Biogeochemistry **36:** 43–65, 1997.

Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ^{13}C and ^{14}C

S.L. SCHIFF[1], R. ARAVENA[1], S.E. TRUMBORE[2], M.J. HINTON[1], R. ELGOOD[1] & P.J. DILLON[3]

[1] *Waterloo Centre for Groundwater Research, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada;* [2] *Department of Earth System Science, University of California-Irvine, Irvine, California 92717 USA;* [3] *Dorset Research Centre, Ontario Ministry of Environment and Energy, Dorset Ontario P0A 1E0 Canada*

Key words: dissolved organic carbon, forested catchments, lakes, ^{14}C, ^{13}C, carbon isotopes, carbon cycling

Abstract. Export of dissolved organic carbon (DOC) from forested catchments is governed by competing processes of production, decomposition, sorption and flushing. To examine the sources of DOC, carbon isotopes (^{14}C and ^{13}C) were analyzed in DOC from surface waters, groundwaters and soils in a small forested catchment on the Canadian Shield in central Ontario. A significant fraction (greater than 50%) of DOC in major inflows to the lake is composed of carbon incorporated into organic matter, solubilized and flushed into the stream within the last 40 years. In contrast, ^{14}C in groundwater DOC was old indicating extensive recycling of forest floor derived organic carbon in the soil column before elution to groundwater in the lower B and C soil horizons. A small upland basin had a wide range in ^{14}C from old groundwater values at baseflow under dry basin conditions to relatively modern values during high flow or wetter antecedent conditions. Wetlands export mainly recently fixed carbon with little seasonal range. DOC in streams entering the small lake may be composed of two pools; an older recalcitrant pool delivered by groundwater and a young labile pool derived from recent organic matter. The relative proportion of these two pools changes seasonally due the changes in the water flowpaths and organic carbon dynamics. Although changes in local climate (temperature and/or precipitation) may alter the relative proportions of the old and young pools, the older pool is likely to be more refractory to sedimentation and decomposition in the lake setting. Delivery of older pool DOC from the catchment and susceptibility of this older pool to photochemical decomposition may consequently be important in governing the minimum DOC concentration limit in lakes.

Introduction

In comparison with the annual fixation and release of carbon by the terrestrial biomass, the export of dissolved organic carbon (DOC) is a small number in the annual carbon budget of forested terrestrial catchments (Figure 1). For downstream aquatic systems, however, DOC can be an important component in the acid-base balance (Eshleman & Hemond 1985) and the food web

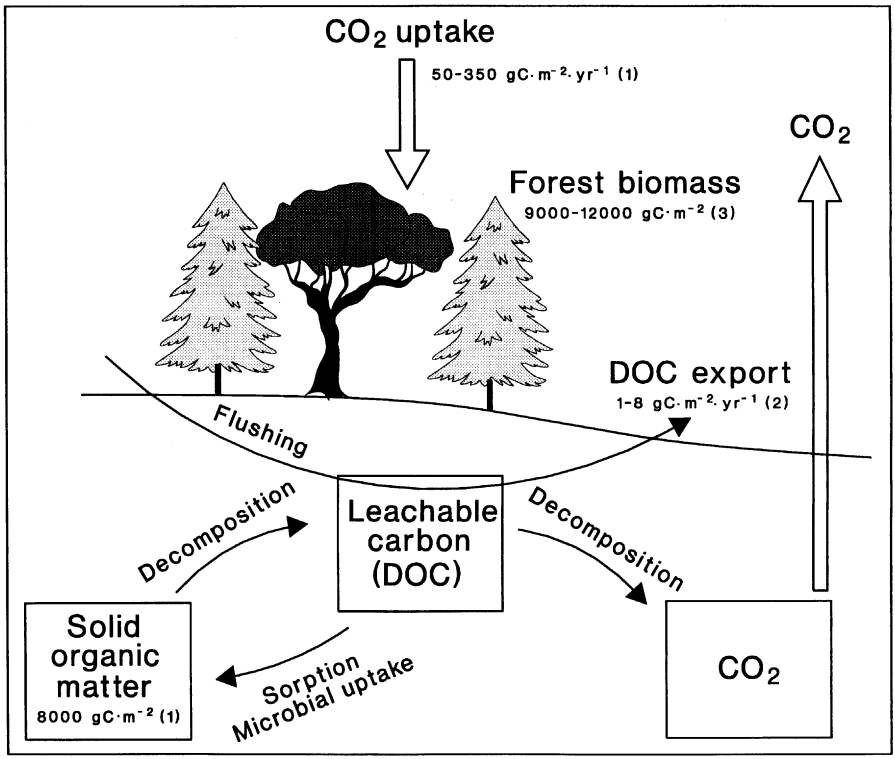

Figure 1. Schematic showing the size of some of the organic carbon pools and the important processes affecting dissolved organic carbon (DOC) in the terrestrial catchment. Decomposition from solid organic matter includes microbial exudates. Production of DOC from decomposition, microbial uptake/sorption, decomposition of DOC and flushing are competing processes affecting the export of DOC in streams of forested catchments (1. Trumbore et al. 1992; 2. Dillon & Molot 1995; 3. Hudson et al. 1994).

(Hobbie & Wetzel 1992), has a major role in the mobility and toxicity of trace metals and other contaminants (Thurman 1985), affects light penetration and offers protection to aquatic organisms from the effects of UV radiation (Lean & Scully 1994).

In forest soils, DOC is produced principally from microbial activity, root exudates and leaching of organic matter. From 25 to 50% of the total annual loss of surficial forest floor material is via production and leaching of DOC (Cronan 1985; Vance & David 1991). Although some of the DOC is transported to and sorbed in the upper B horizon, the ultimate fate of DOC is decomposition to CO_2 and loss to the atmosphere (Trumbore et al. 1992). DOC is thus an intermediary in the carbon cycle of a forest. For DOC to be exported from the terrestrial catchment via a surface stream, the DOC

must be produced but then flushed from the system in order to escape subsequent decomposition and sorption on particulate soil surfaces. Hydrological processes which flush DOC into surface streams and out of catchments vary seasonally and from storm to storm (Hinton et al. 1997a). Production, decomposition, sorption and flushing are competing processes in the fate of DOC (Figure 1). Export of DOC from the terrestrial catchment depends on the complex interplay between these processes with dynamics that change seasonally and spatially.

Alterations in local climate as a consequence of global change could alter the dynamics of DOC export by changing not only the temperature (affecting the competing rates of production and decomposition) but also the flushing by altering the quantity, intensity and seasonal pattern of precipitation (Hinton et al. 1997a).

Most of the research on DOC in forested watersheds has been related to the evaluation of DOC budgets and the export of DOC in streams. Some studies have focussed on the effects of disturbance such as forest clear cutting (Meyer & Tate 1983; Moore 1989) and the role of hydrology on the concentration and fluxes of DOC (Jardine et al. 1990; Hinton et al. 1997a). However studies of DOC concentrations yield little information about sources, unless tied to flowpath analyses (e.g. Hinton et al. 1997b), and yield no information on turnover rates of DOC in forested watersheds.

Research approach

Here, we report data from a research program that has as the main objective the examination of carbon cycling and turnover times of various carbon reservoirs in forested watersheds on the Canadian Shield (Schiff et al. 1990; Aravena et al. 1992; Trumbore et al. 1992).

Our approach involves the use of ^{13}C and ^{14}C, the stable and radioactive isotopes of carbon, respectively. The carbon isotopic composition of DOC in surface water in forested watersheds reflects the sources of DOC including stemflow, throughfall, litter, soil organic matter and wetlands. The ^{13}C composition of these sources is similar to the predominant plants in the watershed. Plants that follow the Calvin photosynthetic pathway (C3 plants) are characterized by $\partial^{13}C$ values ranging between –25‰ and –30‰ with an average of –28‰ (O'Leary 1988). In contrast, the C4 plants (Hatch-Slack photosynthetic cycle) range in $\partial^{13}C$ between –8‰ and –13‰ with an average value of –11‰ (O'Leary 1988). C3 and C4 plants predominate in temperate and dry regions, respectively.

