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Sources of organic and inorganic carbon in a headwater stream: Evidence from carbon isotope studies

SHEILA M. PALMER[1*], DIANE HOPE[2], MICHAEL F. BILLETT[1], JULIAN J.C. DAWSON[1] & CHARLOTTE L. BRYANT[3]
[1]*Department of Plant and Soil Science, Cruickshank Building, University of Aberdeen, Aberdeen AB24 3UU, U.K.;* [2]*Centre for Environmental Studies, Arizona State University, PO Box 873211, Tempe, AZ 85287-3211, U.S.A.;* [3]*NERC Radiocarbon Laboratory, Scottish Enterprise Technology Park, Rankine Avenue, East Kilbride, Glasgow G75 0QF, U.K.*
*(*author for correspondence, Dept. of Civil and Environmental Engineering, Syracuse University, 220 Hinds Hall, Syracuse, NY 13244-90, U.S.A. e-mail: shpalmer@syr.edu)*

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Abstract. A combination of stable isotope studies and ^{14}C dating were used to identify the main sources and processes controlling streamwater DOC and TIC in a temperate non-forested watershed. δ^{13}C values for terrestrial (−24.9 to −29.1‰) and aquatic (−30.5 to −33.5‰) plants were similar to values reported in the literature for similar ecosystems. δ^{13}C values for DOC in soil solution and streamwater were consistent with soil and terrestrial vegetation, indicating that the terrestrial ecosystem is the dominant source of aquatic DOC in this watershed. δ^{13}C values of soil atmosphere CO_2 (−17.2 to −25.2‰) were slightly less negative than would be expected for production via aerobic soil microbial decomposition and root respiration. There was a close correspondence between δ^{13}C values (−15.5 to −21.5‰) for streamwater TIC and soil atmospheric CO_2 in the central part of the catchment where the stream drains CO_2-rich peats. ^{14}C dating showed that although peat has been accumulating in the watershed for at least 2700 years, DOC in soil pore water and streamwater contains carbon of predominantly recent origin (post-AD 1955).

Introduction

The relative importance of terrestrial and aquatic processes in contributing to DOC and TIC (including CO_2) was investigated in a typical non-forested headwater stream in Scotland. This was done using carbon isotopes. δ^{13}C values were obtained for plant and soil carbon, soil atmosphere CO_2 ($\delta^{13}C_{CO_2}$), soil and streamwater DOC ($\delta^{13}C_{DOC}$) and streamwater TIC ($\delta^{13}C_{TIC}$), and ^{14}C data was obtained for soil carbon and DOC in soil and streamwater.

In small streams, particularly in upland and wetland areas, organic carbon supply has been found to be typically dominated by allocthonous, terrestrial organic matter (Wetzel 1992; Hope et al. 1997a, b). Inorganic carbon (HCO_3^-, CO_3^{2-}, free CO_2) in streams may be derived from several sources, including i) dissolution of carbonate and weathering of silicate minerals in soils and underlying bedrock, ii) in-stream respiration by aquatic plants and heterotrophic respiration of allocthonous and autochthonous organic matter, iii) shallow groundwater inputs from elevated levels of soil CO_2, and iv) atmospheric draw-down (Wetzel 1983, 1992). Although it is commonly assumed that CO_2 saturation is controlled by mineral weathering and in-stream biotic activity (Cole 1983; Wetzel 1983; Wetzel & Likens 1991), CO_2 concentrations in the soil atmosphere from root respiration and soil heterotrophic activity may be greatly elevated with respect to the above-ground atmosphere (Hope unpublished; Skiba & Cresser 1991). It might therefore be expected that drainage of CO_2-rich shallow groundwaters into streams would be a dominant source of and control on the concentration of dissolved inorganic carbon in streamwaters.

Stable carbon-isotope measurements can provide a useful tool for identifying the main carbon pools in natural environments and have been used extensively to investigate carbon cycling in forested catchments (Aravena et al. 1992, 1993; Trumbore et al. 1992; Charman et al. 1994; Schiff et al. 1997). ^{14}C measurements can also provide useful information about the main sources of carbon transported in streams (e.g. Schiff et al. 1997, 1998) and has been used as a tracer in various systems, including soils (O'Brien & Stout 1978; Harkness et al. 1986, Harkness & Harrison 1989; Trumbore et al. 1989; Beckerheidmann & Scharpenseel 1992).

Methods

Study site location

The Brocky Burn watershed is situated in Glen Dye, North East Scotland, approximately 40 km south-west of Aberdeen. The stream is 2.7 km in length and is a headwater tributary of the River Dee. Streamwater chemistry is typical of an acid, upland stream, being characterized by low mean pH, low Ca^{2+} and Mg^{2+} concentrations and high DOC concentrations (Dawson et al., in press). The watershed is underlain by granite and granite-derived colluvial and fluvio-glacial material. The main soil types (Figure 1) are histosols (59%), spodosols (22%) and inceptisols (19%), with fluvents (riparian soils) contributing $<1\%$ of the total catchment area (Billett, unpublished). The watershed covers 1.3 km^2 and is characterised by a central area of low relief and by steeper slopes in the upper and lower sections. The peats, which are extensively developed in the central part of the watershed and reach depths of >5 m, are typically aerobic in the upper 50 cm. Fluvents occur adjacent to the stream along most of the length of the main channel. The land is managed for grouse, and the vegetation is dominated by heathers (*Calluna vulgaris*, *Erica tetralix* and *Eric cinerea*). *Sphagnum* and *Eriophorum* spp. are also present, with *Juncus effusus* common in the narrow riparian zone. Aquatic mosses and liverworts (mainly *Fontinalis antipyretica* and *Scapania subalpina*) exist within the stream throughout the year; filamentous algae are only present during late spring and summer months.

