaseous oxygen. This model would require water table conditions near the present oxidized–unoxidized zone contact, overlain by partially saturated conditions. Hendry et al. (1986) modeled the water table response and atmospheric oxygen diffusion into the tills and concluded that the open system oxidation mechanism would have occurred above the water table, which was near the oxidized–unoxidized zone boundary during the warmer, dry Altithermal climatic period in western Canada ($\sim$ 8–6 Ka B.P.).

A second SOM sink in the oxidized till zone may be the recycling of SOM to DOC through microbial or abiotic decomposition processes (cf. Atlas and Bartha, 1987). The mean DOC content in porewaters of the oxidized zone ($24\,mg\,C\,l^{-1}$ porewater) is statistically higher than in the unoxidized zone ($17\,mg\,C\,l^{-1}$). This DOC difference, however, amounts to an increase of only 0.003 g of DOC per liter of till in the oxidized zone (using a porosity of 0.4).

The relative importance of the two SOM sinks can be determined using simple organic carbon mass balance calculations. The overall mass balance equation for SOM loss to DOC and CO_2 in the oxidized till zone can be approximated by:

$$SOM_i - SOM_f = (DOC_f - DOC_i) + CO_{2(gas)} \tag{5}$$

where i represents initially unoxidized conditions, and f represents the final conditions observed at present. Organic carbon mass balance results using eqn. (5) are summarised in Fig. 7. In the calculations it was assumed that initial conditions are represented in the unoxidized till zone, and that all SOM losses in the oxidized zone occurred under lowered water table conditions during the Altithermal period to produce the present-day organic carbon distribution.

The results of mass balance calculations show that oxidation to CO_2 gas was the principal SOM sink (99.9%), producing 26.5 g of CO_2 gas per liter of till (Fig. 7). The average molar rate of CO_2 gas production per liter of till during the Altithermal period ($\sim$ 2000 year) is estimated to be $3.0 \times 10^{-4}\,mol.\,year^{-1}$. Only 0.003 g of SOM was transferred to the DOC pool of the oxidized zone, representing < 0.05% of the total SOM loss. The oxidation of fossil SOM and subsurface production of CO_2 gas has serious implications for radiocarbon dating of dissolved inorganic carbonate (DIC) species in these till porewaters.

Implications for groundwater DIC dating

Radiocarbon dating of groundwater using conventional ^{14}C dating of the dissolved inorganic carbon content of slowly permeable deposits has only recently become feasible with the commercial availability of accelerator mass spectrometry (AMS) for radiocarbon dating of small samples. Radioactive decay of atmospheric and soil CO_2 dissolved in advecting groundwater provides the foundation for conventional DIC ^{14}C dating of groundwater (Münnich,
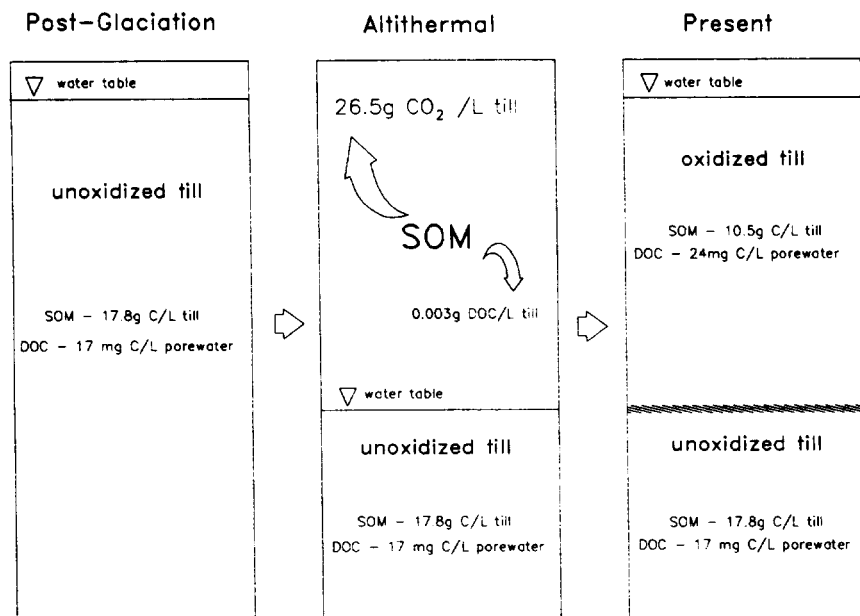
Fig. 7. Conceptual model for the loss of SOM from oxidized zone. Model assumes till was initially unoxidized following deglaciation. A lower water table during the Altithermal period (8–6 Ka B.P.) allowed aerobic oxidation of SOM to CO_2 gas, and minor conversion to DOC to occur. After about 6 Ka the water table rose to present-day conditions.

