

EVALUATING DISSOLVED INORGANIC CARBON CYCLING IN A FORESTED LAKE WATERSHED USING CARBON ISOTOPES

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ABSTRACT. Dissolved inorganic carbon (DIC) is the main acid buffer in forested lake watersheds in Canada. We used carbon isotopes (¹³C, ¹⁴C) to evaluate the production and cycling of DIC in an acid-sensitive lake watershed of the Precambrian Shield. Soil CO₂, groundwater and stream DIC were characterized chemically and isotopically. Soil CO₂ concentration profiles reflect both changes in production and in losses due to diffusion. δ¹³C soil CO₂ profiles (δ¹³C values of -23‰ in summer, slightly enriched during the fall and -25‰ during the winter) are a reflection of the isotopic composition of the sources and changes in isotopic fractionation due to diffusion. Carbon isotopic composition (¹³C, ¹⁴C) of the groundwater and stream DIC clearly indicate that weathering of silicates by soil CO₂ is the main source of DIC in these watersheds. ¹⁴C data show that, in addition to recent groundwater, an older groundwater component with depleted ¹⁴C activity is also present in the bedrock. The carbon isotope pattern in the groundwater also implies that, besides the main springtime recharge events, contributions to the groundwater may also occur during late winter/early spring.

INTRODUCTION

Growing concerns about the global carbon cycle and the natural and anthropogenic sources and sinks of carbon have fostered renewed research interest in the cycling of carbon in natural systems (*e.g.*, Quay *et al.* 1986; Hedges *et al.* 1986; Cicerone & Oremland 1988). Northern temperate forest watersheds cover a large part of northern Canada. An understanding of the carbon cycle in these systems is critical in predicting the anthropogenic influences, such as acid rain and climate modifications, on the cycling and fluxes of carbon.

This paper constitutes part of an ongoing research project whose main objective is the evaluation of carbon cycling in Harp Lake, a forested watershed in the acid-sensitive region of the Precambrian Shield, southeastern Ontario, Canada (Schiff *et al.* 1990; Aravena & Schiff 1990; Trumbore *et al.* 1992). Our approach involves the use of carbon isotopes, ¹³C and ¹⁴C, as tracers to evaluate sources and sinks of the main carbon pools: dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and solid organic carbon (SOC). We discuss here the sources of DIC in groundwater and streams of a forested watershed of the Precambrian Shield. DIC production and cycling are important in the acid neutralization capacity of these systems because DIC is the main acid buffer in these acid-sensitive lake watersheds.

Study Area

Harp Lake, located in the District of Muskoka, Ontario (45°23'N, 79°08'W) (Fig. 1), is one of several Precambrian Shield lakes studied as part of the Acid Precipitation in Ontario Study (APIOS) (Dillon *et al.* 1978; Scheider, Jeffries & Dillon 1979). Harp Lake catchment, with an area of 506 ha, is forested by mixed deciduous coniferous forest. The underlying bedrock consists primarily (68%) of biotite and hornblende gneiss with amphibolite and schist in the western portion of the basin (Jeffries & Snyder 1983). The overburden consists of a minor till plain and rock ridges (88%), with wetlands covering the rest of the catchment. The dominant soils are weakly developed podzols formed upon the thin, sandy basal tills. The essential mineralogy of the soils should be similar to Plastic Lake watershed, located in the same area, the dominant minerals

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of which include quartz, plagioclase feldspar, potassium feldspar, amphibole, vermiculite and iron oxides (Kirkwood & Nesbitt 1991).

The Harp Lake basin is divided into six small subcatchments, each instrumented with a gauging weir (Fig. 1). The groundwater and soil CO₂ studies were mainly carried out in Harp subcatchment 4, which has been the focus of extensive hydrological and geochemical studies (e.g., Seip *et al.* 1985; Rustad *et al.* 1986; Dankevych *et al.*, in press).