Sample collection and preparation for isotope analysis

Streamwater was sampled from three routinely monitored points on the main channel (Figure 1). Samples of soil material, soil atmosphere and soil solution were collected from two representative sites within the central part of the catchment. The peat site was located in an area of 2–3 m deep histosols approximately 50 m from the upstream sampling point, and the riparian site in an area of fluvents adjacent to the stream (Figure 1). Stream discharge was measured continuously at the lower stream sampling point.

1) Plant material and soil samples

Samples of the main species of terrestrial (*Calluna vulgaris*, *Juncus effusus*, *Eriophorum augostifolium*) and aquatic plants (*Scapania subalpina*, *Fontinalis antipyretica*, filamentous green algae) were collected from the catchment in June 1998. δ^{13}C analyses were carried out on samples of non-woody stems and leaves only. Plant material was oven-dried at 40 °C for 7 days, finely ground using a ball mill, and stored in glass vials. Soil samples were collected with an auger from two depths at the peat (0.25 and 1.0 m) and riparian (0.25 and 0.75 m) sites described above. The samples were then dried in a vacuum oven at 40 °C for 48 hours prior to analysis for both δ^{13}C and ^{14}C.

2) DOC in soil and streamwater

Soil and streamwater samples for $\delta^{13}C_{DOC}$ and ^{14}C analysis were collected on two separate occasions (February and June 1998). Soil solution was collected from piezometer wells constructed of 32 mm diameter PVC tubing, perforated with 2 mm diameter holes at 0.20–0.45 m depth (shallow wells), or 0.65–0.95 m depth (deep wells). For each site (peat and riparian) and at each depth, water from 3 replicate wells was combined to give a composite sample for isotope analysis. Samples were withdrawn from piezometer wells using Nalgene tubing attached to plastic syringes, and transferred immediately to

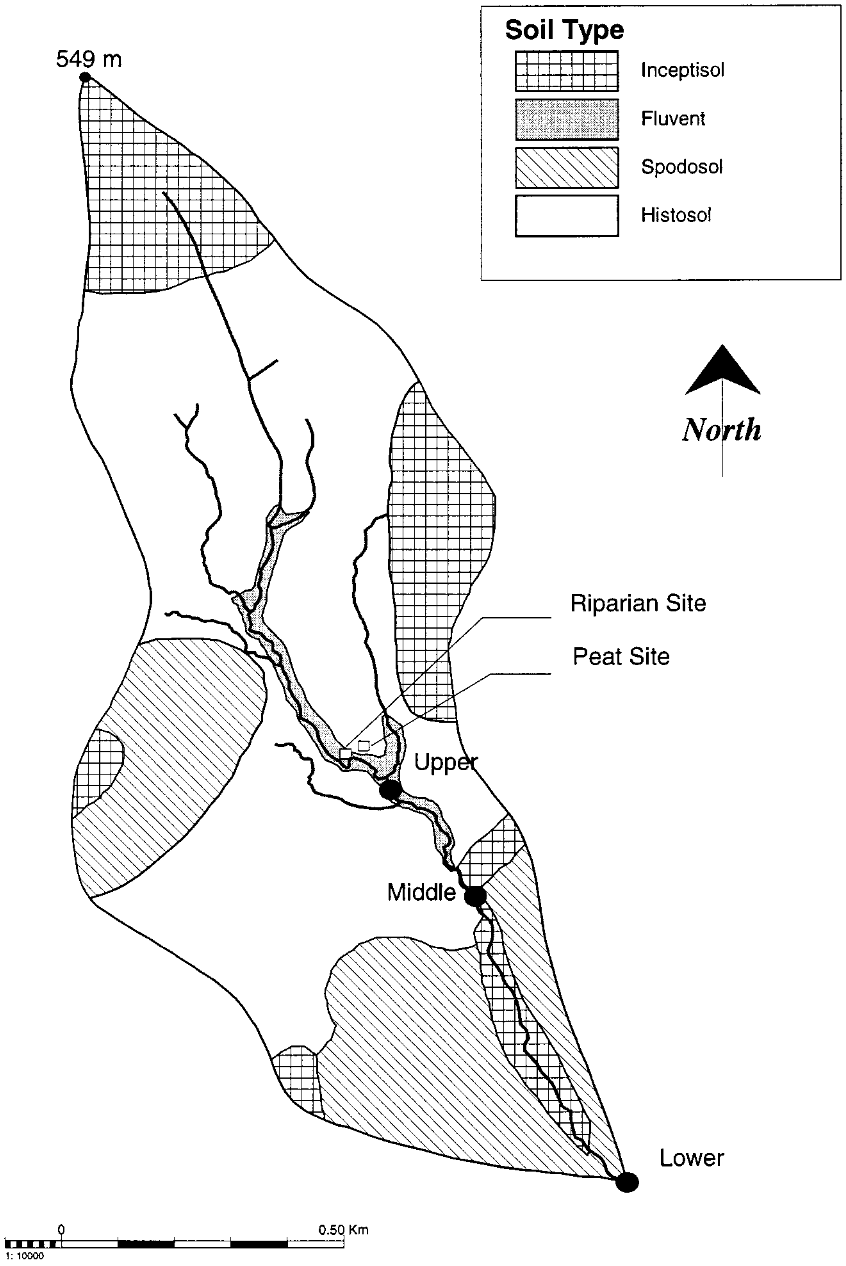


Figure 1. The Brocky Burn watershed showing the distribution of the soils and the location of the wells (□) and stream sampling points (●).

