Biogeochemistry **41:** 175–197, 1998.

Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield

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Accepted 29 September 1997

Key words: carbon cycling, dissolved organic carbon (DOC), forested catchments, nutrient export, Precambrian Shield streams, storm runoff

Abstract. Dissolved organic carbon (DOC) concentrations and export were studied in two small catchments in central Ontario to examine DOC sources and to assess the hypothesis that organic matter adjacent to the stream is a significant contributor of DOC during storms. Different DOC dynamics and exports were observed according to the depth of the riparian water table. In Harp 4-21, riparian flowpaths were predominantly through A and upper B soil horizons and riparian soils contributed between 73 and 84% of the stream DOC export during an autumn storm. In Harp 3A, riparian flowpaths were predominantly through lower B horizons. Consequently, riparian soils were less important and hillslopes contributed more than 50% of the stream DOC export in subcatchments without wetlands during storms. Wetlands and adjacent soils contributed significantly to DOC export in Harp 3A; 8% of the total catchment area exported 32 to 46% of the storm runoff DOC. DOC export dynamics in wetlands and riparian soils were distinctly different. In wetlands, transport was affected by leaching and flushing of DOC at the wetland surface leading to lower DOC concentrations with successive storms. In riparian soils, groundwater flowpaths were more important and stronger positive relationships between discharge and DOC concentration were observed. Precipitation, throughfall and stemflow were minor sources of stream DOC during storms and contributed less than 20% of the total export.

Introduction

Recent reviews have highlighted the ecological significance of groundwater interactions with streams (Brunke & Gonser 1997) and the incomplete understanding of the sources, fluxes and pathways of groundwater dissolved organic carbon (DOC) contributions to streams (Kaplan & Newbold 1993). While several studies have observed groundwater DOC concentrations that exceed stream DOC (Rutherford & Hynes 1987; Fiebig 1995) and several authors recognize the significance of subsurface flowpaths (Hemond 1990; Kaplan

& Newbold 1993), few studies actually relate stream DOC dynamics with groundwater flowpaths (Easthouse et al. 1992).

An issue closely associated with that of groundwater flowpaths is the geographical location of DOC sources within watersheds. Hemond (1990) suggested that in glaciated catchments with shallow soils and bedrock, riparian wetlands and soils are the dominant sources. Using an annual organic carbon budget for a watershed in the Atlantic Coastal Plain, Dosskey & Bertsch (1994) demonstrated that 90% of the DOC originated in riparian wetlands that occupy only 6% of the watershed area. Even though uplands cover a greater area within the watersheds, they are thought to contribute a small proportion of the exported DOC because DOC sorbs to mineral soils prior to reaching the stream.

To examine DOC sources, it is necessary to consider storms since storm runoff exports much of the DOC from small watersheds (Grieve 1984; Hinton et al. 1997). Conceptual hydrological models of stormflow generation emphasize hydrological processes with different water flowpaths in the riparian zone (Freeze 1974; Ward 1984; Wood et al. 1990). Hemond (1990) and Kaplan & Newbold (1993) discuss the significance of subsurface flowpaths near the stream on DOC sources and flowpaths. Because the relative importance of water flowpaths through different soil horizons can vary with soil moisture and groundwater levels, DOC pathways and fluxes may differ substantially from baseflow to stormflow conditions and produce changes in both DOC quality and quantity during storms (Jardine et al. 1990; Easthouse et al. 1992). Similarly, the dominant sources and pathways of stream water and DOC may differ among catchments or even within a single catchment during different storms (McDowell & Likens 1988). Therefore, it is necessary to study DOC dynamics in areas where flowpaths have been delineated.

Harp Lake has been the focus of several investigations examining the hydrologic flowpaths (Dankevy 1989; Hinton et al. 1993, 1994; MacLean, 1992; MacLean et al. 1995; Devito et al. 1996) and carbon cycles (Schiff et al. 1990, 1997; Aravena et al. 1992; Trumbore et al. 1992; Molot & Dillon 1996; Dillon & Molot 1997; Hinton et al. 1997) of watersheds with uplands or wetlands. This paper examines DOC concentrations and export in relation to water flowpaths during runoff events in two small catchments of Harp Lake. The purposes are 1): to compare the transport of DOC along different hydrologic pathways during runoff events; 2) to compare the relative DOC contributions from riparian and upland hillslope areas; and 3) to examine some of the hydrological and physical controls on DOC transport to streams.

Site description

Hydrologic response to storms and DOC concentrations were monitored in two small and adjacent catchments in central Ontario, Canada (Figure 1). Both catchments, Harp 4-21 with an area of 3.7 ha and Harp 3A with an area of 21.7 ha, have podzolic soils and mixed forests dominated by sugar maple (*Acer saccharum*) (Lozano et al. 1987). Harp 4-21 and the northern half of Harp 3A are underlain by Precambrian Shield amphibolite and schist bedrock, whereas the southern half of Harp 3A is underlain by granitized biotite and hornblende gneiss (Jeffries & Snyder 1983). The shape and steepness of the hillslopes and the total sediment thickness differs between the catchments. Most hillslopes in Harp 4-21 are gentle to moderately steep (≈8 to 30%) and are slightly concave towards the stream. In Harp 3A, hillslopes are steeper (≈20 to 50%), straighter, and end in nearly flat valley bottoms. Glacial till is up to 15 m thick in Harp 4-21 whereas the soils and till along the hillslopes of Harp 3A rarely exceed 1.5 m. The lower 50 m of the Harp 3A stream is incised in 2 m of sand and is underlain by approximately 2 m of clay.

Harp 4-21 and Harp 3A are subdivided into two (S1 and S4) and five (W1-W5) subcatchments respectively (Figure 1). All subcatchments drain predominantly hillslope areas; less than 1% of Harp 4-21 and 4% of Harp 3A are covered by surface water (including streams and wetland ponds). Wetlands 2 and 3 occupy the flat valley bottoms of W3 and W4 respectively. Although subcatchment W1 only has small areas of ponded water, it is influenced by wetland runoff from W3 and W4. An ephemeral stream draining the easternmost hillslopes of Harp 3A flows over a bedrock outcrop at B1.