The main DOC sources, decomposing organic matter in soils and wetlands, are composites of both recently fixed and accumulated older carbon. ^{14}C is a useful tracer for distinguishing the relative importance of different aged DOC

sources. DOC derived from carbon fixed prior to 1950 will be depleted in ^{14}C due to radioactive decay of the isotope ($\Delta^{14}C \leq 0‰$). Since 1950, the atmospheric ^{14}C activity has been strongly enhanced by the production of ^{14}C due to upper atmospheric testing of thermonuclear weapons. Atmospheric ^{14}C peaked in the mid-1960's (the peak of bomb testing) at approximately 900‰ and has since declined as the excess atmospheric ^{14}C mixed into the biosphere and oceanic carbon reservoirs (Burcholadze et al. 1989). Contemporary ^{14}C activity measured in leaves at the Harp Lake field site in 1991 was 179 $\pm$ 10‰. DOC derived from atmospheric carbon fixed by plants within the last 40 years will thus has positive ^{14}C values ($\geq$180‰). A mixture of different-age sources will be reflected in the measured ^{14}C content of DOC; a predominance of young carbon will result in positive $\Delta^{14}C$, while DOC derived mostly from old carbon sources will have negative ^{14}C. Radiocarbon measurements on organic carbon integrate the different inherent ages of the carbon pool and are a result of all sources and processes affecting that pool (Trumbore 1993).

Most of the carbon isotope research on DOC in natural waters has been done in groundwater (Murphy et al. 1989; Wassenaar et al. 1991; Aravena & Wassenaar 1993) and a few studies have also been reported on lake and marine environments (Druffel et al. 1989; Schiff et al. 1990). In these studies, carbon isotopes yield information that is not obtainable from the study of carbon mass and flux alone.

In this paper, carbon isotope data on groundwaters, streams and soils are combined with DOC concentration patterns in streams to provide information on the sources of DOC exported from the terrestrial catchment.

Methods

The Harp Lake basin is located on the Precambrian Shield, approximately 200 km north of Toronto, Canada (Figure 2). The terrestrial catchment area has been divided into six major subcatchments (Figure 2). Each stream is gauged with a weir at a convenient location proximal to the lake edge. Harp 4–21, a subbasin within the Harp 4 basin, has been the site of intensive investigations on the role of groundwaters in streamflow generation (Dankevy et al. 1991; MacLean 1993; Hinton et al. 1994).

Underlying bedrock consists primarily (69%) of biotite and horneblende gneiss with amphibolite and schist (28%) in the remaining portion of the basin. The bedrock is covered by glacial till deposits varying in thickness from 0 to 15 metres (Jeffries & Snyder 1983). Soils are poorly developed Podzols formed upon the generally thin, sandy basal tills. Vegetation in the Harp basin is mixed deciduous-coniferous forest dominated by maple and

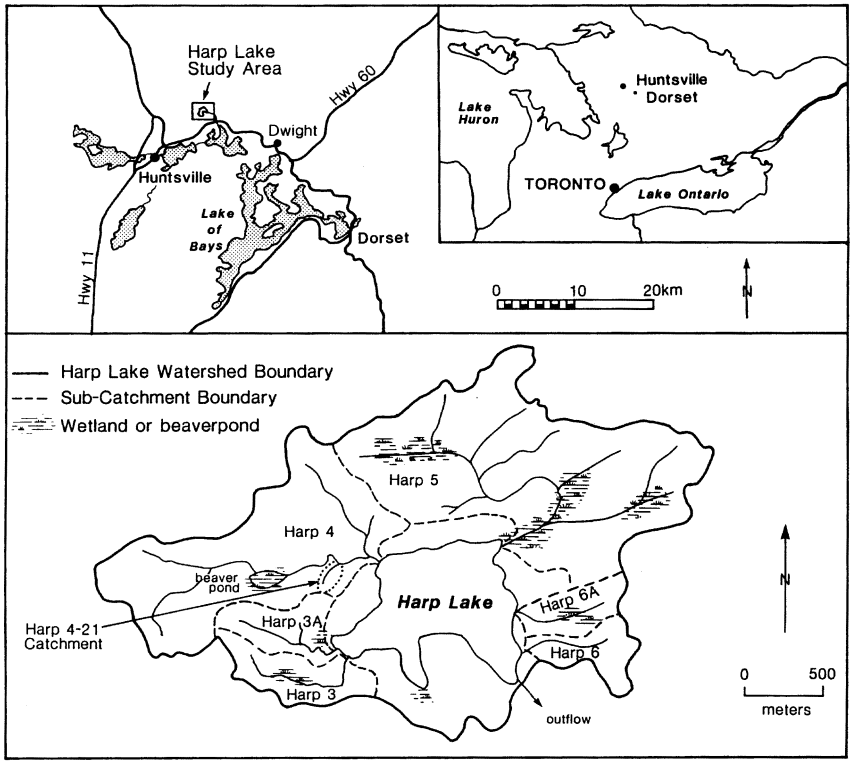

Figure 2. Location of the Harp Lake Basin. Wetland areas within the subbasins are shaded. The areas of the entire catchment and the subbasins are: Harp Basin (506 ha), Harp 3 (22.6), Harp 3A (22.4), Harp 4 (139.0), Harp 5 (204.8), Harp 6 (21.5), Harp 6A (18.9).

birch. Wetlands are present in most subcatchments (Figure 2). The main wetland types are beaverponds and conifer swamps.

Water samples for carbon isotopic analyses of DOC were collected in glass bottles, filtered in the field using sequential 10 μm and 0.5 μm Balston glass fibre filters and acidified to pH 2 to 3. DOC-^{14}C samples were subsequently dried using a Labconco freeze-dry system, transferred to pyrex glass tubes with CuO and Ag wire, vacuum sealed and combusted at 550 °C (Boutton et al. 1983). The resulting CO_2 was cryogenically purified and two aliquots were collected in glass breakseals for analysis of ^{13}C and ^{14}C.

Analysis of ^{13}C was performed at Environmental Isotope Laboratory of The University of Waterloo using either a VG Micromass 903 or a VG Prism mass spectrometer. The ^{13}C data are reported in ∂‰ units relative to PDB with analytical errors less than $\pm$ 0.2‰ between independently field sampled replicates.

For the analysis of ^{14}C, the CO_2 was reduced to graphite for accelerator mass spectrometric (AMS) determination at Lawrence Livermore National Laboratory according to the method described in Vogel et al. (1987). A few samples were submitted for ^{14}C analysis to Isotrace at the University of Toronto and PSI/ETH accelerator facility Zurich Switzerland. The ^{14}C data are reported in Δ notation in ‰ relative to 95% of the activity of oxalic acid standard in 1950 after correction for isotopic fractionation to a $\partial^{13}C$ of –25‰ using the measured $\partial^{13}C$ according to Stuiver and Polach (1977).

Analytical errors in the ^{14}C measurements vary between 6 and 30‰ depending on the laboratory and date when the analyses were performed; most are less than 12‰. Replicate samples, including those sampled independently in the field, were always within the reported individual sample errors.

Samples collected for DOC concentration were filtered in the field using 80 μm (surface water) and 44 μm (groundwater) polyester screens and analyzed by the Ontario Ministry of Environment using standard procedures (OME 1983).

Results and Discussion

a. Interaction of hydrology and carbon reservoirs in DOC export

An evaluation of the sources and export of DOC from forested basins requires an understanding of the interplay between the hydrological and geochemical processes that govern the input of DOC to streams. The main sources of DOC in forested watersheds are stemflow and throughflow and the leaching of litter and organic carbon from soils and wetlands. Flowpaths of water through shallow organic rich horizons of the forest floor and through wetlands should be important contributors to DOC export in streams. Therefore, the interactions between watershed hydrology and carbon reservoirs are key components in the understanding of DOC export in streams of forested catchments.