0.5 litre glass bottles. Grab samples of streamwater were collected in 1 litre glass bottles at the three monitoring sites on the main stream (Figure 1). All samples were stored in the dark at 4 °C and were filtered with 0.7 μm glass fibre filters (Whatman GF/F). The samples were rotary evaporated until less than 5 ml of solution remained in each case and were then freeze-dried.

3) Soil atmosphere samples

Samples of the soil atmosphere were collected from gas diffusion wells on three occasions (December 1997; February and June 1998). The diffusion wells were constructed of 10 mm internal diameter brass tubing, screened at depths of 0.15–0.20 m (shallow) and 0.45–0.50 m (deep) with fine gauge brass gauze covered with a thin layer of latex to form a waterproof gas-permeable membrane (Clymo & Pearce 1995). The top of the well was capped with a gas-tight rubber septum and brass nut and gas samples were collected using a hypodermic needle and high density nylon syringe. For both site types (peat and riparian) and at each depth, two composite samples for stable isotope analysis were collected by combining samples from five individual wells. Composite samples were transported to the laboratory in pre-evacuated glass vials and analyzed within 48 hours.

4) Streamwater TIC

Grab samples of streamwater for analysis of $\delta^{13}C_{TIC}$ were collected on two separate occasions (December 1997; February 1998) at each of the three sites on the stream. To prevent loss of any excess CO_2, samples were collected in 650 ml glass conical flasks that were sealed without headspace under water. Analyses were carried out on unfiltered samples. Particulate inorganic carbon in this acidic upland system is unlikely to be present. From each flask, a 60–100 ml sub-sample was extracted using a syringe and injected into a reaction vessel connected to a vacuum line. The sample was acidified with orthophosphoric acid and the CO_2 released was captured cryogenically in glass vials.

$\delta^{13}C$ analyses and ^{14}C dating

$\delta^{13}C$ analyses of plant material, soil atmosphere CO_2 and streamwater TIC were all carried out at the stable isotope laboratory at the Scottish Crop Research Institute, Dundee. Plant samples were analyzed by continuous flow isotope ratio mass spectrometry using a Europa Scientific ANCA-NT 20–20 Stable Isotope Analyser with ANCA-NT Solid/Liquid Preparation Module. Gas samples were analyzed for $\delta^{13}C$ using a Europa Scientific Tracermass IRMS and GIMS gas sampling system. The precision (1 SD) for $\delta^{13}C$ was ±0.1‰ based on repeated measurement of standards throughout the run.

Stable isotope ratios are expressed as $\delta^{13}C$ values where:

$$\delta^{13}C = [(^{13}C/^{12}C_{\text{sample}})/(^{13}C/^{12}C_{\text{standard}}) - 1] \times 1000‰$$

and ‘standard’ refers to $CaCO_3$ from the Pee-Dee Belemnite or a secondary standard related to it.

Sample preparation for ^{14}C-dating and analysis for stable isotopes of soil samples and DOC in soil and streamwater were carried out at the NERC Radiocarbon Laboratory, East Kilbride, U.K. Dried, homogenised soil samples and stream DOC samples were combusted to CO_2 in sealed quartz tubes by heating with copper oxide to 900 °C in a muffle furnace (Boutton et al. 1983). Carbon dioxide was purified by cryogenic separation from other combustion products. A sub-sample of CO_2 was used to measure stable carbon isotope ratios using a dual-inlet gas source mass spectrometer (VG OPTIMA) calibrated with international reference materials (Craig 1957) relative to the Pee-Dee Belemnite carbonate standard, and with an overall precision of $\pm 0.1‰$, based on repeated measurements of standards.

A further sub-sample was converted to a graphite/iron mixture by iron/zinc reduction (Slota et al. 1987) and sent to the NSF-AMS Facility, University of Arizona, Tuscon, USA for ^{14}C analysis (Donahue 1990). Accelerated mass spectrometry results are reported as conventional radiocarbon years BP (before AD 1950) and % modern absolute ^{14}C with an overall analytical precision of 1σ. The use of % modern absolute takes into account the ongoing radioactive decay of the international reference standard (oxalic acid) since AD 1950 (Stuiver & Polach 1977). ^{14}C enrichment $>100\%$ modern absolute indicates unambiguously the presence of ^{14}C from atomic weapons testing (i.e. post AD 1955). Values between 97–100% modern absolute cannot be interpreted as unambiguous dates because of the dilution of atmospheric ^{14}C concentrations, due to the release of CO_2 from the combustion of fossil fuels that effectively contain no ^{14}C.