Methods

Samples of precipitation, throughfall, stemflow, overland flow, groundwater, water ponded in wetlands and stream water were collected in autumn 1992 (September 27 to November 20) and spring 1993 following snow melt (May 2 to June 4). Throughfall, groundwater and stream samples from Harp 4-21 were also collected during selected storms between March 1989 and April 1990. Precipitation was collected at a meteorological station less than 500 m north of the Harp 4-21 catchment. In 1992 and 1993, throughfall volumes were measured and samples were collected from four sites: two beneath a deciduous canopy (one in Harp 4-21, one in Harp 3A) representative of hillslopes and two beneath a coniferous canopy of cedars (*Thuja occidentalis*) and black spruce (*Picea mariana*) that predominate in wetland 2 of Harp 3A. Precipitation and throughfall samples were collected in polyethylene funnels that drained into 20 l glass bottles. Although polyethylene screening (1 mm

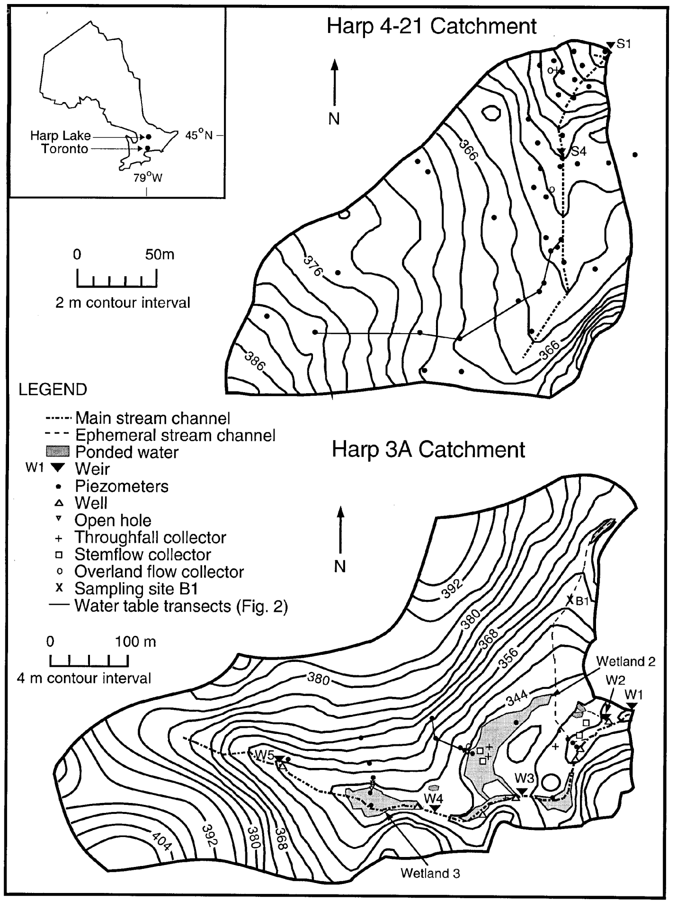

Figure 1. Location and instrumentation of the Harp 4-21 and Harp 3A catchments.

mesh) was placed at the neck of the funnels to prevent falling leaves from entering the bottles, at least four throughfall samples were likely to have been contaminated by leaves and organic matter that fell into the funnels between or during storms. Stemflow samples were collected from one sugar maple, one white birch (*Betula papyrifera*) and two cedar trees using polyethylene tubing that drained into 1 l polyethylene bottles.

Stemflow from deciduous trees overflowed the 1 l collection bottles except during the smallest storms. For the purpose of calculating DOC fluxes, the depth of stemflow from deciduous trees is estimated from the empirical relationship SF = 0.062 P − 0.13 where stemflow (SF) and precipitation (P) are expressed in mm (Helvey & Patric, 1965). Measured water depths of stemflow from the cedars were negligible ($<$0.2 mm). The empirical relations for throughfall (TF), TF = 0.92 P − 0.54 and TF = 0.88 P − 3.0 (expressed in mm) for the deciduous and coniferous stands respectively, were calculated on a storm basis and compare well with those of Helvey & Patric (1965).

Overland flow was sampled from two collectors in Harp 4-21 and one collector in Harp 3A. Collectors were made from PVC pipe that was cut in half lengthwise, screened, capped at both ends, inserted at ground surface below the litter, and drained by gravity to 1 l polyethylene bottles.

Groundwater samples were collected from piezometers that were screened at various depths (0.04 to 7.8 m) along the hillslopes, in the streams, in riparian areas and in the wetlands. Screen lengths varied from 0.08 to 0.5 m and some shallow piezometers were constructed to collect groundwater flowing through the A or upper B soil horizons. Groundwater levels were measured manually in piezometers, wells and shallow (0.15 to 0.2 m) open holes.

Streams were sampled several times during each storm at W1-W5, S1, S4, and B1 during the autumn, and at W1, W3-W5, S1 and S4 during the spring (Figure 1). Stream discharge was monitored continuously using V-notch weirs and water level recorders at all sites except B1 where instantaneous measurements of discharge were made. Rating curves were calibrated from numerous instantaneous measurements of discharge and stage during storms. Stream DOC exports were calculated by interpolating DOC concentrations according to stream discharge as described in Hinton et al. (1997).

Stream, wetland, stemflow and groundwater samples were prefiltered in the field through 80 μm (44 μm for groundwater) polyester screening into site-designated polyethylene bottles. Precipitation, throughfall and overland flow samples were not prefiltered. All 1992 and 1993 samples were filtered within 24 hours through 0.45 μm Sartorius® cellulose nitrate membranes (25 mm diameter) into glass scintillation vials. Cellulose nitrate membranes were rinsed by passing a minimum of 75 ml of sample through the filter prior to sample collection. Experiments with deionized (Nanopure) water and with a HCl solution (pH = 4.3) demonstrated that the cellulose nitrate membranes rinsed in this way contributed only 0.04±0.07 mg/l and 0.06±0.03 mg/l respectively to the filtrate. Samples were acidified with HNO_3 to a pH near 2 and kept refrigerated in darkness until analyzed by high temperature combustion with a Dohrmann DC-190 total carbon analyzer. The instrument blank measured 0.1 mg/l. All results are reported in mg C/l.

DOC concentrations reported from 1989 and 1990 were analyzed by the Ontario Ministry of the Environment (MOE) by the persulfate oxidation method (MOE 1983). All MOE samples were prefiltered as described above but were not passed through the 0.45 μm membranes. To account for differences in analytical methods, filtering and preservation, 33 pairs of samples were compared. The results demonstrated that MOE samples were lower than the 0.45 μm filtered samples by an average of 0.8 $\pm$ 0.4 mg/l in the range of 2–12 mg/l. It is not apparent whether the difference is due to differences in sample treatment or analytical method. All 1989 and 1990 MOE results have been normalized by +0.8 mg/l for comparison with the other analyses.