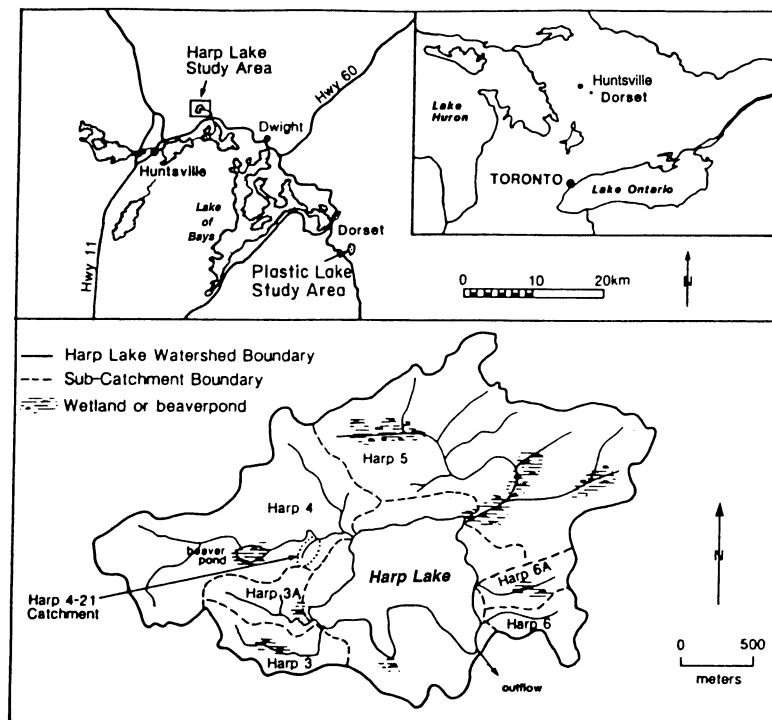


Fig. 1. Study area, Harp Lake watershed

Methodology

We collected soil CO₂ samples for CO₂ concentration and ¹³C analysis on a monthly basis, using a nest of individual metal probes that penetrate the first 100 cm of the soil. The probe inlets were at 10-cm intervals. Samples were collected in glass syringes, stored under water, refrigerated and analyzed within a few days after sampling. Standard gas chromatographic techniques were used for analyzing CO₂ concentration at the Water Quality Laboratory, University of Waterloo. For ¹³C analyses, the CO₂ was purified in a standard vacuum line and run in a VG Micromass 903 or a VG PRISM. These analyses were carried out at the Environmental Isotope Laboratory (EIL), University of Waterloo, with an analytical reproducibility better than 0.2‰. ¹³C analyses are reported using the δ notation defined as

$$\delta^{13}\text{C} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] * 1000 \quad (1)$$

where the R's are the ¹³C/¹²C ratio in the sample and international standard PDB, respectively.

We collected groundwater samples from wells located close to the recharge areas, in the middle of the basin and in discharge areas. Streams were sampled at the gauging weirs located at the bottom of each subcatchment, with the exception of Harp 4-21, which is located in the middle of the basin (Fig. 1). CO₂ produced by direct acidification of the water was purified and subsampled for ¹³C and ¹⁴C analyses. ¹³C analyses were carried out at EIL by mass spectrometry and ¹⁴C analyzed at Lawrence Livermore National Laboratory by tandem accelerator mass spectrometry (AMS) (Davis *et al.* 1990). ¹⁴C results are expressed in percent modern carbon (pMC) normalized to a δ¹³C of -25‰ PDB (Stuiver & Polach 1977). Typical analytical errors are ± 1 pMC for ¹⁴C.

RESULTS AND DISCUSSION

Soil CO₂

Soil CO₂ concentration profiles collected from spring 1990 (May) to the end of winter 1991 (March) show three distinct patterns (Fig. 2): first, an increase in CO₂ concentration that reaches a maximum (1.2%) at mid-summer; second, a decrease in CO₂ concentration occurs between July and December, reaching a minimum concentration of 0.3%; finally, we observed a slight increase from 0.3%–0.5% between December and March 1991. More than 1 m of snow covered the field area during this last period.

The CO₂ trends shown in Figure 2 result from CO₂ cycling in the soil zone. The sources of soil CO₂ are root respiration and oxidation of organic matter (*e.g.*, Solomon & Cerling 1987). Thus, CO₂ concentration in soils depends on the rate of production, which is a function of soil temperature and moisture content and rate of loss. (*e.g.*, Dörr & Münnich 1987). CO₂ concentration