Sample collection and methods for routine chemical analyses

Samples that were analyzed for streamwater pCO_2, soil and streamwater DOC, DIC, pH and alkalinity, and soil atmosphere CO_2, were collected biweekly during the period September 1997 to August 1998. Soil solution and soil atmosphere samples were collected as described previously except that samples collected from individual wells were not composited. Gas samples for the determination of free CO_2 in streamwater were collected using a headspace equilibration method (Kling et al. 1991). Streamwater pH was determined on samples collected in nylon syringes sealed under water, and grab samples were collected for all other streamwater analyses.

Dissolved organic carbon and DIC were determined on filtered samples (0.7 μm, GF/F) by ultra-violet oxidation (LABTOC, Pollution and Process Monitoring Ltd). Analysis of carbon dioxide in headspace and soil atmosphere samples was carried out by GC-FID (Chrompak 9001) with attached methanizer. The pH of streamwater samples was measured using a combined glass/reference electrode (Radiometer model GK2401C) in a system closed to the atmosphere to prevent outgassing of CO_2. Soil solution pH was measured on samples that were open to the atmosphere. Gran alkalinity was measured by titration with 0.005 M H_2SO_4 to 2 endpoints (pH 4.5 and 4.0) using a combined glass/reference electrode.

Results

Isotope analyses

1) Plant and soil material

δ^{13}C values for terrestrial (-24.9 to -29.1‰) and aquatic (-30.5 to -33.5‰) plant species (Table 1) were consistent with values reported in the literature for similar ecosystems (O'Leary 1988; Farquhar et al. 1989). At both sampling depths, soil values were -26.8‰ for the peat site and -27.7‰ for the riparian site (Table 1). Others have reported similar δ^{13}C values for soil organic matter (Aravena et al. 1992), and in this study the measured values for soil organic matter are in the middle of the range measured for terrestrial vegetation.

For all samples, ^{14}C dates almost certainly represent an average age of composite material and reflect a mix of carbon sources from different years. However, for comparison, it is convenient to assume that the ^{14}C date of a particular sample is its definite age. The soil ^{14}C ages indicate that peat has been accumulating in the watershed for more than 2700 years. Soil dates for both the shallow and deep riparian samples (1665 and 2795 ^{14}C yrs BP, respectively) were slightly older than those for the peat samples (1355 and 2605 ^{14}C yrs BP, respectively); a period of 1100–1300 ^{14}C years separated the two sampled soil depths.

2) Soil and streamwater DOC

On both occasions, streamwater DOC had similar δ^{13}C values to soil solution DOC (Table 2). $\delta^{13}C_{DOC}$ values for both streamwater (-27.4 to -28.0‰) and soil solution (-27.0 to -27.9‰) were close to the values found for soils and terrestrial vegetation from the watershed (Table 1). There were no clear differences between riparian and peat sites, between different points on the stream, or between the two sampling dates. ^{14}C values for DOC in soil

Table 1. $\delta^{13}C$ (‰) values of plant material and soil samples, and ^{14}C age (yrs BP) and ^{14}C enrichment (% modern absolute) of soil samples collected from the Brocky Burn watershed.

	$\delta^{13}C$ ±0.1‰	^{14}C age (yrs BP) $\pm 1\sigma$	^{14}C enrichment (% mod. abs.) $\pm 1\sigma$	Publication code
Terrestrial plants				
Calluna vulgaris (shoots)	−29.1			
Juncus effusus (shoots)	−27.8			
Eriphorum vaginatum (shoots)	−24.9			
Aquatic plants				
Scapania subalpina	−33.5			
Fontinalis antipyretica	−33.0			
Filamentous green algae	−30.5			
Soils				
Peat 0.25 m	−26.8	1355 ± 40	83.99 ± 0.44	AA-29887
Peat 1.00 m	−26.8	2605 ± 65	71.88 ± 0.59	AA-30837
Riparian 0.25 m	−27.7	1665 ± 45	80.82 ± 0.45	AA-30838
Riparian 0.70 m	−27.7	2795 ± 50	70.20 ± 0.42	AA-30838

solution varied from 89.49 to 122.01% modern absolute (Table 2) with no obvious differences that could be related to soil type or depth (Table 2). ^{14}C dates show that DOC in the soil solution (Table 2) is significantly younger than the soil organic matter itself at all depths (Table 1). All soil solution samples collected in February contain some carbon from post-1955 ($>100\%$ mod. abs.), although samples from the shallow peat wells were significantly younger than samples collected on the same date from either the deep peat or riparian wells (Table 2, Figure 2(a)). In June, although DOC from the shallow riparian wells was younger, DOC from deeper wells was older, compared to samples collected from the same wells in February (Table 2, Figure 2(a)). As with soil solution, DOC in streamwater at all three sampling points contained carbon of recent origin (i.e. post-1955) on both occasions. There were no clear differences in the ^{14}C values of DOC for the three different points on the stream, but the range in values (102.44 to 105.67% mod. abs.) was somewhat less than that shown for soil solution DOC (Table 2).