1957). However, subsurface and deep vadose zone production of small amounts of fossil CO_2 gas (e.g. Haas et al., 1983; Wood and Petraitis, 1984) by oxidation of SOM poses an additional problem for estimating corrected ^{14}C DIC ages for prairie till porewaters. Because gaseous transport in the vadose zone is dominated by diffusion, steady state production of minor amounts of CO_2 by oxidation of SOM could generate high partial pressures of fossil CO_2 gas in the vadose zone, effectively masking any atmospheric and soil CO_2 component. This variable age CO_2 gas not only diffuses from the oxidized zone to the atmosphere, but dissolves into vadose zone porewater, and reacts to dissolve [14]C 'dead' carbonate minerals (Reardon et al., 1980). Thus, any attempts to correct conventional DIC ^{14}C ages must account for ^{14}C dilution of the atmospheric and soil CO_2 component by oxidation of fossil SOM, carbonate dissolution, and any other geochemical redox processes that produce DIC.

Computed partial pressures of CO_2 gas from porewater chemistry at Sites 1–3 are extremely high, and frequently exceed 0.1 atm. This suggests that the large amounts of CO_2 gas produced by aerobic or bacterial oxidation of SOM during the Altithermal period may have significantly affected the DIC chemistry of the oxidized till porewaters (e.g. Keller and Hendry, 1988). In addition, the stable carbon isotope content of DIC in unoxidized till zone porewaters at Sites 1–3, and other clayey deposits (Desaulniers, 1984), are often depleted, having a

strong biogenic ^{13}C signature ($\delta^{13}C$ as low as -25‰). The effects of CO_2 gas production by SOM oxidation and other redox processes affecting the inorganic geochemistry of prairie till porewaters, as well as rigorous attempts to correct DIC ^{14}C data at Sites 1–3 will be presented elsewhere (Hendry et al., 1990).

CONCLUSIONS

Tills in the Western Great Plains and their associated porewaters are characterized by high organic carbon contents. SOM in the tills is represented by variable mixtures of organic matter emplaced during till deposition and Cretaceous age coal fragments. SOM was likely oxidized during lowered water table conditions of the Altithermal climatic period, resulting in the present day zone of brown, low SOM, oxidized till overlying a zone of grey, high SOM, unoxidized till. Oxidation of SOM during this climatic event resulted in an estimated annual subsurface CO_2 production rate of about 3.0×10^{-4} mol. CO_2 gas per liter of till. This historical subsurface production of fossil CO_2 would pose an additional problem for the correction of conventional DIC ^{14}C age dating in prairie tills of western Canada. Transformation of SOM to DOC during the Altithermal is shown to be insignificant.

High concentrations of DOC in the till porewaters mainly originated during emplacement of the tills, ~ 11–14 Ka B.P. Because groundwater movement in the unoxidized till is neglible, DOC ^{14}C ages are likely to be representative of groundwater ages. The DOC content of oxidized zone porewater is slightly higher than in the unoxidized zone. HMW and especially LMW DOC fraction ^{14}C activities are affected to varying degrees by organic or microbial contamination from 'dead' coal fragments that occur in the oxidized till zone.

ACKNOWLEDGEMENTS

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