In the major streams in the Harp Lake catchment (Harp 3A, 4 and 5), the DOC is labelled with a significant proportion of recent (bomb) carbon. Most values are in excess of 80‰ (Figure 3; except one notable exception for August 1991 in Harp 3A) indicating that at least 50% of the carbon has been incorporated into organic matter, transformed to a soluble organic form and flushed from the terrestrial watershed within the last 40 years (Schiff et al. 1990). Values less than that of contemporary carbon measured in maple leaves at Harp in 1991 (179 ± 10‰) indicate that the DOC exported from these catchments is of mixed age. The high proportion of modern carbon shows the potential for alteration of processes that control DOC export on a

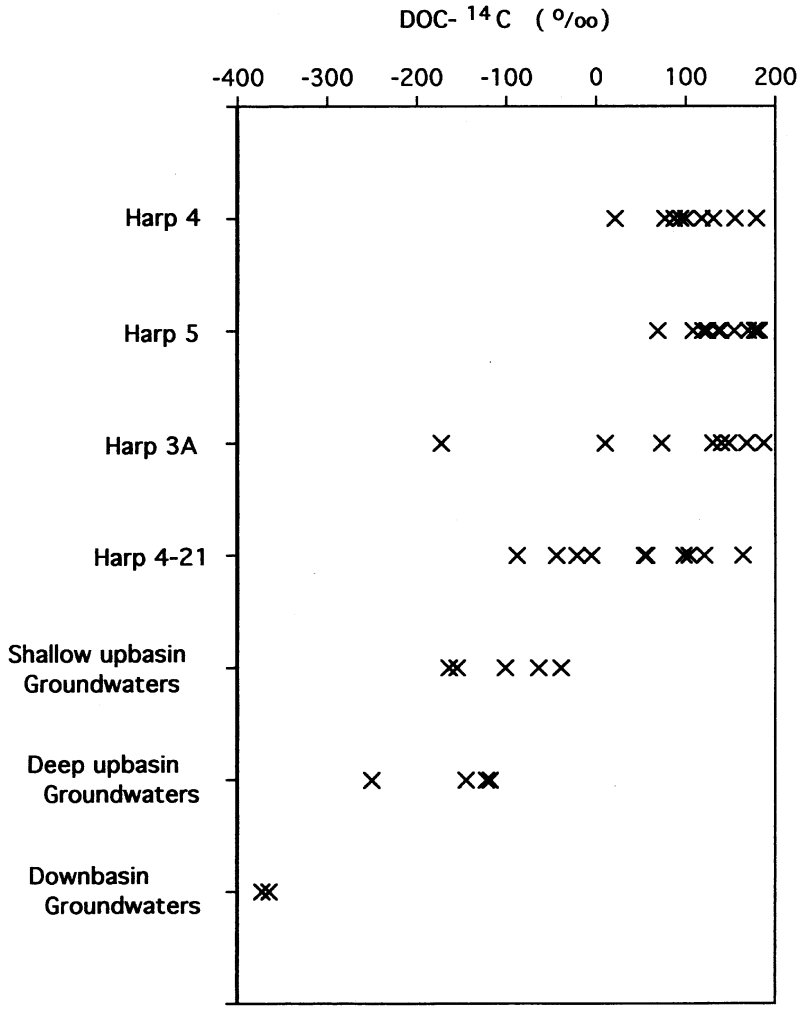

Figure 3. DOC-^{14}C in streams and groundwaters in the Harp Watershed. Shallow basin piezometers are located in Harp 4–21, the small upland basin (Figure 2) and are screened for 30 cm at various depths ranging from 0.5 metres to 2.5 metres below ground surface. Deep upbasin piezometers are screened below 2.5 metres from ground surface. Downbasin piezometers are located just below the Harp 4 weir proximal to the lake edge. Errors in Δ^{14}C are less than the symbol size on the figure.

short timescale in response to changes in climate, land use or precipitation chemistry.

In contrast to surface streams, groundwaters from the lower B or C soil horizons in all locations, even at the top of the flow system in the small headwater basin, have DOC-^{14}C less than 0‰ (Figure 3). DOC concentra-

tions in groundwaters are low; typically less than 1 to 2 mg/l. These values are much lower than DOC concentrations observed within the litter layer or A soil horizons (up to 120 mg/L, Hinton et al. 1997b). Therefore, because of the low bomb carbon content, the DOC in the groundwaters below the upper B horizon is not a fraction of the recently formed DOC which bypasses the sorption/decomposition process in the upper soil zone due to preferential infiltration. Groundwater recharge rates are high. Annual precipitation is 1033 mm/yr (1976–1989 MOE unpublished data) with the loss of approximately one half to evapotranspiration. Based on hydrogeologic studies, the groundwater residence time in the Harp 4–21 subcatchment was estimated to be approximately 4 years (Dankevy et al. 1990). Thus, because of the high infiltration rate which flushes soluble organic carbon downwards through the soil profile, the low bomb carbon content of groundwater DOC is not a result of extremely slow leaching. This DOC is the output of extensive recycling, the soluble fraction of the reworked soil organic carbon, and as a result, probably has less microbially labile functional groups than newly formed DOC (e.g. Thurman 1985).

The low ^{14}C content of groundwater DOC in contrast to the higher ^{14}C observed in DOC from streams suggests that most of the DOC exported from these major catchments is not derived from groundwaters located below the upper B soil horizon.

Terrestrial DOC from all streams and groundwaters is confined to a narrow range of $\partial^{13}C$ from –25.5‰ to –28.6‰ with 80% of the values falling within 0.5‰ of –27.0‰ (Figure 4). Fresh deciduous leaves in August 1990 in the Harp 4–21 basin had an average $\partial^{13}C$ of –30.4‰. Litter was measured at –28.9‰ in the top cm and –27.8‰ immediately above an A1 soil horizon (0–5 cm) with a $\partial^{13}C$ of –26.4‰ (Trumbore et al. 1992). Even though there appears to be a slight enrichment in the $\partial^{13}C$ of organic matter from leaves through the litter to the organic soil horizon, the majority of the measured DOC-^{13}C values in the streams are well above the values measured in the organic matter from the B2 horizon (–25.6‰ at 25–40 cm; Trumbore et al. 1992) consistent with a near surface source for the majority of the stream and groundwater DOC if there is no significant fractionation of ^{13}C upon decomposition and leaching of soil organic matter. The restricted ^{13}C range in DOC coupled with the uncertainty and small size in the magnitude of the isotopic fractionations affecting DOC cycling limits the usefulness of DOC-^{13}C measurements to separate sources of DOC on the basin scale.

a. Export of DOC from upland catchments

Harp 4–21 is a small headwater upland subbasin devoid of wetland areas. This upland deviates from the pattern of the other major inflows to Harp Lake.

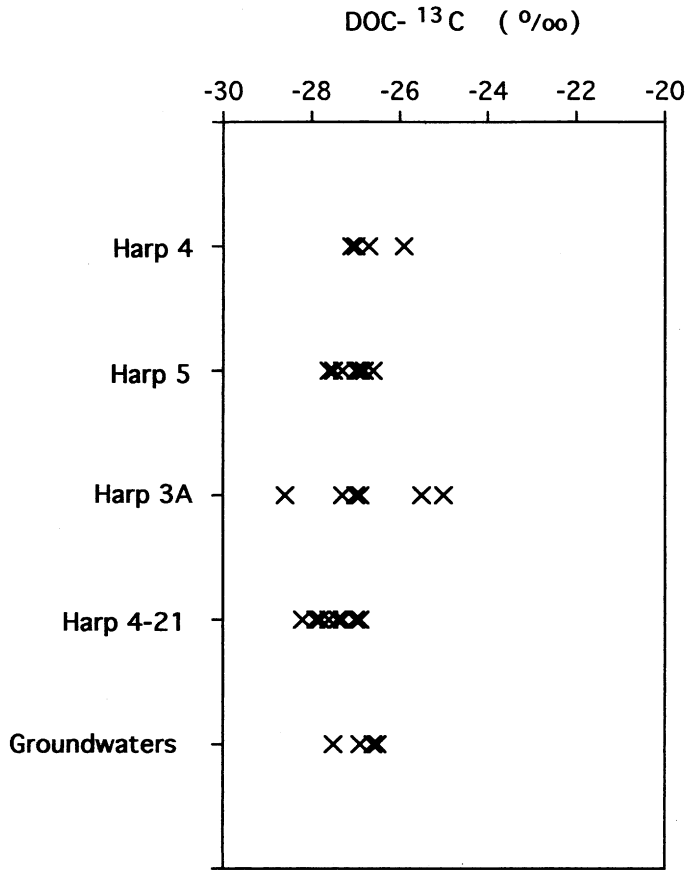

Figure 4. DOC-^{13}C in streams and groundwaters in the Harp Watershed. The number of analyses for each sampling location is not clear in the figure because of the narrow range in ∂^{13}C. The numbers of analyses plotted on this figure are as follows: Harp 4 (n = 9), Harp 5 (n = 12), Harp 3A (n = 10), Harp 4–21 (n = 8) and groundwaters (n = 9). Errors in ∂^{13}C are less than the symbol size on the figure.