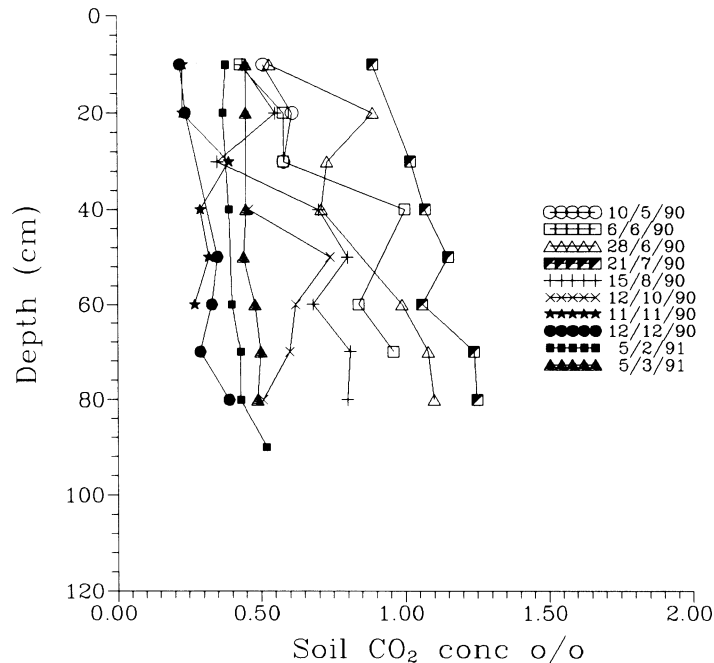


Fig. 2. Soil CO₂ concentration profiles, Harp Lake watershed

gradients with depth in a soil environment are mainly due to movement of CO₂ from production zones to the atmosphere and toward the water table (e.g., Reardon, Allison & Fritz 1979).

The soil CO₂ concentration profiles at Harp Lake can be explained by an increase in CO₂ production during the summer, a decrease in CO₂ production from July to December, and finally, an accumulation of CO₂ during winter, when the area is covered by snow. During winter, photosynthetic activity and microbiological respiration rates are at a minimum. However, the snow cover reduces the diffusive loss of soil CO₂ to the atmosphere, explaining the slight increase in soil CO₂ during the winter.

¹³C Composition of Soil CO₂

In the δ¹³C profiles for soil CO₂ (Fig. 3), δ¹³C values are about -22‰ during the summer, with a trend to more enriched values (~-21‰) in the early fall. This trend reverses from October, with δ¹³C values approaching -25‰ during winter. These trends must be associated with processes that control the concentration of CO₂ in soil environments.

The ¹³C composition of soil CO₂ is related to the isotopic composition of the sources (root respiration and oxidation of organic matter), which, in turn, is a function of the photosynthetic cycle of the vegetation and the isotopic fractionation that occurred during CO₂ losses to the atmosphere by diffusion (Dörr & Münnich 1980; Cerling 1984; Cerling *et al.* 1989). Plants that use the Calvin photosynthetic cycle (C₃ plants) are characterized by a range in δ¹³C between -24‰ to -29‰. Other plants that use the Hatch-Slack photosynthetic cycle (C₄ plants) range in δ¹³C values between -10‰ to -16‰ (Deines 1980).

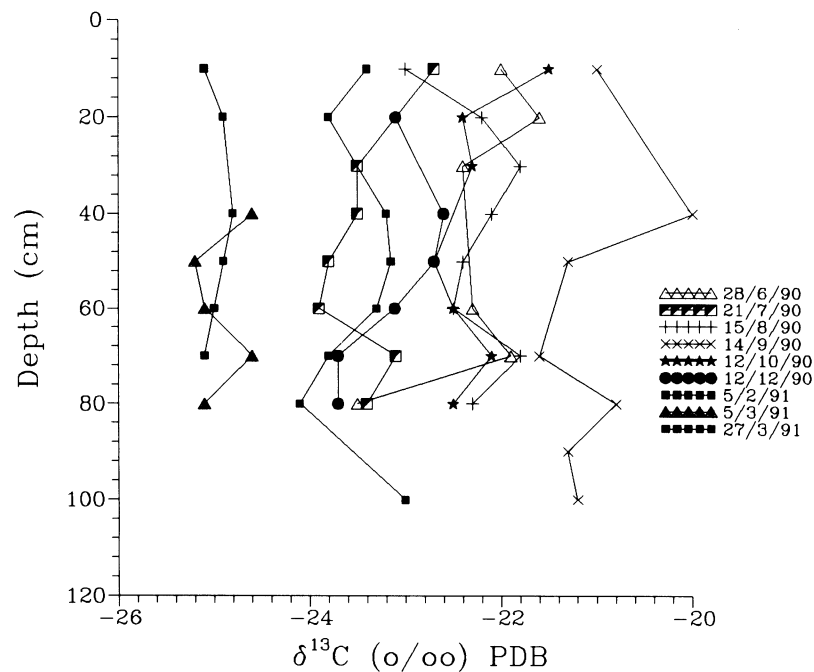


Fig. 3. Soil CO₂ δ¹³C profiles, Harp Lake watershed

TABLE 1. ^{13}C and ^{14}C data of soil CO_2 and tree leaves, Harp Lake catchment