3) Soil atmosphere CO_2 and streamwater TIC

At between −17.2 to −25.2‰ the $\delta^{13}C_{CO_2}$ values in the soil atmosphere (Figure 3a) were slightly heavier than the range reported for terrestrial vegeta-

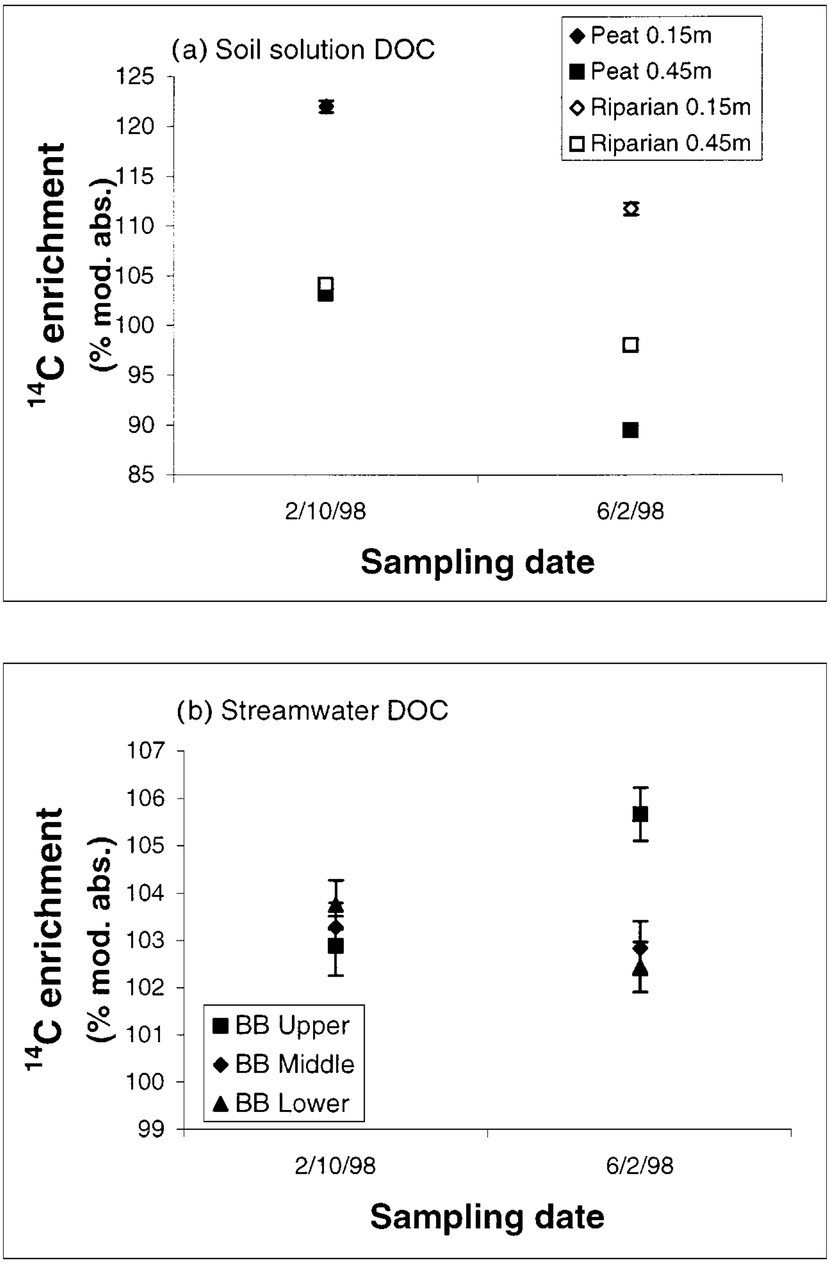


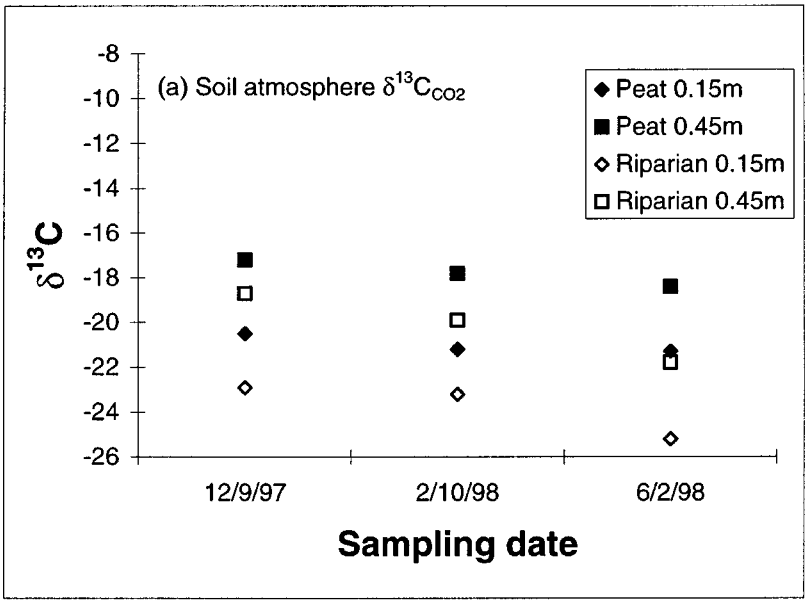
Figure 2. ^{14}C enrichment in DOC in (a) soil solution and (b) streamwater. Error bars represent $\pm 1\sigma$.