A significant fraction of samples have ^{14}C activities less than 0‰ (Figure 3). The lowest values are similar to the ^{14}C activity of groundwater DOC suggesting that groundwaters may be an important DOC source in upland streams.

DOC concentrations in this small stream range from 1.3 mg/L at base-flow during dry antecedent conditions to a high of 15 mg/L during stormflow (Hinton et al. 1997a). Routine stream chemistry sampling programs may not fully characterize the DOC concentration -discharge relationship because storm events are often missed (Hinton et al. 1997a). During storms, the general pattern in Harp 4–21 is an increase in DOC with increasing discharge

(Hinton et al. 1997a). Imprinted upon this general pattern are seasonal differences in flowpaths and perturbations in the availability of soluble organic carbon throughout the year due to seasonally differing rates of decomposition, changes in the frequency of events which govern prior leaching of the organic matter and seasonal differences in the relative contributions of DOC sources especially the input of fresh litter in the fall. The result is changes in DOC concentrations during an individual storm event and also between successive storms. Thus at any specific discharge value the stream DOC concentration is quite variable depending on the position in the stream hydrograph and the season.

At baseflow the stream DOC is delivered by groundwater of low DOC concentration discharging directly through the streambed. Autochthonous production of DOC is low in this small stream and the streambed is composed of sand and larger sized material. Any increases in stream DOC above groundwater concentrations under baseflow conditions are likely the result of the interaction of discharging groundwater within the stream bed or hyporheic zone or at the fringes of the streambed where organic matter is present.

During storm events, however, the Harp 4–21 streamflow is also composed principally of discharging groundwater. Hydrograph separations using ^{18}O (Hinton et al. 1994) indicate that stream stormflow contains 75–85% pre-event water. Throughfall DOC concentrations (typically less than 5 mg/l after leaffall, Hinton et al. 1997b) are too low to account for high stream DOC concentrations observed during autumn storms. Stemflow, although elevated in DOC concentration (up to 90 mg/l, Hinton et al. 1997b) is insufficient in quantity to significantly raise the stream DOC. Groundwater DOC even at shallow depths below the A horizon (greater than 10 cm below surface) is in general much lower than stream concentrations during stormflow. An evaluation of DOC concentrations and flowpath analysis (Hinton et al. 1997b) indicates that as low DOC groundwater discharges into upper soil horizons in riparian zones near streams, this water is leaching DOC from the litter layer and the A soil horizon. During storms, the area in the catchment where groundwater discharges through shallow soil and litter horizons expands upslope from the stream edge, and stream DOC concentrations increase correspondingly (Hinton et al. 1997b).

The pattern of $\Delta^{14}C$ with DOC (Figure 5b) is consistent with this analysis of water flowpaths and DOC sources, and with the measured ^{14}C in soils. In a study of water-leachable carbon in a soil profile from the Harp 4–21 basin, Trumbore et al. (1991) reported that ^{14}C in both leached DOC and in the residual soil organic carbon declined rapidly with depth. In the litter layer the ^{14}C activity of the leached carbon (170 + 10‰) matched the values measured in maple leaves at Harp in 1991 (179 $\pm$ 10‰). Activities of ^{14}C in leached

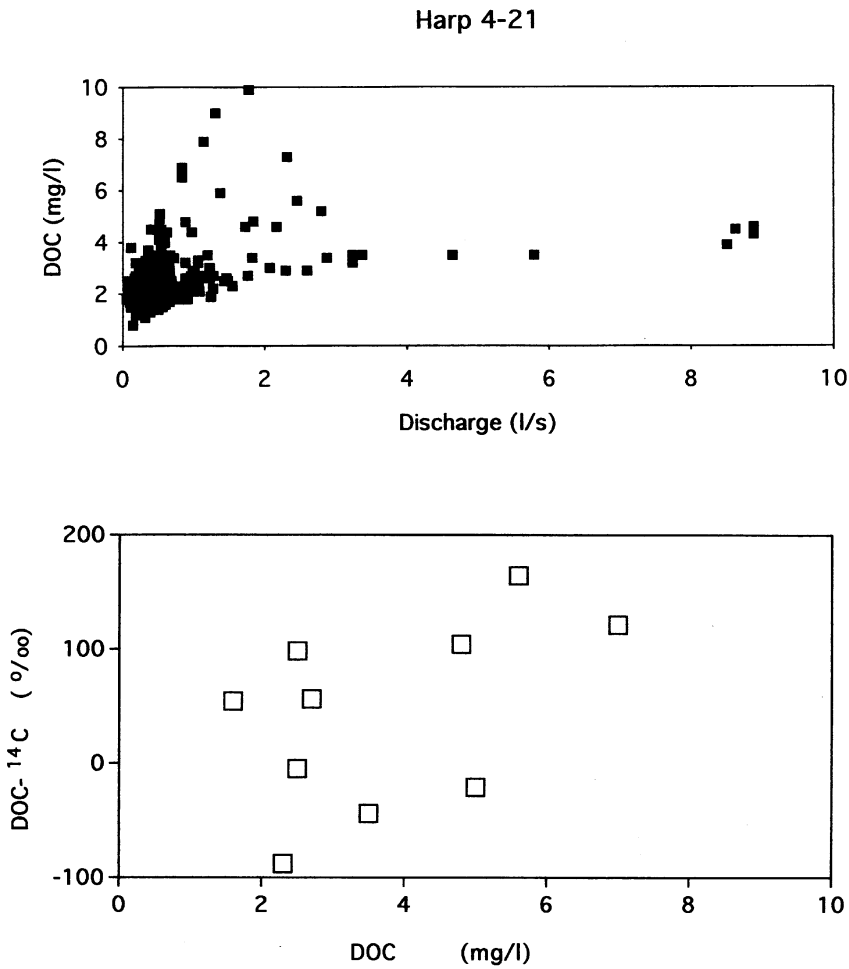

Figure 5. a) DOC concentration versus average daily discharge for Harp 4–21 in 1990–92. All discharge values above 2.5 l/s are spring samples. All DOC values above 6 mg/l are all autumn samples. b) DOC-^{14}C versus DOC concentration for Harp 4–21. Errors in Δ^{14}C are less than the symbol size on the figure.

carbon from the A horizon (120 ± 10‰), although significantly less than the litter values, are still quite high. In the A to B soil transition and upper B horizon (10–25 cm), ^{14}C activities in the leached carbon were +10‰; particulate carbon was less than –150‰ During extremely dry antecedent conditions, the stream at baseflow has low DOC concentrations and DOC-^{14}C values typical of discharging groundwaters, less than 0‰. Seasonal changes in the availability of DOC for flushing near the stream edge probably result in the range of DOC-^{14}C values at low DOC concentrations.

During storms, the corresponding increase in DOC with an increase in DOC-^{14}C to values greater than +100‰ indicates that the source of the DOC flushed during storm events must be the litter or A horizons. Under wet antecedent conditions in the Harp 4–21 basin, the discharging water leaches sufficient DOC in wet riparian areas that late fall and late spring DOC streamwater concentrations, even at baseflow, are higher (Hinton et al. 1997b) and should have significant amounts of bomb ^{14}C.

A natural upper limit exists for the ^{14}C content of the streamwater DOC in Harp 4–21. Because pre-event water is such a large component of stormflow, a portion of the stream DOC must come from discharging groundwaters. Even at the highest DOC concentration measured in conjunction with the ^{14}C samples (7 mg/l; Nov 1990), discharging groundwater with a DOC of 1.5 mg/L contributes at least 15% of the total DOC with a ^{14}C signature similar to the lowest observed value in the stream at baseflow of –88‰. The maximum observed value for the example of Nov 1990 should be 134‰ and is similar to the measured value of 121 $\pm$ 7‰. Thus an input of fresh DOC at contemporary atmospheric ^{14}C activity will always be diluted by the old groundwater component.

The ^{14}C activity of the stream DOC reflects the spectrum of ages of the DOC sources. Although DOC leached from small soil or litter subsamples in the laboratory could conceivably have ^{14}C activities equal to the longterm 1960–1990 average (+395‰) or even above if the organic matter from which the DOC is derived was fixed only during the era of peak atmospheric ^{14}C activity, the litter and A horizons in the entire catchment represent a spectrum of organic matter accumulation rates. In one soil profile (Trumbore et al. 1992), the historical atmospheric signal has been integrated to 170‰ for the litter and 120‰ for the A horizon. A sample of DOC collected from a stream or groundwater will be an average of the DOC reaching that location from all upstream sources. Small scale spatial variations will be averaged out. Values for ^{14}C of upland stream DOC in catchments where the hydrologic flow occurs predominantly at soil depths below the A horizon will always be less than current atmospheric value.