	Sampling date	$\delta^{13}\text{C}\text{‰}$ (PDB)	^{14}C pMC
Tree leaves	June/1990	-28.0	117.9
Soil CO_2 30 cm	August/1990	-20.9	117.0
	March/ 1991	-24.9	116.4
Soil CO_2 70 cm	August/1990	-21.3	116.3
	March/1991	-25.1	119.7
Atmospheric CO_2	August/1990	-11.3	116.5

Plants in the study area have $\delta^{13}\text{C}$ values around -28‰ (Table 1). Further, $\delta^{13}\text{C}$ values for DOC in Harp Lake catchment water, which is related to the isotopic composition of the soil organic matter (SOM), range between -25‰ and -28‰ (Schiff *et al.* 1990). The isotopic differences observed between soil CO_2 ($\delta^{13}\text{C} = -22\text{‰}$ during the summer) and soil-respired CO_2 at Harp Lake watershed ($\delta^{13}\text{C} = \sim -27\text{‰}$) can be attributed to the effect of diffusion. This process enriches the soil CO_2 by about 4.4‰ relative to the CO_2 sources (respired CO_2) (Cerling 1984; Cerling *et al.* 1991). The $\delta^{13}\text{C}$ values obtained during winter, which are closest to the isotopic composition of the sources, could be due to a reduction in CO_2 loss by diffusion when the site is covered by snow.

Besides diffusion, the other possible mechanism that could shift the soil CO_2 values seasonally is a change in the sources of soil CO_2 . Natelhoffer and Fry (1988) found some evidence that SOM is enriched in ^{13}C compared to the parent plant matter. Further, Dörr and Münnich (1986) postulated that lower ^{14}C values in soil CO_2 in winter than in summer were due to the predominance of oxidation of SOM in winter as a source of CO_2 . Therefore, if SOM (more enriched $\delta^{13}\text{C}$ values and maybe older compared to root respired CO_2) is the dominant source of soil CO_2 during the winter at Harp Lake basin, this should be reflected in the $\delta^{13}\text{C}$ and ^{14}C content of the soil CO_2 . This hypothesis is highly speculative because no direct ^{13}C data are available to differentiate between soil CO_2 generated by root respiration and by oxidation of organic matter.

A $\delta^{13}\text{C}$ profile for SOM at Harp 4-21 subcatchment agrees with the data reported by Natelhoffer and Fry (1988), which show a $\delta^{13}\text{C}$ change from -29‰ at the surface to -25‰ at a depth of 35 cm (Trumbore *et al.* 1992). However, ^{14}C results indicate that any CO_2 produced by the oxidation of the deeper enriched ^{13}C organic carbon seems to be an insignificant component of the soil CO_2 . ^{14}C data of the SOM show recent carbon (114–118 pMC) at the very shallow part of the soil, with values close to 100 pMC at a depth between 5 and 10 cm. Older carbon, with ^{14}C content equal to or less than 80 pMC, is present at depths below 15 cm (Trumbore *et al.* 1992). In comparison, ^{14}C data obtained on soil CO_2 show no significant changes in ^{14}C content between summer and winter months (Table 1). These values, ranging between 116.5 and 119 pMC, are similar to the ^{14}C data obtained on atmospheric CO_2 and tree leaves from the same area (Table 1). The average ^{14}C activity in the atmospheric CO_2 for 1990 in Canada was close to 118 pMC (Schiff *et al.* 1990). Thus, the soil CO_2 carbon isotope data obtained at Harp Lake watershed suggest that diffusion is the dominant isotopic fractionating process in these soil environments, and the top 15 cm of the soil is the zone where CO_2 is produced by oxidation of organic matter. The hypothesis that reduction of soil CO_2 losses by diffusion explains the $\delta^{13}\text{C}$ shift toward depleted values during winter is supported by the CO_2 concentration profiles, which show an increase of CO_2 concentration from December to March under continuous snowcover.