Table 2. $\delta^{13}C$ (‰) values, ^{14}C age (yrs BP) and ^{14}C enrichment (% modern absolute) of DOC in Brocky Burn stream and soil solution samples collected on 2 separate occasions.

	Sampling date	$\delta^{13}C$ ±0.1‰	^{14}C age (yrs BP) ±1σ	^{14}C enrichment (% mod. abs.) ±1σ	Publication code
Streamwater DOC					
Brocky Burn Upper	10/02/98	−27.9	Modern	102.89 ± 0.63	AA-29884
	02/06/98	−28.0	Modern	105.67 ± 0.56	AA-30834
Brocky Burn Middle	10/02/98	−27.4	Modern	103.28 ± 0.52	AA-29885
	02/06/98	−28.0	Modern	102.84 ± 0.57	AA-30835
Brocky Burn Lower	10/02/98	−27.8	Modern	103.76 ± 0.52	AA-29886
	02/06/98	−28.0	Modern	102.44 ± 0.53	AA-30836
Soil solution DOC					
Peat shallow	10/02/98	−27.6	Modern	122.01 ± 0.57	AA-29880
	02/06/98	−27.4	No data	No data	AA-30830
Peat deep	10/02/98	−27.1	Modern	103.20 ± 0.52	AA-29881
	02/06/98	−27.0	845 ± 45	89.49 ± 0.51	AA-30831
Riparian shallow	10/02/98	−27.7	Modern	103.70 ± 0.47	AA-29882
	02/06/98	−27.6	Modern	111.73 ± 0.59	AA-30832
Riparian deep	10/02/98	−27.5	Modern	104.12 ± 0.47	AA-29883
	02/06/98	−27.4	115 ± 45	98.04 ± 0.55	AA-30883

tion and soil carbon in this study (Table 1). Soil atmosphere samples from the deeper wells (mean −18.9‰) were consistently enriched in ^{13}C compared to samples from shallower wells (mean −22.4‰). Riparian well gas samples were ^{13}C-depleted compared to samples from peat wells (means −21.9 and −19.4‰, respectively). There was also a trend of ^{13}C depletion between successive sampling dates; this was most apparent for the riparian samples (Figure 3(a)).

Streamwater $\delta^{13}C_{TIC}$ became heavier with distance downstream (Figure 3(b)), and the values for samples collected at the same points on the stream varied between the two sampling dates. In December, the $\delta^{13}C_{TIC}$ value of −21.4‰ at the uppermost site was close to the $\delta^{13}C_{CO_2}$ of the soil atmosphere sampled from shallow soil diffusion wells on the same day (−20.5‰ peat and −23.2‰ riparian). In streamwater collected from the uppermost site in February, TIC was relatively ^{13}C-enriched (−15.5‰) compared to (i) the soil atmosphere $\delta^{13}C_{CO_2}$ values from wells sampled on the same day (Figure 3(a)) and (ii) streamwater TIC collected in December (Figure 3(b)).



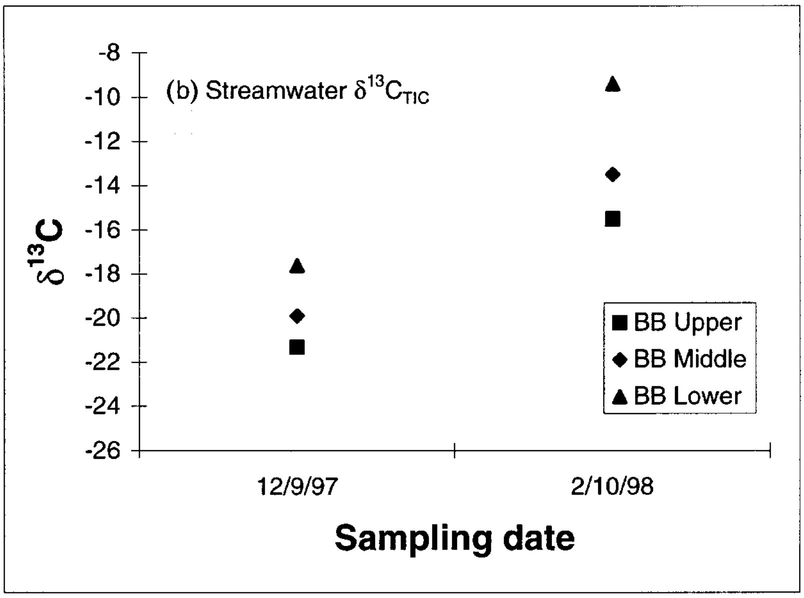


Figure 3. (a) $\delta^{13}C_{CO_2}$ in the soil atmosphere on three sampling dates; (b) $\delta^{13}C_{TIC}$ in streamwater on two sampling dates.

Carbon concentrations, pH and alkalinity in soils and streamwater

Mean annual concentrations of DOC and pCO_2 declined, and pH and alkalinity increased in Brocky Burn with distance downstream (Table 3(a)). The greatest spatial effect was in the mean concentration of free CO_2 which declined by $>$80% between the Brocky Upper (1.8 mg L^{-1}) and Brocky Lower (0.3 mg L^{-1}) sampling sites. Annual means for DOC and DIC were lower and pH higher in streamwater at all three sampling points compared to soil solution from the two sites and depths (Table 3(b)). Mean DOC concentrations were lower in shallow and deep riparian wells (36.3 and 39.2 mg L^{-1}, respectively) compared to peat wells at both depths (45.7 and 43.2 mg L^{-1}), and the only appreciable measure of alkalinity in soil solution was in deeper riparian wells (Table 3(b)). Otherwise there were no obvious patterns in soil solution chemistry between sites and at different depths. At both the peat and riparian sites soil atmosphere CO_2 was considerably elevated (Table 3(b)) with respect to the above-ground atmosphere. Annual mean soil atmosphere CO_2 was greater in peat shallow wells (3.8%) compared both to deeper peat wells (2.8%) and to riparian wells at both depths (Table 3(b)).