The combination of flowpath analysis and ^{14}C content of DOC suggests that the DOC in upland streams is composed of 2 pools. The first DOC pool is carried to the stream by discharging groundwaters. This DOC has been extensively recycled in the soil zone, has a low ^{14}C content and probably has a low proportion of labile functional groups. Although groundwater contributions to streamflow are high even during storm events, groundwater DOC concentrations are low. The relative contribution of this older recalcitrant pool is limited by the amount of soluble carbon which elutes through the overlying soil column. The second pool is composed of recently fixed and potentially

more microbially labile DOC leached from the A horizon or litter layer. The potential contribution of this second pool is very high especially after leaffall. Leaching experiments have shown that 25% or more of the leaf carbon can be lost within one week (McDowell & Fisher 1976, summarized in Thurman 1985). However, this labile pool can only reach the stream via shallow flowpaths that bypass locations where significant soil sorption occurs.

The relative contributions of these two DOC pools to stream DOC export changes as a function of the hydrology of the catchment and the seasonal changes in the availability of leachable carbon in the litter/A horizons. Most of the DOC is exported during high flow conditions when shallow flowpaths predominate in close proximity to the stream. Thus the majority of the DOC leaving this small upland catchment originates from shallow litter and A horizons within a few metres of the stream and will be composed of recently incorporated (young) labile DOC.

b. Export of DOC from wetlands

A wide variety of wetland types exist on the Precambrian Shield landscape. Many of these wetlands are large reservoirs of organic carbon with up to 7 metres of organic peat deposits. Within forested watersheds, most wetland types are net exporters of carbon as DOC in outflowing streams and positive relationships are observed between catchment area covered by peat and DOC export (e.g. Dillon & Molot 1995).

Within these deep organic carbon deposits, the age of the carbon decreases with depth and can range in age from 8,000 years BP to the present. Very often peat older than 1000 years is found within a metre of the surface (e.g. Bunting et al. 1996; Charman et al. 1993). Despite the existence of old carbon at shallow depths in the peat profile, the ^{14}C data on DOC from streams exiting a variety of wetlands all contain a significant fraction of bomb carbon (Figure 6). Even though there are some seasonal differences in DOC-^{14}C, the values are all above 50‰. Inflowing water to these wetlands is runoff from uplands and upstream wetlands with ^{14}C values ranging from contemporary atmospheric levels (179‰) to older values of discharging groundwaters as seen in Harp 4–21 (Figure 3). Although for some wetlands in Figure 6 there are few seasonal data, there is good seasonal sample distribution for Harp 5, where 13% of the subbasin area is covered by wetlands including a beaverpond and a large mixed conifer swamp just above the catchment outflow weir where the samples were collected. The limited range of these data suggests that the presence of wetlands tends to dampen seasonal oscillations in the ^{14}C signature of exported DOC from catchments. Because many wetland types significantly increase the watershed export of DOC, streams in forested catchments that contain wetlands will have higher DOC concentrations and

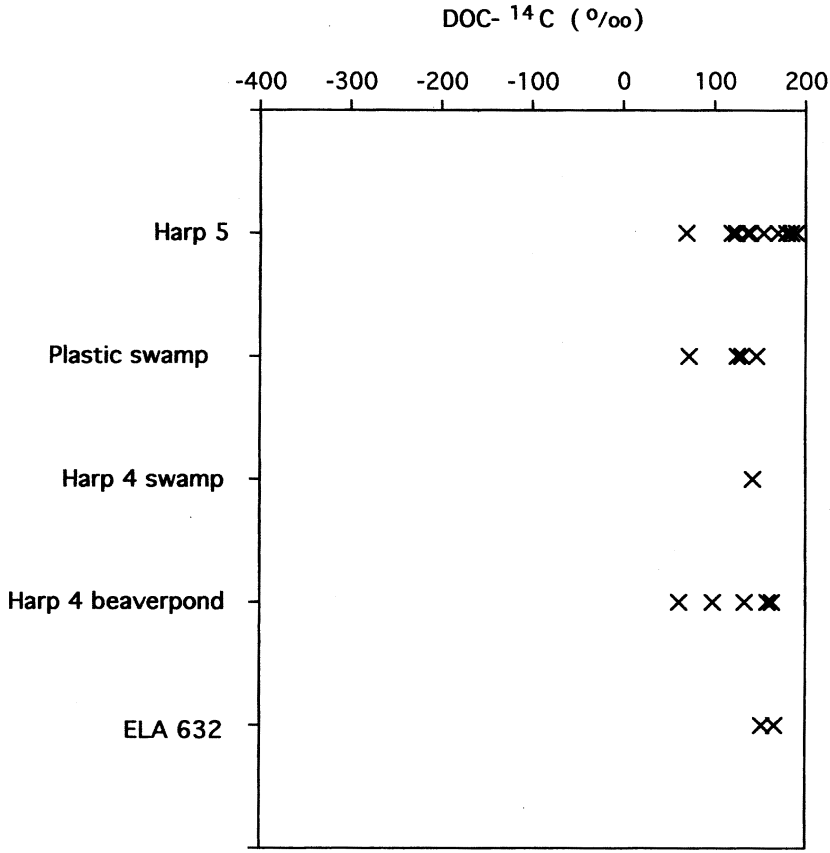

Figure 6. DOC-^{14}C in streams exiting various wetlands. In Harp 5 catchment, 13% of the area is covered by wetlands with the largest wetland, a mixed conifer swamp, located immediately above the gauging weir (Figure 2). Plastic swamp is a conifer swamp located approximately 60 km southeast of Harp Lake. Harp 4 swamp is a mixed hardwood-conifer swamp in the Harp 4 catchment. Harp 4 beaverpond is located in the Harp 4 catchment. ELA 632 is a small bog-poor fen complex located in the Experimental Lakes Area in northwestern Ontario. Errors in Δ^{14}C are less than the symbol size on the figure.

DOC-^{14}C activities. In addition, the dominant flowpaths through wetlands are at or near the wetland surface (e.g. Devito 1994; Mewhinney et al. 1995) resulting in a wetland DOC contribution close to the current atmospheric ^{14}C value. The upper limit for ^{14}C in DOC in wetland outflows should be the ^{14}C of recently fixed carbon.

c. Inflows to Harp Lake

Most catchments in the Precambrian Shield contain wetlands (Dillon & Molot 1997). Often the stream DOC- discharge relationship is a mixture of processes in uplands where DOC increases with increasing discharge and processes in larger wetlands where increased discharge results in a dilution of the wetland DOC pool (e.g. Devito 1994). The Harp 5 stream is the major inflow to Harp lake and discharges to the lake through a large wetland. Highest DOC concentrations occur at low flow (Figure 7a) and the DOC discharge relationship follows a typical dilution curve (e.g. Johnson et al. 1969). Activities of ^{14}C in DOC from Harp 5 are all greater than 100‰ (Figure 7b) indicating a substantial input of recently fixed (and subsequently leached) organic carbon with no strong seasonal pattern.

Harp 4 stream, the second largest inflow to Harp lake drains a mixture of several types of wetlands and upland areas similar to and including Harp 4–21, the beaverpond (Figure 6) and a conifer swamp (Figure 6). The resulting discharge-DOC relationship (Figure 8a) is a composite of increasing DOC with discharge from uplands and dilution curves (decreasing DOC with an increase in discharge) typical of wetlands such as the beaverpond. The relative contribution of uplands and wetlands changes seasonally. DOC-^{14}C in Harp 4 exhibits more seasonality (Figure 8b) than in Harp 5 with values ranging from 21 $\pm$ 13‰ (April 1989) to 179 $\pm$ 28‰ (August 1989). Seasonality is more important than flow in controlling DOC concentration and DOC-^{14}C activity in Harp 4 in contrast to Harp 5.