The mass of DOC transported along flowpaths is calculated by multiplying the volume of flow by the average DOC concentration. The volume of water that originated from a particular hillslope between November 2 and 9, 1992 is estimated as the total stream discharge minus the volume of precipitation that fell onto the riparian area. This calculation is justified by time domain reflectometry measurements of soil water in riparian areas which demonstrate that there is almost no net storage of water during storms. The extent of riparian areas was delineated by the occurrence of the water table within the organic-rich soil horizons (A, O and upper B) adjacent to the stream.

Results

Hydrological flowpaths

In Harp 4-21, the depth to the water table increased with increasing distance from the stream. At baseflow, the water table was positioned within the upper B or lower A horizons adjacent to the stream, within the middle to lower B horizon in the lower portion of the hillslopes, and within the till in the upper hillslopes (Figure 2) (Hinton et al. 1993). Groundwater discharging from the till into the soils near the stream maintained high water table levels, creating saturated conditions and maintaining stream baseflow throughout the year along the Harp 4-21 stream. Baseflow was sustained by deep groundwater flowing from the till directly through the stream bed and through the lower B horizons of riparian soils. During storms, groundwater levels near the stream and along the lower hillslope rose into soil horizons so that most of the subsurface flow to the stream passed through shallow soil horizons (A and upper B) (Figure 2).

In Harp 3A, the water table remained near the base of the B horizon along the length of the hillslope. The water table generally intersected the A or O horizons for a small distance at the edge of the stream or wetlands (Figure 2). During storms, the water table in the hillslope usually remained within the lower B horizon and subsurface flow during storms occurred mostly in the lower B horizon (40–60 cm depth). Riparian water tables and flowpaths varied within Harp 3A and the extent of subsurface flowpaths through shallow soil horizons was limited to the lower 1 to 10 meters of hillslopes in most areas. Only during the very large storms on November 13 (88 mm of precipitation) did hillslope groundwater levels rise into the upper B horizon. During dry

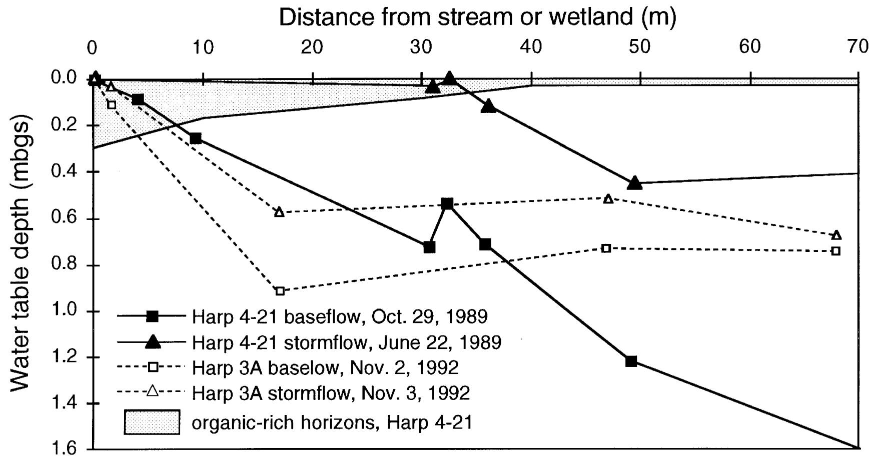

Figure 2. Depth to water table during baseflow and stormflow conditions in Harp 4-21 and Harp 3A. Stippled area shows the approximate depth of organic-rich horizons in Harp 4-21. Locations of transects are shown in Figure 1.

summer conditions, the entire hillslopes became unsaturated and most of the Harp 3A stream was dry.

Hydrograph separations using ^{18}O and dissolved Si concentrations demonstrated that more than 75% of the storm runoff in Harp 4-21 consisted of soil water or groundwater (Hinton et al. 1994). High Si concentrations in deep groundwaters and stream discharge showed that a significant proportion (up to 70%) of the runoff involved deep groundwater that flowed through the till, discharged into soil horizons near the stream where it mixed with soil water, and flowed to the stream. Hydrograph separations in Harp 3A during the November 2, 1992 storm suggest that groundwater and soil water contributed approximately 85% of peak runoff. Thus, in both Harp 4-21 and 3A, stream stormflow is dominated by subsurface water.

DOC concentrations

The pattern of DOC concentrations through the hydrologic cycle (Figure 3) are typical of those reported in other catchments (McDowell & Likens 1988; Moore 1989). DOC concentrations of precipitation were low; throughfall and stemflow concentrations increased from contact with live vegetation. Overland flow and groundwater in the A horizon typically had similar or higher DOC concentrations than throughfall which indicates production of DOC in litter and high organic matter soil horizons. DOC removal as a result of sorption or decomposition within the soil is suggested by lower DOC concentrations in groundwaters from the B horizon or deeper. In wetlands,

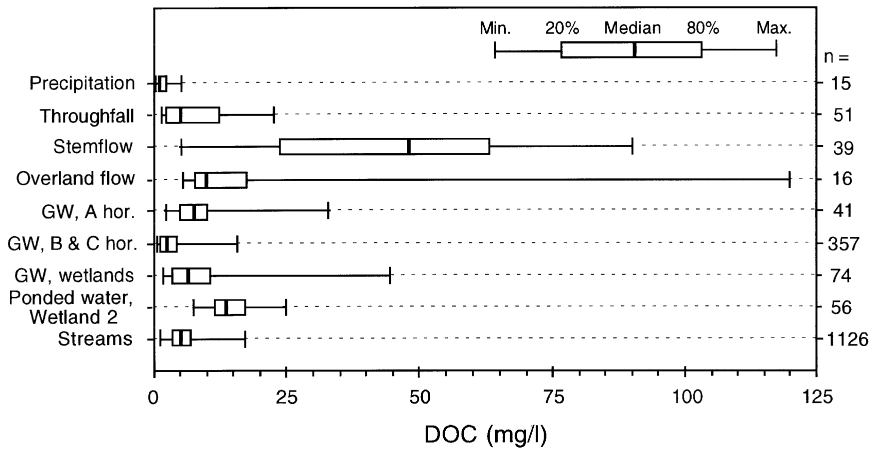

Figure 3. DOC concentrations of waters in Harp 4-21 and Harp 3A (1989-1993) (GW = groundwater, hor. = soil horizon, and *n* = number of samples).

groundwater DOC concentrations varied substantially but were generally higher than those in the hillslope. Similarly, higher DOC concentrations in surface water within wetland 2 may have been caused by production of DOC and/or leaching of litter, organic matter and vegetation within the wetland.