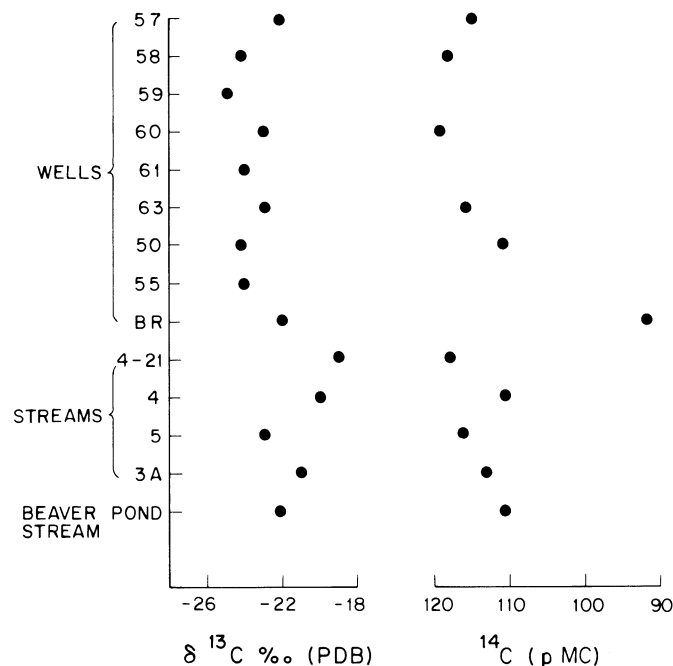


Fig. 4. ^{13}C and ^{14}C data for groundwater and streams, Harp Lake watershed

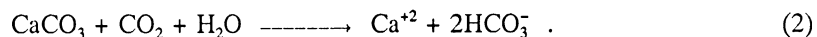
Carbon Isotope Data in Groundwater

Figure 4 shows the carbon isotopic composition of groundwater DIC. Wells sampled for groundwater are close to recharge areas (Wells 57, 58), in the middle of the basin (Wells 59, 60, 61, 63) and in the discharge areas close to the lake (Wells 50 and 55 and BR).

In general, the $\delta^{13}\text{C}$ values of the groundwater DIC are very similar throughout the basin, ranging from -22 to -24‰ . This pattern is a reflection of the chemical reactions that control the production of DIC in the aquifer sediments at Harp Lake watershed.

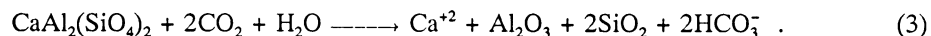
The main reactions that produce DIC in groundwater are dissolution of carbonates and weathering of silicates. The extent of both reactions is a function of the concentration of soil CO_2 (PCO_2) in the recharge areas and the mineralogy of the sediments. These reactions generate DIC within a characteristic range in carbon isotopic composition.

Dissolution of carbonates can be described by



This reaction under closed-system conditions generates DIC with an isotopic composition around -11‰ and 59 pMC in ^{13}C and ^{14}C , respectively. This assumes a soil CO_2 of -22‰ and 118 pMC and a carbonate of 0‰ and free of ^{14}C . If this reaction occurs under open-system conditions, DIC should display $\delta^{13}\text{C}$ values between -19‰ and -13‰ , depending on the pH and temperature (Deines, Langmuir & Harmon 1974; Wigley 1975) and a ^{14}C DIC activity close to 118 pMC.

In the case of weathering of silicates, for example, anorthite,



DIC generated by this reaction should have a ^{14}C activity similar to the soil CO_2 and $\delta^{13}\text{C}$ values enriched by about 1‰ relative to the soil CO_2 (1‰ is the isotopic fractionation between gas and aqueous CO_2 (Fontes 1983)). The ^{13}C data from Harp Lake watershed groundwater ($\delta^{13}\text{C} = \sim -23\text{‰}$) clearly indicate that the production of DIC is controlled by weathering of silicates. Although isotopic evidence of this process has been observed in groundwater (Hufen, Lau & Buddemeir 1974; Gallo 1979), the Harp Lake data are the first to illustrate the effect of a pure silicate-weathering reaction, in the absence of carbonates, on the carbon isotopic composition of DIC in groundwater. This has important implications for the neutralization of acidic precipitation. Silicate weathering is much slower than carbonate weathering. The lack of even a small amount of residual carbonate undetectable by mineralogic analyses severely limits the production rate of acid neutralization capacity (ANC) in these catchments.

It can also be argued that DIC in Harp Lake groundwater reflects only dissolution of soil CO_2 in recharge water, and not weathering. However, the geochemical evolution of the groundwater from recharge to discharge areas is clear evidence of weathering processes in the aquifer. The geochemical pattern shows increases in pH, alkalinity, major cations and silica from shallow to deep groundwater and discharge areas (Dankevy *et al.*, in press).

The main recharge events occur during spring melt and, to a lesser extent, during the fall (Hinton, Schiff & English, ms.). The average $\delta^{13}\text{C}$ of -22‰ in the groundwater DIC agrees with this recharge scenario. It seems that warmer temperatures preceding the main spring event cause trees to become active, which should activate more production of soil CO_2 from root respiration and/or CO_2 produced during the winter. As soon as some snow cover recedes, diffusive CO_2 losses should also increase, which enriches the soil CO_2 in ^{13}C . The April 1991 data on soil CO_2 ($\delta^{13}\text{C}$ values $\sim -22\text{‰}$) confirm this. However, the slightly depleted $\delta^{13}\text{C}$ values of around -24‰ obtained in some groundwater suggest the contribution of recharge events occurring before the loss of snow cover during late winter/early spring, when the soil CO_2 is characterized by $\delta^{13}\text{C}$ values of -25‰ . These selective recharge events could be due to infiltration of heavy rains that percolate through the snow pack.