Harp 3A is a smaller catchment characterized by the presence of organic rich areas located along the riparian stream zone. Harp 3A differs from Harp 4–21 in the shallower depth of soil horizons and the absence of deeper tills which, in Harp 4–21, sustain streamflow from the upland portions of the basin during summer conditions of higher evapotranspiration rates (Hinton et al. 1997b). Although the discharge – DOC relationship (Figure 9a) indicates that any DOC concentration up to a maximum of 6.3 mg/l is possible at low flow conditions, DOC concentrations can reach 9 mg/l during storms (Hinton et al. 1997a). DOC increases with discharge during storms with a slope that is dependant on season and on the frequency of preceding storm events (Hinton et al. 1997a).

Activities of ^{14}C in DOC from Harp 3A are above 0‰ except one value of –173 $\pm$ 5‰ in August 1990 (Figure 9b). This extremely low value corresponds to a period when the stream discharge is at the annual low and the streamwater is derived entirely from the lower 75 metres of the stream (5% of the catchment area) where a thicker deposit of glacial lacustrine silts and clays with sufficient storage capacity slowly releases stored groundwater of low DOC concentration.

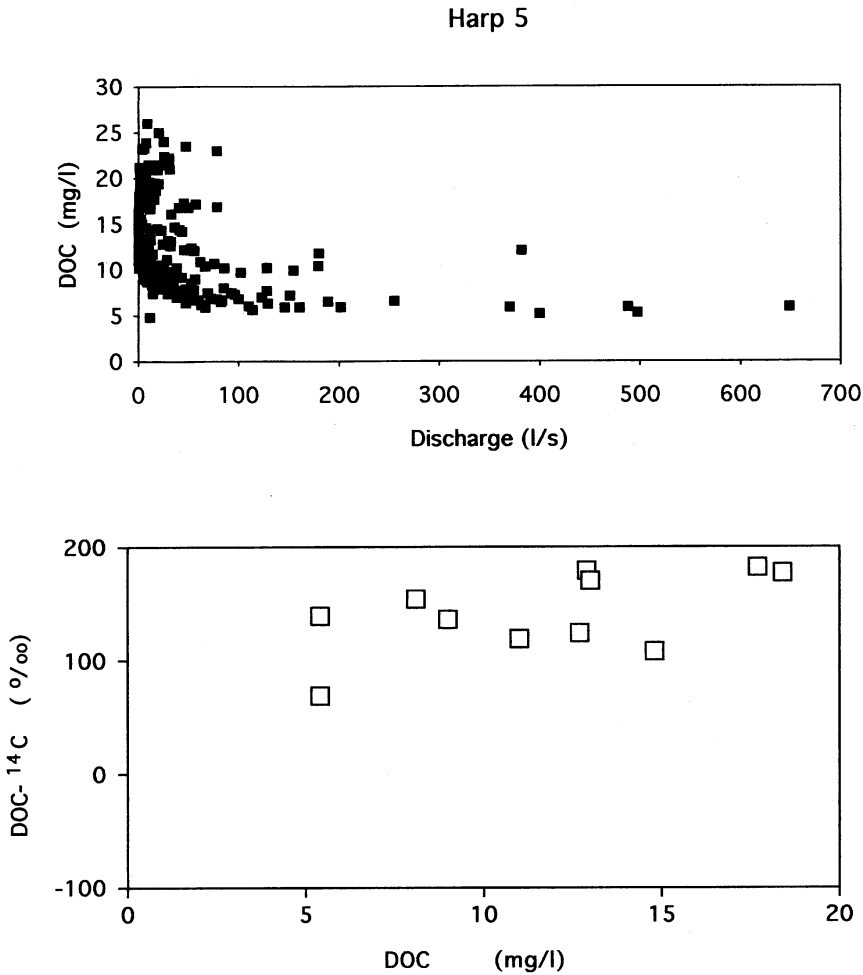

Figure 7. a) DOC concentration versus average daily discharge for Harp 5 in 1990–92. b) DOC-^{14}C versus DOC concentration for Harp 5. Errors in Δ^{14}C are less than the symbol size on the figure.

d. DOC input to Harp Lake

Harp 5 stream dominates the hydrologic inflow to Harp Lake and, because of the high DOC concentrations, the DOC load (Figure 10). A rough estimate of the annual flow weighted DOC-^{14}C input to Harp Lake can be calculated by using the DOC load (Figure 10), the measured DOC-^{14}C values (Figure 3), and interpolating linearly between sampled values for missing ^{14}C data. Contributions from the smaller subcatchments were minor (Figure 10). Monthly values for these subcatchments were extrapolated from ^{14}C analyses on the

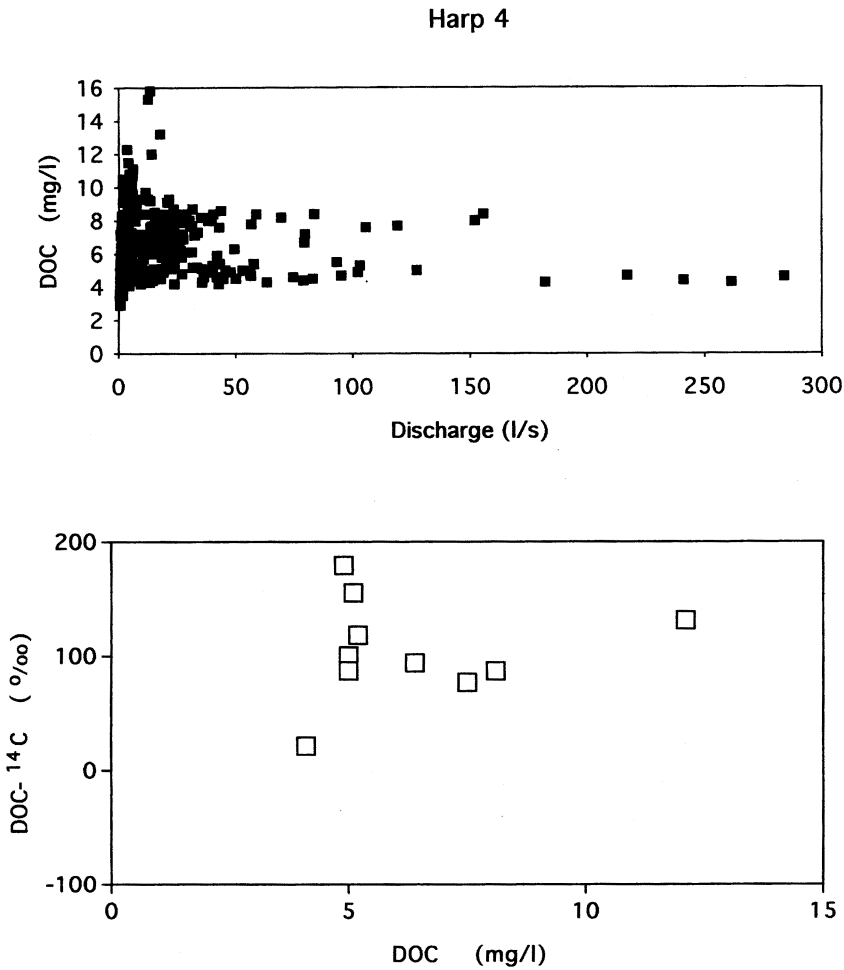

Figure 8. a) DOC concentration versus average daily discharge for Harp 4 in 1990–92. b) DOC-^{14}C versus DOC concentration for Harp 4. Errors in Δ^{14}C are less than the symbol size on the figure.

main subcatchments augmented by analysis of a few DOC-^{14}C samples which agreed well with the major inflow values. Because the Harp 5 stream DOC contains a significant portion of bomb carbon with little seasonal variation, the weighted DOC input to Harp Lake is predominantly modern (Figure 10) with an annual flow weighted average of +139‰.

Problems that plague the construction of whole lake mass balances are even more apparent in the construction of the ^{14}C-DOC mass balance. Loads from gauged/monitored areas must be extrapolated to ungauged areas. At Harp, the ungauged area corresponds principally to the area below the stream weirs.