Stream DOC concentrations and concentration changes during storms differed between the subcatchments. Harp 3A subcatchments showed variable increases in DOC concentrations during storms with no response to spring storms at W5 (Figure 4, Table 1). In Harp 4-21, both S1 and S4 showed larger increases in DOC concentrations during storms (Table 1) that were more closely related to discharge. Whereas seasonal regressions between DOC concentration and discharge were significant ($P < 0.01$) at S1 and S4, similar regressions at W3 and W4 (subcatchments with wetlands) were not significant (Hinton et al. 1997). In Harp 3A, the wetlands were obvious sources of DOC to the stream as average DOC concentrations increased from W5 to W4 to W3 in both seasons during baseflow and stormflow conditions (Table 1).

Groundwater DOC concentrations varied spatially along flowpaths (Table 2). In Harp 4-21, the DOC concentrations within the till were low both along the hillslopes (mean = 2.3 mg/l) and in deep piezometers near the stream (mean = 1.5 mg/l) but increased as groundwater flowed through the B (mean = 4.7 mg/l) and A (mean = 8.9 mg/l) soil horizons near the stream. In Harp 3A, there were larger temporal variations in DOC concentrations within individual piezometers and larger spatial variations among piezometers than in Harp 4-21. Piezometers within the lower B horizon and within the till along the hillslopes of Harp 3A had a mean DOC concentration of 5.1 mg/l. Within the sandy horizons beneath the wetlands and the clays in the lower

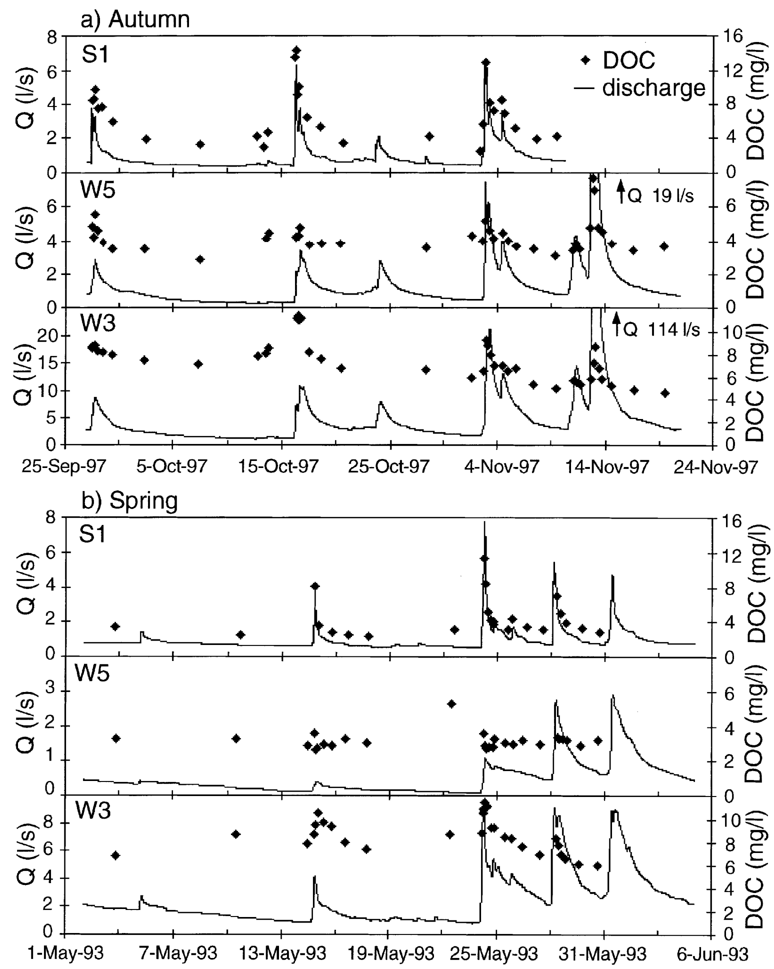

Figure 4. Stream DOC concentrations at S1, W5 and W3 during the a) autumn and b) spring sampling periods.

portion of the catchment, the groundwater DOC concentration averaged 2.8 mg/l. However, moderate to low hydraulic conductivities within the wetlands and in the clays suggest that these groundwaters are minor contributors to streamflow. Wetland DOC concentrations were higher with average values of 7.6 mg/l within the organic soils of wetlands, and 14.0 mg/l at the surface of wetland 2.

Table 1. Flow-averaged DOC concentrations for periods of stormflow, baseflow and total flow during the autumn and spring sampling periods (Hinton et al. 1997).

	Average DOC concentration (mg/l)					
	Autumn 1992			Spring 1993		
Site	Stormflow	Baseflow	Total flow	Stormflow	Baseflow	Total flow
W1	6.5	4.8	5.8	6.0	4.7	5.2
W2	5.5	3.4	4.6	–	–	–
W3	7.4	6.4	6.9	8.5	7.6	7.8
W4	6.4	5.0	5.7	5.8	5.1	5.3
W5	5.0	3.6	4.4	3.2	3.2	3.2
S1	8.0	4.1	5.7	5.8	3.1	3.8
S4	7.1	3.9	5.2	–	–	–

DOC contributions along flowpaths

Throughfall and stemflow were minor contributors to stream DOC and discharge. Hydrograph separations using ^{18}O indicate that they contributed 23% of the total runoff during the October 31, 1989 storm onto a leafless canopy in Harp 4-21 (Hinton et al. 1994). With a measured throughfall DOC concentration of 4.1 mg/l and an assumed stemflow concentration of 34 mg/l (the volume-weighted mean concentration from autumn 1992 for deciduous trees), the total DOC export that originated from throughfall and stemflow was approximately 18% (12% and 6% respectively). During the dormant season in Harp 3A, the mean throughfall DOC concentrations (2.3–4.0 mg/l) were lower than stream baseflow by 1.0 mg/l to 2.4 mg/l with the exception of one storm (Nov. 4, 1992, 10.4 mg/l) where throughfall samples may have been contaminated by fallen leaves in the collectors. Lower throughfall DOC would contribute to a net dilution of stream DOC yet all these storms exhibited increases in stream DOC concentrations.