The ^{14}C data from these waters agrees with the ^{13}C scenario. All the wells closer to the recharge areas have ^{14}C values between 116 and 118 pMC. These values are similar to the ^{14}C data on soil CO_2 , atmospheric CO_2 and tree leaves from the same area (Table 1). The average ^{14}C activity in the atmospheric CO_2 for 1990 in Canada was close to 118 pMC (Schiff *et al.* 1990). A comparison of the ^{14}C data of the groundwater at the discharge areas (110 pMC) with the fallout ^{14}C curve for Canada suggests that these waters could have a residence time of at least 30 years between recharge and discharge areas (assuming piston flow). However, tritium data on groundwater indicate a shorter average residence time for the groundwater. It is more likely that the ^{14}C data reflect a mixture of waters with differing ^{14}C content prior to reaching discharge areas.

A groundwater component depleted in ^{14}C relative to shallow groundwater is indeed present in Harp Lake aquifer. Groundwater collected in a well tapping the bedrock has a ^{14}C activity of 92 pMC, which, when translated into ^{14}C years, yields a minimum residence time of about 1 ka. However, this water is tritiated, which indicates a younger average age of the water. The older ^{14}C component could be a mixture of a small amount of water of much longer residence time and containing high DIC and/or the input of older carbon from carbonate minerals. This last possibility can be analyzed, assuming the following scenarios: 1) the source of the older inorganic carbon is primary carbonate with a ^{13}C composition close to 0‰ and free of ^{14}C ; or 2) the source can be

secondary carbonates with a ^{13}C composition close to DIC and with an unknown ^{14}C content. Because the ^{13}C remains unchanged despite a shift in the ^{14}C content (bedrock $^{14}\text{C} = 92$ pMC, mean $\delta^{13}\text{C} = -22\text{‰}$), the first possibility can be eliminated. For the second scenario, the boundaries for the $\delta^{13}\text{C}$ isotopic composition of possible secondary carbonate should be between -12‰ (in the case that primary carbonate and soil CO_2 were the precursors of the secondary carbonate) and -21‰ , if only soil CO_2 were the secondary carbonate precursor. Because the ^{13}C content of the bedrock water is similar to the other groundwater, the existence of ^{13}C -enriched secondary carbonate can be eliminated. The only possibility left is ^{13}C -depleted secondary carbonate, which implies a DIC generated by silicate weathering. However, it is unlikely that ^{13}C -depleted secondary carbonate could have been deposited in these temperate forested watersheds, because the groundwater is very much undersaturated with respect to calcite (Dankevy *et al.*, in press). Thus, the carbon isotope composition of the bedrock points to older groundwater in the basin, and suggests that the bedrock and tills were devoid of carbonate minerals before the onset of acid precipitation in the study area.

Carbon Isotopic Composition of Stream Water

The stream water shows the same carbon isotopic pattern as the groundwater. The $\delta^{13}\text{C}$ DIC values range from -19‰ to -23‰ . The slightly enriched $\delta^{13}\text{C}$ values for some of the streams seem to be associated with DIC affected by isotopic exchange with atmospheric CO_2 . This process tends to enrich the DIC in ^{13}C (Broecker & Walton 1959). The effect of this process can be observed in the evolution of the ^{13}C composition in streams during the complete season (Aravena & Schiff 1990). Some streams change from -22‰ at high flow during the rainy season, to -15‰ at low flow during the dry season.

The ^{14}C activity for the stream water ranges from 119 pMC in Harp 4-21 to 110 pMC in Harp 4 and the beaver pond (Fig. 1). The high ^{14}C in stream water implies the input of recent groundwater to stream-flow generation. The slightly lower pMC in the beaver pond is a result of carbon cycling in this pond, probably related to conversion of DOC to DIC. DOC in the beaver pond is one of the oldest carbon pools in Harp Lake watershed (Schiff *et al.* 1990). Further, Harp 4 reflects the contribution of beaver-pond water and possibly the discharge of older groundwater (associated with bedrock) into the stream bed in areas close to the weir.