Discussion

Streamwater DOC

The δ^{13}C results in this study clearly show that terrestrial inputs dominate the supply of DOC to Brocky Burn, a finding that is consistent with the well-established link that exists between DOC transported in streams and soil carbon pools (Aitkenhead et al. 1999; Hope et al. 1997b; Schiff et al. 1997). The younger ^{14}C age of DOC in the soil solution relative to soil organic matter is likely to be due to the continual supply and movement of water containing relatively young DOC from near-surface soil sources down the soil profile. Dissolved organic carbon in streamwater was also dominated by young (post-1955) carbon on both sampling dates, suggesting that the primary source of DOC to Brocky Burn is from organic matter in the upper part of the soil profile (Tables 1 and 2). This is consistent with the strong covariation seen between DOC concentrations in shallow piezometer wells and streamwater with time (Billett unpublished), and is likely to be related to the production of mobile DOC via the oxidation of soil organic matter in the upper aerobic part of the peat profile (Clymo & Pearce 1995). In a similar study in Canada, Schiff et al. (1997, 1998) found that in forested watersheds with wetland areas, surface soils were the dominant source of DOC in streamwater, whereas in upland catchments devoid of wetlands the age of exported DOC

Table 3. (a) Annual means (± standard deviation) for streamwater DOC, DIC, CO_2, pH, and total and HCO_3^- alkalinity at three points on Brocky Burn. (b) Mean (± standard deviation) DOC, DIC, pH, and total alkalinity in soil water and mean CO_2 in the soil atmosphere at two depths and two locations.

(a) Streamwater

	Discharge $m^3\ s^{-1}$	DOC mg L^{-1}	DIC (HCO_3^-) mg L^{-1}	Free CO_2 mg L^{-1}	pH	Total alkalinity μEq L^{-1}	HCO_3^- alkalinity μEq L^{-1}
Brocky Upper		16.6 ± 7.9	0.86 ± 0.7	1.8 ± 0.5	4.80	39.3 ± 56.4	26.9 ± 57.8
Brocky Middle		15.3 ± 7.8	1.09 ± 0.9	1.0 ± 0.2	4.97	59.6 ± 73.0	54.2 ± 68.5
Brocky Lower	0.0440 ± 0.0913	13.7 ± 7.1	0.8 ± 0.7	0.3 ± 0.0	5.07	45.3 ± 55.0	36.6 ± 58.2

(b) Soil

	Soil water				Soil atmosphere
	DOC mg L^{-1}	DIC (HCO_3^-) mg L^{-1}	pH	Total alkalinity μEq L^{-1}	CO_2 % v/v
Peat Shallow	45.7 ± 12.6	1.55 ± 1.0	3.9	−58.6 ± 8.7	3.8 ± 1.2
Peat Deep	43.2 ± 3.9	2.03 ± 1.6	4.1	−34.3 ± 7.4	2.8 ± 0.6
Riparian Shallow	36.3 ± 16.2	1.29 ± 1.0	4.4	−17.2 ± 13.1	2.7 ± 1.0
Riparian Deep	39.2 ± 6.9	2.56 ± 1.8	3.6	56.2 ± 19.0	3.1 ± 0.7

was controlled by antecedent moisture conditions, with older carbon being exported when soils are drier.

Soil atmosphere CO_2

$^{13}CO_2$ diffuses more slowly in air, and to a lesser extent in water, compared to the lighter $^{12}CO_2$. Consequently, if molecular diffusion dominates exchange, the δ^{13}C values of soil CO_2 may be ^{13}C-enriched by at least 0.7 to 4.4‰ (Hersteberg & Siegenthaler 1991; Cerling 1984; Cerling et al. 1991) relative to the CO_2 produced by root respiration or oxidation of soil organic matter. In this study, the average enrichment (3.7‰) of riparian shallow soil atmosphere samples (mean −23.8‰) compared to measured riparian soil (−27.7‰) and terrestrial vegetation (mean −27.3‰), is consistent with isotopic fractionation associated with CO_2 diffusion through soil. Findings from other studies suggest that the greater δ^{13}C enrichment in the peat and deeper riparian soil atmosphere samples in Brocky Burn watershed may result from the release of some CO_2 as a by-product of methanogenesis via acetate fermentation under anoxic conditions (Herzceg 1988; Charman et al. 1994). Carbon dioxide produced in this way is strongly enriched in ^{13}C and may have a δ^{13}C value as high as −5‰ (Charman et al. 1994) or +9‰ (Waldron et al. 1999). Anoxic conditions that support methanogenesis are likely to be found around the deeper wells, which were frequently below the water table (Hope unpublished).