Similar calculations for the June 22, 1989 storm indicate that throughfall and stemflow contributions to stream discharge and DOC were also minor in the growing season. Together, they contributed 17% of the total runoff (Hinton et al. 1994) and approximately 12% of the total DOC flux in Harp 4-21. The DOC flux was estimated by using the measured throughfall DOC concentration of 2.3 mg/l and the weighted mean stemflow DOC concentration of 55 mg/l from spring 1993. The low throughfall DOC concentration may result from the high rainfall intensity of this storm or spatial variability in throughfall DOC concentrations. In Harp 3A, the small proportion of throughfall and stemflow in stream runoff ($<15\%$) suggests that throughfall and stemflow were also insufficient in volume to contribute much of the total stream DOC export.

Table 2. Average DOC concentrations of groundwaters and ponded water in Harp 4-21 and Harp 3A.

Harp 4-21	Depth range[1] (m)	Average [DOC] (mg/l)	*np*	*n*	Harp 3A	Depth range[1] (m)	Average [DOC] (mg/l)	*np*	*n*
Hillslope, till	0.9–6.8	2.3 ± 1.3	14	61	Hillslope, B horizon	0.27–1.6	5.1± 2.3	11	56
Riparian, lower B or till	0.69–2.9	1.5 ± 0.5	11	100	Riparian and beneath wetlands, C horizon	1.5–2.9	2.8 ± 1.3	5	38
Riparian, middle B horizon	0.16–0.53	4.7 ± 1.7	7	62	Riparian and lower hillslope, A or upper B horizon	0.04–0.08	14.3 ± 13.1	4	11
Riparian, A or upper B horizon	0.12–0.13	8.9 ± 3.2	3	27	Wetlands, organic sediments	0.08–1.23	7.6 ± 5.7	10	74
					Wetland 2, ponded water	0.00	14.0 ± 3.3	–	56

Mean DOC concentrations of individual piezometers are averaged. Total number of piezometers (*np*) and samples (*n*) are indicated.
[1] piezometer mid-screen depths.

Overland flow was observed in both Harp 3A and Harp 4-21 during storm events. Whereas the extent of overland flow varied seasonally in both catchments, the temporal and spatial distribution of overland flow was much more variable in Harp 3A. The overland flow collector in Harp 3A was poorly located and malfunctioned so that only one overland flow sample with a DOC concentration of 90 mg/l was collected from the October 16, 1992 storm. The two overland flow collectors in Harp 4-21 were more successful and collected samples with DOC concentrations that range from 5.5 mg/l to 120 mg/l. Nearly all these results were greater than stream DOC concentrations (Figure 3) and suggest that overland flow could have been an important pathway of DOC to streams during storms if the volumes were substantial. The large spatial and temporal variability of overland flow volumes and DOC concentrations make it difficult to estimate reasonably the input of DOC to streams along this flowpath. Because overland flow in these basins includes both groundwater discharge and throughfall, hydrograph separations of the streams cannot be used to distinguish overland flow from soil or groundwater flow.

Groundwater flow through the shallow soil horizons adjacent to the stream represents a major flowpath for DOC in Harp 4-21. If we assume that the entire increase in soil water and groundwater discharge (i.e. above baseflow) during the October 31, 1989 storm flowed through the A and upper B horizons and had the average DOC concentration of 11.0 mg/l (n = 6) measured in piezometers P34-01 (0.03–0.19 m depth) and P46-01 (0.06–0.22 m depth) prior to and during that storm, the mass of DOC flowing through the shallow riparian horizons would equal 73% of the total DOC exported by the stream.

Riparian and wetland vs. hillslope sources of DOC

To demonstrate the significance of DOC production in riparian and wetland areas, DOC export from hillslopes and streams are compared for storms between November 2 and 9, 1992 (Table 3). The range of hillslope DOC export was calculated by assuming that the average DOC concentration of groundwater in hillslope ranged between that of stream baseflow (at S1 and W5) and that of hillslope piezometers. In Harp 4-21, the hillslope accounted for between 16 and 27% of the total DOC export from the stream. Therefore, most of the DOC exported during storms must have originated either in riparian areas or within the stream.

Hillslope transport of DOC to the riparian and wetland areas was more important in Harp 3A than in Harp 4-21 and varied between 37 and 68% of the total stream DOC export (Table 3). In the subcatchments without wetlands, W1 and W5, between 50–93% and 62–115% respectively of the stream DOC export originated from the hillslope. Even the lower ranges of these estimates

Table 3. Hillslope and stream export of DOC between November 2 and 9, 1992.

	Hillslope			Stream	
	Water volume (m^3)	DOC export[1] (kg)	% of stream export	Water volume (m^3)	DOC export (kg)
Harp 4-21					
S1	350	0.51–0.91	15–26	430	3.5
S4	320	0.47–0.82	16–28	530	3.0
Total	670	0.98–1.73	16–27	960	6.5
Harp 3A					
W1	1920	5.4–9.9	50–93	2240	10.7
W3	1260	3.5–6.5	22–40	1710	16.2
W4	1170	3.2–6.0	35–64	1570	9.4
W5	1120	3.1–5.7	62–115	1240	5.0
Total	5470	15.2–28.1	37–68	6760	41.3

Total precipitation during this period was 46 mm. Results are net values for each subcatchment (e.g. W4 values are calculated from W4–W5).
[1] Using a range of DOC concentrations based on stream baseflow and groundwater (1.5–2.6 mg/l in Harp 4-21 and 2.8–5.1 mg/l in Harp 3A).

in Harp 3A exceeded the upper ranges of estimates from S1 and S4 in Harp 4-21.

The wetlands were a significant source of DOC near the stream in Harp 3A. Whereas riparian areas in W5 contributed less than 38% of DOC export, the riparian areas and wetlands in subcatchments W3 and W4 contributed between 60–78% and 36–65% of the subcatchment stream DOC (Table 3). These areas exported 32–46% of the total DOC export from Harp 3A even though they occupy only 8% of the total catchment area. The effect of wetlands and riparian areas on DOC export is also evident when the seasonal DOC yields are compared for the different subcatchments (Table 4). The DOC yields from subcatchments with wetlands (W3 and W4) were comparable to those with riparian DOC sources (S1) and were much larger than the yields from subcatchments without wetlands (W1 and W5).