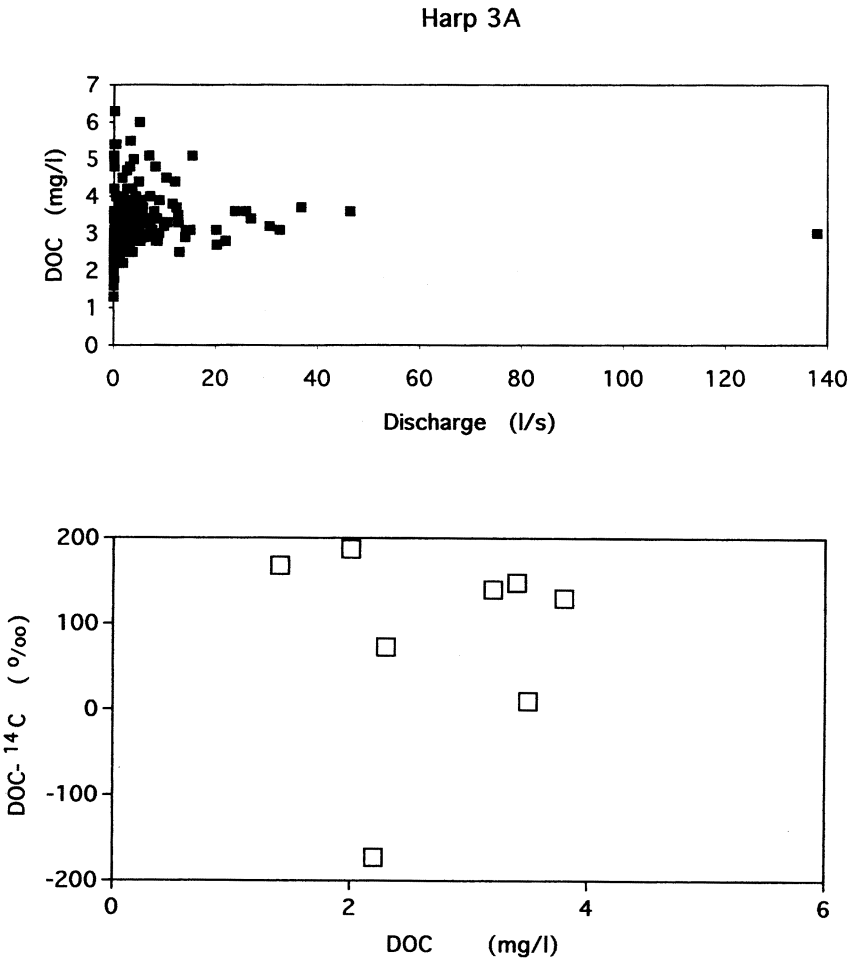

Figure 9. a) DOC concentration versus average daily discharge for Harp 3A in 1990–92. b) DOC-^{14}C versus DOC concentration for Harp 3A. Errors in Δ^{14}C are less than the symbol size on the figure.

This portion is among the smallest in the lakes sampled intensively in the region as part of the Lakeshore Capacity Study (Dillon et al. 1986). However, the ungauged portion is still an important component of the water budget (11.6%, Dillon et al. 1986). Chemical concentrations assigned to inflow from ungauged areas are usually prorated from measured stream concentrations. In the case of DOC, the actual DOC concentrations will depend on whether the water enters via a surface or shallow subsurface flow route (high DOC) or through direct seepage into the lake (low DOC). In addition, in Harp the prorating includes the large contribution by Harp 5 which has high DOC

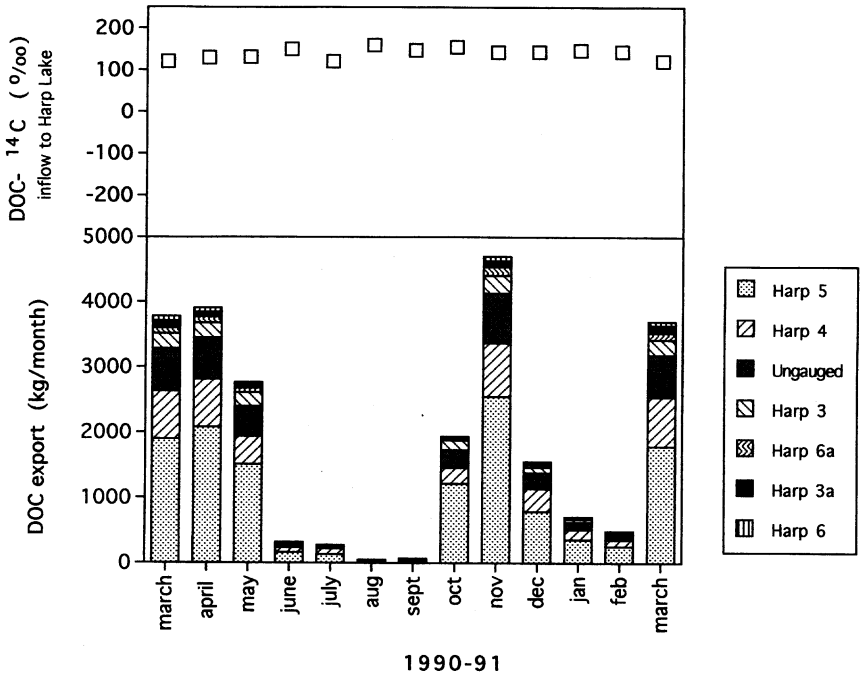

Figure 10. Monthly DOC export from the subcatchments at Harp Lake and the monthly export-weighted DOC-^{14}C input to Harp Lake in 1990–91.

concentrations resulting from the large wetland just above the stream weir. Thus although the ungauged area contributes 11.6% of the water, it contributes 15.3% of the DOC load. However, because a significant portion of DOC export occurs during storms (50% in upper 10% of flow values; Hinton et al. 1997a), and storms are often missed by sampling schedules, the potential overestimate in DOC in the ungauged area will be somewhat balanced by the underestimate due to lack of stormflow values. The same considerations and perhaps balancing of errors holds for the DOC-^{14}C assigned to the ungauged area. In any case, the weighted DOC-^{14}C input calculated for Harp Lake must be viewed with some caution.

The weighted DOC-^{14}C input to Harp Lake although containing a significant component of bomb carbon has less ^{14}C than the measured ^{14}C in deciduous leaves in the Harp basin (179 $\pm$ 10‰). Thus DOC entering Harp Lake is also composed of two pools; a young labile fraction derived from organic matter recently produced and leached comprising most of the DOC and an older recalcitrant pool which is the endproduct of extensive recycling in the soil zone. Lakes are large sinks for dissolved organic carbon, consuming up to one half of the total DOC input (Dillon & Molot 1997). Because

this second pool has undergone extensive recycling in the soil zone where higher rates of microbial activity and high degree of contact with sorbing surfaces occur, it is possible that this second old pool will also be recalcitrant to sorption and decomposition in the lake setting where particle concentrations and microbial biomass are lower. However, this soil-derived DOC has not been exposed to direct sunlight. Decomposition of the older pool DOC in lakes, wetland pools and streams of longer reach may arise from photolysis or interaction with photochemicals (e.g. De Haan 1993; Salonen 1995) but the DOC may also pass largely unperturbed out the lake outflow for lakes without abnormally long water residence times. The young labile pool will be much more susceptible than the older pool to alteration via either decomposition or sedimentation in the lake.

e. Implications for predicting effects of climate change

In lakes, DOC offers protection for aquatic organisms from direct effects of exposure to UV radiation by decreasing UV penetration in the water column (Scully & Lean 1994). Alterations in the DOC budgets of lakes due to climate change and the effects of altered DOC budgets on UV attenuation in lakes is one of the themes of this special issue of Biogeochemistry (Schindler 1997). Quantitative prediction of changes in the hydrologic balance and DOC export of small watersheds is difficult because of the interplay between evapotranspiration, seasonality in the production and export of DOC, and the uncertainties in the magnitudes of potential change in the temperature or the amount and seasonal distribution of precipitation.

The relative importance of the various removal mechanisms for DOC in lakes is largely unknown. Changes in temperature and precipitation will affect both water residence time of the lakes and the export of DOC from catchments. Although Schindler et al. (1997) and Dillon and Molot (1997) have shown that DOC retention is related to water renewal time, these relationships cannot be used to predict DOC retention under altered temperature and precipitation regimes without independent knowledge of in-lake removal decoupled from changes in terrestrial catchment export of DOC.

In spite of these uncertainties, there is likely a lower limit for the DOC concentration in lakes similar to Harp Lake. As long as there is a hydrologic inflow to the lakes from catchments with sufficient soil depth to export some old pool DOC, there will continue to be an input of old pool DOC to the lake. If this old pool DOC is largely recalcitrant to decomposition and sedimentation in the lake setting, the lower limit to the lake DOC concentration will be a function of the export of the old DOC pool to the lake, the water residence time of the lake and the susceptibility of this old pool to photodecomposition by UV radiation. However, photobleaching decreases the photoreactivity of

DOC so that protection of sensitive aquatic resources from direct effects of UV exposure by old DOC may be limited.