Streamwater TIC

Previous studies on DIC in freshwater have found δ^{13}C values that are typically in the range 0 to −16‰ (e.g. Atekwana & Krishnamurthy 1998; Pawellek & Veizer 1994; Yang et al. 1996). Such studies have, however, been carried out on large river systems where the δ^{13}C signature reflects a variety of inorganic carbon sources and where production of CO_2 in the water column is likely to be significant. In headwater streams such as Brocky Burn, stream flow is fed dominantly by shallow groundwaters draining deep peat deposits, giving rise to low streamwater pH. This results in approximately 70–95% of the TIC being in the form of free CO_2 (Wetzel 1983). The $\delta^{13}C_{TIC}$ data for Brocky Burn show that the majority of inorganic carbon in the stream is either derived from respired organic matter in surface soil horizons, or from respiration of DOC in the stream itself. Although limited seasonal data are presented, the relative ^{13}C enrichment in TIC in February when stream flow was low compared to December, could tentatively be explained either by (i) transport through deeper flowpaths in soils where $\delta^{13}C_{CO_2}$ is less negative, and (ii) fractionation associated with CO_2(gas) $\leftrightarrow$ HCO_3^- under conditions where stream pH is slightly elevated (Dawson et al., in press).

Although soil-derived CO_2 does not equilibrate with the atmosphere immediately upon entry into the stream channel, equilibrium is approached over the relatively short distance between the middle and lower sites. A loss of CO_2 to the atmosphere is evidenced by a marked decline in the DIC (particularly in the form of free CO_2) between soil pore waters and successive sites down the stream channel, along with a rise in pH (Table 3). On the days sampled for this study, pCO_2 values at the lower site were in the range 355 to 398 μatm, slightly higher than would be expected for atmosphere-water equilibrium (311 to 330 μatm). Conservative tracer studies have shown that these downstream changes are significantly greater than can be explained by additional inflows of water with low CO_2 content along the stream channel (Dawson et al., in press). The ^{13}C isotope data also support a relatively rapid exchange and equilibration of CO_2 between streamwater and the atmosphere in the lower reaches, with less negative $\delta^{13}C_{TIC}$ values being seen at successive downstream sites on both sampling dates (Figure 4). If an isotopic value of between -7‰ and -8‰ is assumed for atmospheric CO_2, then the TIC at the lower site would be expected to have an isotopic equilibrium value of between -7.8‰ and -8.8‰. The downstream changes observed are likely to be driven partly by increased atmospheric exchange of CO_2 on passage down the stream, and partly by the isotopic fractionation associated with CO_2(gas) $\leftrightarrow$ HCO_3^- that is driven by the increase in pH as excess CO_2 degasses in the lower reaches of the stream (Dawson et al., in press; Hope et al., in review).

Conclusions

The stable isotope results obtained in this study on a temperate non-forested watershed show that the dominant sources of streamwater DOC and TIC are soil and terrestrial vegetation. The influence of soil atmosphere CO_2 on streamwater TIC is most apparent in the central part of the catchment where the stream drains CO_2-rich peats, although isotopic equilibrium with the atmosphere is approached over the 1.1 km study reach.

The ^{14}C data show that despite the considerable ^{14}C age of soils in this watershed, DOC in soil solution and streamwater contains carbon that is approximately 2500 calendar years younger than peat at 1m depth. Furthermore, it would appear that DOC in streamwater is mainly derived from near-surface soil horizons and transported via shallow groundwater flowpaths to the stream itself.

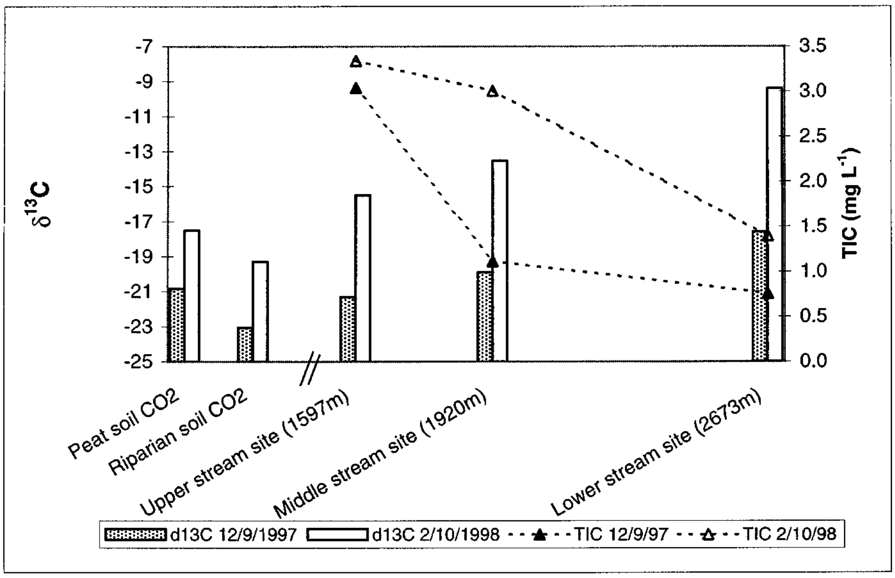


Figure 4. Spatial patterns in δ^{13}C of TIC in soil pore water and streamwater (bars) and TIC streamwater concentrations (triangles) on two sampling dates.

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