Wetlands and in-stream sources of DOC

The increase in average groundwater DOC concentrations from hillslopes to wetlands to ponded water in wetland 2 (Table 2) suggests that the source of DOC within the wetland originates either from organic matter at the wetland surface or from contact of groundwater with organic matter prior to discharg-

Table 4. DOC and water yields within each subcatchment of Harp 3A in the autumn and spring sampling seasons.

	W1	W3	W4	W5	S1
Autumn[1] DOC yield (g m^{-2} y^{-1})	1.1	8.9	4.8	2.6	4.1
Autumn[1] water yield (mm)	97	104	82	80	88
Spring[2] DOC yield (g m^{-2} y^{-1})	−0.1	6.0	2.5	0.8	2.7
Spring[2] water yield (mm)	43	42	36	19	58

Results are net values for each subcatchment (e.g. W4 values are calculated from W4–W5).
[1] September 27–November 10, 1992.
[2] May 2–May 31, 1993.

ing to the wetland surface. The hydraulic conductivities that were measured within the wetlands decrease rapidly with depth ($\approx 10^{-5}$ m/s near the surface at 0.1 m depth, $\approx 10^{-7}$ to 10^{-6} m/s at depths >0.5 m) and suggest limited groundwater flow through the base of the wetland and greater flow through more permeable shallow organic horizons at the wetland edge.

The response of stream DOC during storms at W3 and W4 suggests DOC production by decomposition and leaching of organic matter by ponded water as a source of DOC and episodic flushing as a transport process of DOC from wetlands to the stream. The clockwise loops in Figure 5 show that DOC concentrations were usually higher during the rising limb than on the falling limb of the hydrographs at W3 and W4. Site S1 did not show these loops and site W5 only had small loops during two small autumn storms. Higher DOC concentrations on the rising limbs may have been caused by the flushing of high DOC water from the relatively stagnant portions of the wetland as water levels rose and the pools became more interconnected. The DOC concentrations in wetland 2 during baseflow conditions varied spatially with values that ranged from 5.3 to 17.1 mg/l during one autumn sampling and from 10.3 to 26.5 mg/l during a spring sampling when the pools were poorly interconnected. Samples of water flowing across wetland 2 collected during storms showed that DOC concentrations initially increased as water levels rose and stagnant pools became connected (Figure 6). When water levels were extremely high and all the pools were interconnected during the large storm on November 12, 1992, wetland DOC concentrations remained low as there were no stagnant areas and most pools were continuously flushed. Alternatively, a larger volume of water in the wetland during this storm may simply have diluted the DOC.

With the exception of wetlands, in-stream sources of DOC are unlikely in Harp 3A and Harp 4-21. The stream beds are sandy with little organic matter and no debris dams. In fact, the Harp 3A stream between W3 and

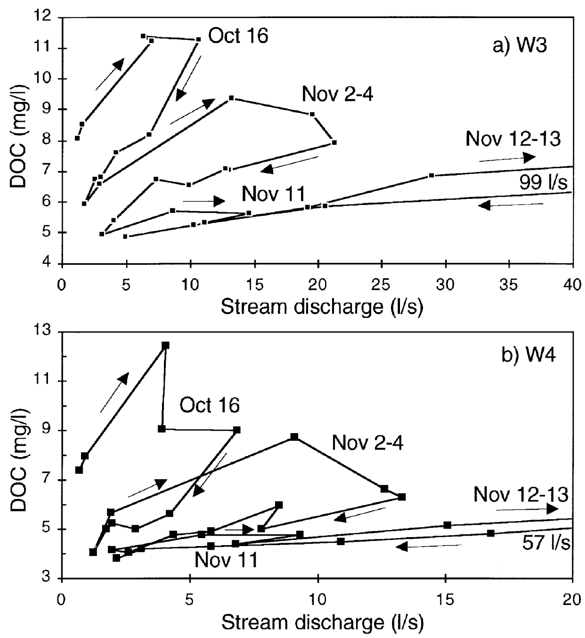

Figure 5. DOC concentrations versus stream discharge during autumn 1992 storms at a) W3 and b) W4. Arrows indicate the progression of time.

W1 was a net sink of DOC. A conservative estimate of the total mass of DOC that entered the stream between W3 and W1 (W3 export + W2 export + B1 stream export + groundwater discharge) exceeded DOC export at W1 by 8 kg in the autumn and 11 kg in the spring or 4% and 27% of total DOC export respectively. In the spring the DOC export at W3 was greater than that measured at W1 so that the loss of DOC between W3 and W1 exceeded the DOC production from the W1 subcatchment to produce a net negative yield (Table 4). Since these estimates only include DOC removal downstream of W3, the total amount of DOC removed along the entire stream length could be larger. Meyer (1990) and Mann & Wetzel (1995) discuss biotic and abiotic utilization of DOC in streams and wetlands. Baseflow sampling along the Harp 4-21 stream did not show downstream increases in DOC concentrations (Hinton, unpublished data).

Discussion

DOC concentrations of the different subcatchments clearly demonstrate the effects of different DOC sources and flowpaths in riparian, hillslope and wetland areas (Figure 4). DOC mass balances show that riparian and wetland