The input of groundwater is not the only factor controlling the DIC pool in Harp Lake streams. The presence of wetlands plays a significant role in both production and consumption of carbon in some subcatchments. This seems to be the case for the beaver pond and the Harp 5 subcatchment streams. The latter stream is the main source of DIC to Harp Lake (P. Dillon, unpublished data).

CONCLUSIONS

Soil CO_2 concentration profiles in Harp Lake watershed, a forested basin located in the Canadian shield, are a result of changes in soil CO_2 production and losses due to diffusion to the atmosphere and toward the water table. Soil CO_2 production rates reach maxima and minima during summer and winter, respectively. Losses by diffusion tend to be reduced during winter because of the snow cover, which allows a slight accumulation of CO_2 in the soil zone.

The carbon isotopic composition of soil CO_2 ($\delta^{13}\text{C} = \sim -23\text{‰}$) in the summer reflects the carbon isotopic composition of the sources and isotopic fractionation due to losses by diffusion. The more depleted $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} = \sim -25\text{‰}$) observed during winter are explained by a reduced diffusion

rate because of the snow cover. These data confirm the role of diffusion as an isotope-fractionating process in soil CO₂.

The carbon isotopic composition (¹³C, ¹⁴C) of the groundwater and streams indicates that silicate weathering by soil CO₂ plays a dominant role in the generation of DIC and alkalinity in Harp Lake watershed. ¹⁴C data show that, besides recent groundwater, an older groundwater component with less ¹⁴C activity is also present in the bedrock. These data show the potential of using carbon isotopes, ¹³C and ¹⁴C, to determine groundwater input from bedrock into surface water, and also rule out the existence of primary carbonate minerals in bedrock and tills before the onset of acid rain in the study area.

Selective and significant recharge events inferred from the carbon isotope pattern of the groundwater were identified at the end of the winter. This finding has important implications for ¹⁴C dating of groundwater systems. One important parameter for geochemical models used to correct ¹⁴C data in groundwater is the ¹³C composition of the recharge water, generally inferred from the ¹³C composition of the soil CO₂. The difference in δ¹³C between selective recharge and spring and fall events is as much as 4‰.

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REFERENCES

- Aravena, R. and Schiff, S. L. 1990 CO₂ production and carbon cycling in Precambrian Shield Watersheds. In Proceedings of the Technology Transfer Conference. *Environment Ontario* 1: 177–180.
- Broecker, W. S. and Walton, A. 1959 The geochemistry of C-14 in fresh water systems. *Geochimica et Cosmochimica Acta* 16: 15–34.
- Cerling, T. E. 1984 The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth and Planetary Science Letters* 71: 229–240.
- Cerling, T. E., Quade, J., Wang, Y. and Bowman, J. R. 1989 Carbon isotopes in soils and paleosols as paleoecologic indicators. *Nature* 341: 138–139.
- Cerling, T. E., Solomon, K. D., Quade, J. and Bowman, J. R. 1991 On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta* 55: 3403–3405.
- Cicerone, R. J. and Oremland, R. S. 1988 Biochemical aspects of atmospheric methane. *Global Biogeochemical Cycles* 2(4): 299–327.
- Dankevy, S. N., Schiff, S. L., English, M. and Dillon, P. J., in press, Groundwater flow and chemistry in a small acid-stressed subcatchment in the Canadian Shield. In *Proceedings of the NHRI Symposium on Groundwater Contamination*, National Hydrologic Research Institute, Environment Canada.
- Davis, J. C., Proctor, I. D., Southon, J. R., Caffee, M. W., Heikkinen, D. W., Roberts, M. L., Turteltaub, K. W., Nelson, D. E., Loyd, D. H. and Vogel, J. S. 1990 LLNL/UC AMS facility and research program. In Yiou, F. and Raisbeck, G. M., eds., Proceedings of the 5th International Conference on Accelerator Mass Spectrometry. *Nuclear Instruments and Methods B52*: 269–272.
- Deines, P. 1980 The isotopic composition of reduced organic carbon. In Fritz, P. and Fontes, J.-C., eds., *Handbook of Environmental Geochemistry* V1: Amsterdam, Elsevier: 329–406.
- Deines, P. D., Langmuir, D. and Harmon, R. S. 1974 Stable carbon isotope ratio and the existence of a gas phase in the evolution of carbonate groundwaters. *Geochimica et Cosmochimica Acta* 38: 1147–1164.
- Dillon, P. J., Jeffries, D. S., Snyder, W., Reid, R., Yan, N. D., Evans, D. and Moss, J. 1978. Acid precipitation in South-Central Ontario: Recent observations. *Journal of Fisheries Research Board Canada* 35(6): 809–815.
- Dörr, H. and Münnich, K. O. 1980. Carbon-14 and carbon-13 in soil CO₂. In Stuiver, M. and Kra, R. S., eds., Proceedings of the 10th International ¹⁴C Conference. *Radiocarbon* 22(3): 909–918.
- _____ 1986 Annual variation of the ¹⁴C content of soil CO₂. In Stuiver, M. and Kra, R. S., eds., Proceedings of the 12th International ¹⁴C Conference. *Radiocarbon* 28(2A): 338–345.
- _____ 1987 Annual variation in soil respiration in selected areas of the temperate zone. *Tellus* 39B: 114–121.