Acknowledgements

We thank A. MacLean for assistance in the field. L. Scott and J. Jones of the Dorset Research Centre provided logistical support. M. C. English and two anonymous offered salient criticisms of the manuscript. We gratefully acknowledge the excellent facility for accelerator mass spectrometry at Lawrence Livermore National Laboratory. Funding was provided by a grant from the Natural Science and Engineering Research Council (to S.S.), Tri-council and Geological Society of America scholarships to Marc Hinton, the Ontario Ministry of the Environment and the Waterloo Centre for Groundwater Research.

References

Aravena R, Schiff SL, Trumbore SE, Dillon PJ & Elgood R (1992) Evaluating dissolved inorganic carbon cycling in a forested lake watershed using carbon isotopes. Radiocarbon 34: 636–645

Aravena R & Wassenaar LI (1993) Dissolved organic carbon and methane in a regional confined aquifer: Evidence for associated subsurface sources. Applied Geochem. 8: 483–493

Boutton PW, Wong WW, Hachey DL, Lee LS, Cabrera MP & Klein PD (1983) Comparison of quartz and pyrex tubes for combustion of organic samples for stable carbon isotope analysis. Anal. Chem. 55: 1832–1833

Bunting JM, Warner BG & Aravena R (1996) Late quaternary vegetation dynamics and hydroseral development in a *Thuja occidentallis* swamp in southern Ontario. Can. J. Earth Sciences (in press)

Burcholadze AA, Chudy M, Eristavi IV, Pagava SV, Povinec P, Sivo A & Togonidaze GI (1989) Anthropogenic ^{14}C variations in atmospheric CO_2 and wines. Radiocarbon 31: 771–776

Charman D, Aravena R & Warner B (1993) Carbon dynamics in a forested peatland in north-eastern Ontario, Canada. J. of Ecol. 82: 55–62

Cronan CS (1985) Comparative effects of precipitation acidity on three forest soils: Carbon cycling responses. Plant Soil 88: 101–112

Dankevy SN, Schiff SL, English MC & Dillon PJ (1991) Groundwater flow and chemistry in a small acid-stressed subcatchment in the Canadian Shield. In: Proc. of the NHRI Symposium on Groundwater Contamination. National Hydrologic Research Institute, Saskatoon, Canada

De Haan H (1993) Solar UV-light penetration and photodegradation of humic substances lake water. Limnol. Oceano. 38: 1072–1076

Devito KJ (1994) Hydrologic control of sulphur dynamics in headwater wetlands of the Canadian Shield. PhD Thesis. York University, Toronto, Canada. 210 pp

Dillon PJ & Molot L (1997) Dissolved organic and inorganic carbon mass balances in central Ontario lakes. Biogeochem. 36: 29–42

Dillon PJ, Nicholls KH, Scheider WA, Yan ND & Jeffries DS (1986) Lakeshore Capacity Study: Trophic Status. Ontario Ministry of Municipal Affairs. Toronto Canada. 89 pp

Druffel ERM, Williams PM, Robertson K, Griffin S, Jull AJT, Donahue D, Toolin L & Linick TW (1989) Radiocarbon in dissolved organic and inorganic carbon from the central North Pacific. Radiocarbon. 31: 523–532

Eshleman KN & Hemond HF (1985) The role of organic acids in the acid-base status of surface waters at Bickford watershed, Massachusetts. Water Resources Res. 21: 1503–1510

Hinton MJ, Schiff S & English M (1994) Examining the contributions of glacial till water top storm runoff using two- and three-component hydrograph separations. Water Resources. Res. 30: 983–993

Hinton MJ, Schiff S & English MC (1997a) The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochem. 36: 67–88

Hinton MJ, Schiff S & English MC (1997b) Sources and flowpaths of dissolved organic carbon during storms in two Precambrian Shield catchments. Biogeochem. (submitted)

Hobbie JE & Wetzel RG (1992) Microbial control of dissolved organic carbon in lakes – Research for the future. Hydrobiologia 229: 169–180

Hudson RJM, Gherini SA & Goldstein RA (1994) Modeling the global carbon cycle: Nitrogen fertilization of the terrestrial biosphere and the "missing" CO_2 sink. Global Biogeochem. Cycles 8: 307–333

Jardine PM, Wilson GV, McCarthy JFM, Luxmoore RJ, Taylor DL & Zelazny LW (1990) Hydrogeochemical processes controlling the transport of dissolved organic carbon through a forested hillslope. J. Contam. Hydrol. 6: 3–19

Jeffries DS & Snyder WR (1983) Geology and geochemistry of the Muskoka-Haliburton study area. Dorset Research Centre Ontario Ministry of Environment Data Report DR 83/2: 101 pp

Johnson NM, Likens GE, Bormann FH, Fisher DW & Pierce RS (1969) A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resources. Res. 5: 1353–1363

Lean D & Scully N (1995) Spectral irradiance and photochemical reactions in lakes. Biogeochem. (submitted)

MacLean RA (1993) The role of vadose zone in the generation of runoff from a headwater basin in the Canadian Shield. MA thesis. Wilfrid Laurier University, Canada. 158 pp

McDowell WH & Fisher SG (1976) Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecol. 57: 561–569

Mewhinney E, Aravena R & Schiff S (1995) The hydrology of two contrasting small boreal forest wetlands in Northwestern Ontario. Intern. Assoc. Hydrogeologists Congress, Edmonton, Canada. June 1995

Meyer JL & Tate CM (1983) The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecol. 64: 33–44

Moore TR (1989) Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. 1. Maimai. Water Resour. Res. 25: 1321–1330

Murphy EM, Davis SN, Long A, Donahue D & Jull AJT (1989) Characterization and isotopic composition of organic and inorganic carbon in the Milk River Aquifer. Water Resources Res. 25: 1893–1905

O'Leary MH (1988) Carbon isotopes in photosynthesis. Bioscience 38: 328–336

OME (1983) Ontario Ministry of Environment. Handbook of analytical methods for environmental samples, Lab. Serv. Branch, Rexdale, Ont.

Salonen K (1995) The significance of light degradation of DOM in humic lakes in Finland. Biogeochem. (submitted)

Schiff SL, Aravena R, Trumbore SE & Dillon PJ (1990) Dissolved organic carbon cycling in forested watersheds: A carbon isotope approach. Water Resources Res. 26: 2949–2957

Schindler DW & Curtis PJ (1997) The role of DOC in protecting freshwaters subjected to climatic warming and acidification from UV exposure. Biogeochem. 36: 1–8

Schindler DW et al. (1997) Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. Biogeochem. 36: 9–28

Schindler DW, Bayley SE, Curtis PJ, Parker BR, Stainton MP & Kelly CA (1992) Natural and man-caused factors affecting the abundance and cycling of dissolved organic substances in Precambrian Shield lakes. Hydrobiologia 229: 1–21

Scully NM & Lean DRS (1994) The attenuation of ultraviolet light in temperate lakes. Arch. Hydrobiol. 43: 135–144

Stuiver M & Polach HA (1977) Discussion: Reporting of ^{14}C data. Radiocarbon. 19: 355–363

Thurman EM (1985) Organic geochemistry of natural waters. Martinus Nijhoff/Dr W. Junk Publishers, 497 pp

Trumbore SE (1993) Comparison of carbon dynamics in two soils using measurements of radiocarbon in pre- and post-bomb soils. Global Biogeochem. Cycles 7: 275–290

Trumbore SE, Schiff SL, Aravena R & Elgood R (1992) Sources and transformation of dissolved organic carbon in the Harp Lake forested catchment: The role of soils. Radiocarbon. 34: 626–635

Vance GF & David MB (1991) Forest soil response to acid and salt additions of sulfate: III. Solubilization and composition of dissolved organic carbon. Soil Science 151: 297–305

Vogel JS, Nelson DE & Southon RJ (1987). ^{14}C background levels in an accelerator mass spectrometry system. Radiocarbon. 29: 323–333

Wassenaar L, Aravena IR, Hendrey MJ & Fritz P (1991) Radiocarbon in dissolved organic carbon- a potential groundwater dating method: Case studies from western Canada. Water Resources Res. 27: 1975–1986