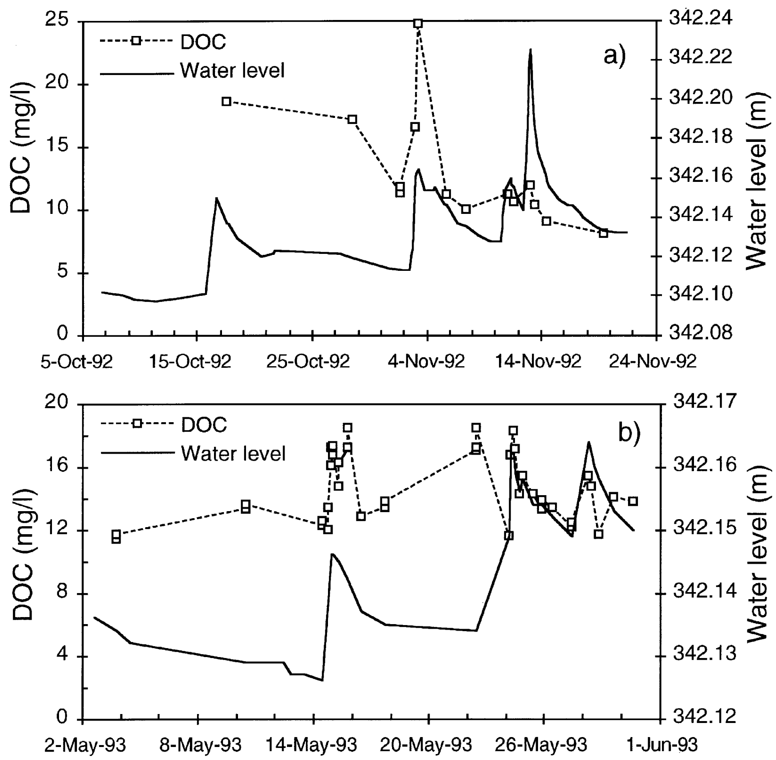

Figure 6. DOC concentrations and water levels in wetland 2 during a) autumn, and b) spring.

sources contributed most of the stream DOC during storms (Table 3), that shallow subsurface flowpaths are capable of contributing most of the stream DOC export, and that in-stream sources of DOC are unlikely. The differences in DOC dynamics among these three areas are examined by comparing results from subcatchments S1 and S4 (riparian), subcatchments W3 and W4 (wetland), and subcatchments W1, W2 and W5 (hillslope). Although wetland areas can be riparian, a distinction between riparian and wetland areas based on the persistence of ponded water in wetland areas is made for the following discussion.

Riparian areas

Riparian areas contributed most of the DOC to the Harp 4-21 stream during storms. Because the DOC originates near the stream, the riparian flowpaths are most important and the hillslope water flowpaths are relatively unimportant. In the riparian areas, the dominant flowpath was lateral saturated flow within the upper soil horizons where hydraulic conductivities are highest. Deeper groundwater from the till is a major contributor to storm runoff. However, discharge of deeper groundwater from the till directly to the stream could not have contributed sufficient discharge during storms to account for streamflow (Hinton et al. 1994). Consequently, most of the deeper groundwater flow from the till discharges to riparian soils, mixes with shallower waters and flows rapidly through shallow soil horizons to the stream during storms. Therefore, both shallow flowpaths that originate near riparian areas, and deeper flowpaths that originate in hillslope areas could have similar flowpaths near the stream and reach the stream with similar DOC concentrations.

Despite their similar riparian flowpaths, there is an important difference between these shallow and deeper flowpaths. In riparian areas, water flowing along shallow flowpaths may reach the stream without substantial interaction with lower soil horizons. In hillslope areas, soil water DOC concentrations decreased from approximately 21 mg/l in the litter and A horizons to 2.2 mg/l in the B and C horizons (LaZerte & Scott 1996). Therefore, waters flowing along deeper flowpaths have been through a cycle of DOC leaching and sorption before they contact riparian soils. This distinction is important for the interpretation of DOC quality. For example, deep groundwater DOC had little modern (bomb) carbon and low ^{14}C activities compared to litter and soil water leachates with higher ^{14}C activities (Trumbore et al. 1992; Schiff et al. 1997). Intermediate stream water ^{14}C activities showed that the stream was composed predominantly of modern, shallow carbon sources but was diluted by old, deeper carbon sources (Schiff et al. 1997). Therefore, quantitative models using chemical fingerprints of DOC (Kaplan & Newbold 1993) would need to consider such flowpaths where low DOC waters from the hillslopes leach riparian DOC sources. These flowpaths are not represented in schematic diagrams by Kaplan and Newbold (1993) and Boyer et al. (1996) but are possible in the hydrological model for the riparian zone presented by Fiebig et al. (1990).

In the debate of whether groundwater dilutes or contributes to stream DOC and whether groundwater DOC is immobilized in the hyporheic zone (Kaplan & Newbold 1993), there have been several comparisons of stream and groundwater DOC concentrations (e.g. Rutherford & Hynes 1987; Ford & Naisman 1989; Fiebig 1995). The difficulty with this approach is that groundwater contributes to the stream along different flowpaths with different DOC concentrations. Stream DOC concentrations in Harp 4-21 are largely controlled by the relative contributions of waters from the different horizons in riparian areas. Average baseflow DOC concentrations (Table 1) were higher than the deep groundwater (Table 2) which indicates that baseflow is a mixture of flow along deep and shallow groundwater flowpaths. During very dry conditions in late August, mostly deep groundwater contributed to the stream and stream DOC concentration (2.3 mg/l) and ^{14}C activity were similar to deep groundwater DOC (Schiff et al. 1997). Consequently, not only are the positioning of the piezometers and their screen lengths relative to the soil horizons and subsurface flowpaths very important, but the relative flow along different flowpaths will change with fluctuating water levels.

Saturated overland flow could also be a significant flowpath for DOC to the stream, particularly near peak discharges during large storms. As overland flow is a mixture of groundwater discharge, throughfall and stemflow, the contribution of the DOC sources will vary and be difficult to quantify. Higher DOC concentrations in overland flow compared to throughfall and groundwater suggest that the leaching of litter may be the main source of DOC along this flowpath. If this flowpath is significant, most of the DOC would likely originate near the stream or wetlands. Further examination of overland flow DOC is warranted.

Riparian vs. hillslope areas

Riparian areas are far more important to storm DOC export in Harp 4-21 than in subcatchments W1, W2 and W5 of Harp 3A (Table 3). The importance of riparian areas depends on the level of the water table relative to the organic-rich soil horizons. During storms there was more flow through high organic matter soil horizons in Harp 4-21 than in Harp 3A. This difference is partly a reflection of the effect of slope angle on the riparian water table. Along the more gentle hillslopes of Harp 4-21, the water table remained closer to ground surface further from the stream than along the steeper slopes of Harp 3A (Figure 2). Therefore, groundwater flowed along shallow flowpaths for a greater distance allowing more contact with organic matter.

Groundwater flow from the hillslopes is also important for its influence on the riparian water table. In Harp 3A, the lack of tills with lower hydraulic conductivities combined with steeper slopes and a rooting zone that extends to bedrock results in faster drainage of the water from the hillslope. Slower groundwater flow through the tills of Harp 4-21 hillslopes maintains high water levels and wetter antecedent conditions near the stream whereas the Harp 3A hillslopes drain more rapidly and dry up in the summer due to lack of flow from hillslope soils and till.