- Fontes, J.-C. 1983 Dating of groundwater. In Guidebook to Nuclear Techniques in Hydrology. IAEA, Vienna. *Technical Report Series* 91: 285–299.
- Gallo, G. 1979 Utilization complémentaire des isotopes de milieu et de l'hydrochimie pour l'étude hydrogéologique des eaux souterraines de la Région de Ribeirão Preto (Brasil). In *Isotope Hydrology* 2: 367–407. IAEA, Vienna.
- Hedges, J. I., Clark, W. A., Quay, P. D., Richey, J. E., Devol, A. H. and Santos, M. 1986 Composition and fluxes of particulate organic material in the Amazon river. *Limnology and Oceanography* 31: 717–738.
- Hufen, T. H., Lau, L. S. and Buddemeir, R. W. 1974 Radiocarbon, ^{13}C and tritium in water samples from basaltic aquifers and carbonate aquifers on the Island of Oahu, Hawaii. In *Proceedings, Isotope Techniques in Groundwater Hydrology* 2: 111–127. IAEA, Vienna.
- Hinton, M. J., Schiff, S. L. and English, M. C. 1992 Physical properties governing groundwater flow in a glacial till catchment. *Journal of Hydrology*, in press.
- Jeffries, D. S. and Snyder, W. R. 1983 Geology and geochemistry of the Muskoka-Haliburton study area. Dorset Research Centre Ministry of the Environment. *Data Report* DR 83/2: 101 p.
- Kirkwood, D. E. and Nesbitt, H. W. 1991 Formation and evolution of soils from an acidified watershed: Plastic Lake, Ontario, Canada. *Geochimica et Cosmochimica Acta* 55(5): 1295–1308.
- Natelhoffer, K. J. and Fry, B. 1988 Control on the natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *Soil Science of America Journal* 52: 1633–1639.
- Quay, P. D., Emerson, S. R., Quay, B. M. and Devol, A. H. 1986 The carbon cycle for Lake Washington – A stable isotope study. *Limnology and Oceanography* 31(3): 596–611.
- Reardon, E. J., Allison, G. B. and Fritz, P. 1979 Seasonal chemical and isotopic variations of soil CO_2 at Trout Creek, Ontario. *Journal of Hydrology* 43: 355–371.
- Rustad, S., Christophersen, N., Seip, H. M. and Dillon, P. J. 1986 Model for streamwater chemistry of a tributary to Harp Lake, Ontario. *Canadian Journal of Fisheries and Aquatic Sciences* 43: 625–633.
- Scheider, W. A., Jeffries, D. S. and Dillon, P. J. 1979 Effect of acid precipitation on Precambrian freshwaters in Southern Ontario. *Journal of Great Lakes Research* 5(1): 45–51.
- Schiff, S. L., Aravena, R., Trumbore, S. E. and Dillon, P. J. 1990 Dissolved organic carbon cycling in forested watersheds: A carbon isotope approach. *Water Resources Research* 26(12): 2949–2957.
- Seip, H. M., Seip, R., Dillon, P. J. and DeGrosbois, E. 1985 Model of sulphate concentration in a small stream in the Harp Lake catchment, Ontario. *Canadian Journal of Fisheries and Aquatic Sciences* 42: 927–937.
- Solomon, D. K. and Cerling, T. E. 1987 The annual carbon dioxide cycle in a montane soil: observations, modeling and implications for weathering. *Water Resources Research* 23: 2257–2265.
- Stuiver, M. and Polach, H. A. 1977 Discussion: Reporting of ^{14}C data. *Radiocarbon* 19(3): 355–363.
- Trumbore, S. E., Schiff, S. L., Aravena, R. and Elgood, R. 1992 Sources and transformation of dissolved organic carbon in a forested catchment: The role of soils. *Radiocarbon*, this issue.
- Wigley, T. M. L. 1975 Carbon-14 dating of groundwater from closed and open systems. *Water Resources Research* 11: 324–328.