Not all the differences in stream DOC response between Harp 4-21 and Harp 3A can be attributed to differences in riparian flowpaths. There may be differences in soil properties both along the hillslopes and in riparian areas. Groundwater in the lower B horizons of Harp 3A hillslopes had higher DOC concentrations than in Harp 4-21 (Table 2). These differences could indicate different DOC sorption capacities along the hillslopes as documented by Nelson et al. (1993) in a paired watershed study. However, there are not any large differences in soil texture or cation exchange capacity that would suggest such differences are due to differences in hillslope soil properties (Lozano et al. 1987). Rather, differences in the thickness and organic content of the riparian soils were observed between Harp 4-21 and Harp 3A, but no thorough investigation of organic matter content or distribution was carried out. Thicker and higher organic matter content in riparian soils of Harp 4-21 probably result from the higher and more persistent saturation. Seasonally dry conditions in Harp 3A allows for more oxidation of organic matter.

Hillslope vs. wetland areas

The subcatchments in Harp 3A have similar topography and vegetation except for the presence of small wetlands in W3 and W4. The DOC concentrations increased from the hillslope to the wetland (Table 2), and DOC concentrations at W3 and W4 were consistently higher than those at W5 during both baseflow and stormflow conditions (Table 1). Consequently, the yield of DOC was much greater from subcatchments with wetlands than those without (Table 4). The presence of wetlands, even small ones, completely dominated the DOC export during both baseflow and stormflow conditions so that the hillslope areas were relatively unimportant compared to the wetlands (Table 3). Therefore, it would be pointless to attempt to relate DOC dynamics in subcatchments W3 and W4 to hillslope flowpaths. This dominance of wetlands over hillslopes as a DOC source is the reason that correlations between wetland area and DOC export are possible (Eckhardt & Moore 1990; Molot & Dillon 1996).

Wetland vs. riparian areas

The DOC dynamics of wetland subcatchments (W3 and W4) are different from riparian subcatchments (S1 and S4) in several ways. Baseflow DOC concentrations were lower at S1 and S4 (Table 1). During storms, S1 and S4 had larger changes in DOC concentrations that were more closely related to flow (Figures 4 and 5, Hinton et al. 1997). Whereas higher groundwater levels during storms generally produced larger peak DOC concentrations for larger discharges at S1 and S4, peak DOC concentrations at W3 and W4 (Figures 4 and 5) and wetland 2 (Figure 6) were smaller for progressively larger storms. Higher DOC concentrations on the rising limbs of hydrographs (Figure 5) suggest that flushing of organic sources at the wetland surface during storms may be important. These results suggest that most of the DOC in W3 and W4 originates at the wetland surface rather than at the wetland edge in a manner similar to riparian areas in S1 and S4. Consequently, the processes and the dynamics of DOC in riparian areas are not the same as those in wetlands, and riparian areas cannot simply be treated as wetland areas.

Conclusions and implications

Riparian and wetland areas were the major sources of stream DOC during storms in two small catchments of glacial sediments. A significant proportion of DOC export originated in these areas (Table 3) and DOC yields were highest from these areas (Table 4). These results support the hypothesis by Hemond (1990) that 'stream channel wetlands' are the main source of stream DOC. Riparian DOC sources are not restricted to areas of ponded water; most of the DOC export from Harp 4-21 during storms originated in the shallow organic-rich soils adjacent to the stream that do not have ponded water. In this study, the response of stream DOC concentrations during storms were different between riparian and wetland areas because the DOC export in riparian areas is related to flowpaths whereas the DOC export in wetlands is related to DOC production and leaching in ponded water.

The results of this study emphasize the need to focus on the dynamics of DOC in riparian and wetland areas during storms. Some of the important hydrologic processes that control DOC dynamics only occur during storms and would not be observed from studies with longer sampling intervals. Because the sources of DOC in watersheds can be localized (within 5–25 meters of the stream channel in Harp 4-21), the geographic locations of instrumentation are very important. Traditionally, most studies have relied on soil lysimeters and piezometers located in midslope positions or have failed to recognize different flowpaths in riparian areas. Recognition of the difference in flowpaths between hillslope and riparian areas needs to be incorporated into project design. Studies are also needed to examine how differences in soil properties in the immediate area near the stream (0–25 m) affect stream DOC dynamics.

DOC sources cannot be equated with water flowpaths. Water flowing along different flowpaths can acquire DOC from similar sources in riparian and wetland areas. The use of multiple organic markers in mixing models as suggested by Kaplan & Newbold (1993) may be complicated by the discharge of deeper groundwater through shallow riparian flowpaths. First, if groundwater acquires the same concentration as soil water then the marker will not serve to distinguish the two. Second, not all markers will be affected similarly in riparian areas so that the markers may record the degree of interaction with riparian soils rather than the relative fluxes along different flowpaths. Conversely, such markers could help identify interactions in riparian areas.

The importance of riparian soils as a source of DOC ultimately depends on the water flowpaths near the stream. Where flowpaths intersect riparian soils of high organic matter content for a significant distance before discharging to the stream, stream DOC export will be higher. Several hydrologic and physical factors affect these flowpaths but the most critical factor is the water table fluctuation near the stream. Where riparian DOC sources are important, DOC dynamics will vary from catchment to catchment and may vary within a catchment during different storms. However, we hypothesize that positive correlations between DOC concentrations and stream discharge will be strongest in watersheds with large riparian DOC sources and without significant wetland areas.

Acknowledgements

We wish to thank A. MacLean, A. Meyer, P. Overduin, S. Alpay, J. Patterson and R. Fagan for field assistance, M. Schultz for digitizing stream charts, R. Elgood for laboratory expertise, and P. and G. Kyryluk for permitting research on their property. S. Alpay and five anonymous reviewers provided valuable comments. L. Scott of the Dorset Research Centre, M. Stone of Wilfrid Laurier University, and R. Elgood of the Waterloo Centre for Groundwater Research provided valuable logistical support. Funding was provided by the Natural Science and Engineering Research Council of Canada, the Ontario Ministry of Environment, and Eco-Research (Tri-Council Secretariat) and Geological Society of America scholarships to M.J. Hinton.

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