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Sources and sinks of dissolved organic carbon in a forested swamp catchment

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Abstract. Concentrations of dissolved organic carbon (DOC) were measured in precipitation, throughfall, stemflow, and soil, peat and stream water in a 50 ha catchment with a central 5 ha swamp at Mont St. Hilaire, Quebec. DOC concentrations in precipitation were low (2.0 mg L^{-1}), but increased in passage through the tree canopies as throughfall (9.1—14.6 mg L^{-1}) and stemflow (23.1—30.1 mg L^{-1}). For the period July 1—November 15, 1987, 0.5 g DOC m^{-2} was imported as precipitation, and forest canopies contributed a further 1.4—1.7 g m^{-2} to the soil surface. DOC concentrations were higher (46.0 and 67.6 mg L^{-1}) in upland soil organic horizons, but decreased with depth because subsoil mineral horizons acted as a major sink of DOC. A laboratory experiment using leaf leachate revealed that subsoil horizons were able to adsorb DOC, with equilibrium DOC concentrations ranging from 3 to 19 mg L^{-1}. Soil organic carbon appeared to be an important determinant of equilibrium DOC concentrations. The swamp was a major source of DOC, with an overall average DOC concentration of 58.6 mg L^{-1} and showed strong spatial and temporal variations related to hydrologic and thermal regimes. During base flow periods, stream DOC concentrations were small (<3 mg L^{-1}), dominated by water fed from springs draining upland soils. During high flows, stream DOC concentrations increased through the contribution of DOC-rich water originating in the swamp. Sources, sinks and transport of DOC are thus a function of a complex set of inter-related biotic and abiotic process.

Introduction

Dissolved organic carbon (DOC) is composed of a wide range of organic compounds, ranging from short-chain acids to large molecules such as fulvic and humic acids (Thurman 1985). DOC in soil and stream water can reach concentrations of 50 mg L^{-1} or more, and thus may influence water acidity, the mobility and toxicity of metals, and nutrient availability. DOC exports from catchments range from <1 to >20 g m^{-2} y^{-1}, with differences related to catchment features, such as soils, topography, vegetation and runoff sources and hydrologic pathways (e.g. Eckhardt &

Moore 1990; Mulholland & Watts 1982; Schlesinger & Melack 1981; Urban et al. 1989).

The major sources and sinks of DOC have been identified in a few forested ecosystems (see data presented in Fig. 6 for a summary). Precipitation generally contains small concentrations of DOC (<2 mg L^{-1}) which increase with the passage of rainfall through the tree canopy as throughfall and stemflow into the organic horizons of the soil, where it commonly reaches values of 50 mg L^{-1}. Subsoils, especially those containing low concentrations of organic carbon and high concentrations of extractable iron and aluminum, exhibit the capacity to adsorb DOC as water percolates down through the soil profile, resulting in smaller DOC concentrations. Because of the presence of large amounts of organic matter, and the absence of strong adsorption mechanisms, water extracted from wetland soils, such as peatlands, commonly shows high concentrations of DOC. Stream DOC concentrations often reflect the proportion of well-drained and wetland soils in the catchment (e.g. Eckhardt & Moore 1990; Mulholland & Kuenzler 1979; Urban et al. 1989).

Although the major sources and sinks of DOC have been identified and quantified in a few studies (e.g. McDowell & Likens 1988), little attention has been directed at the examination of the spatial and temporal variations of these sources and sinks within catchments, and the relative importance of the factors that contribute to DOC production and transport. In this study, we report on results obtained in a small, forested catchment in southern Quebec, consisting of steep ($\approx 25°$) slopes around a central peatland swamp. We identify the major sources, sinks and temporal variations of DOC and how these reflect seasonal, vegetation and pedologic characteristics.

Materials and methods

The catchment is located at Mont St. Hilaire (45° 10′N, 73° 10′W), a Monteregian Hill, 35 km east of Montreal, which is covered with essentially undisturbed vegetation typical of the mixed northern hardwood forest (Phillips 1972). The catchment covers about 50 ha on the northeastern edge of the mountain and contains a central swamp, 5.5 ha in area, with an average width of 100 m and 550 m long, underlain by a bedrock of limestone (Fig. 1). The northeastern slope of the catchment, rising to an elevation of about 280 m a.s.l. from 240 m, is underlain by hornfels. The western and northwestern slopes, which rise up to 350 m, are underlain by syenite, with a thin exposure of limestone at the foot of the steep western slope adjacent to the swamp. The climate is cool con-

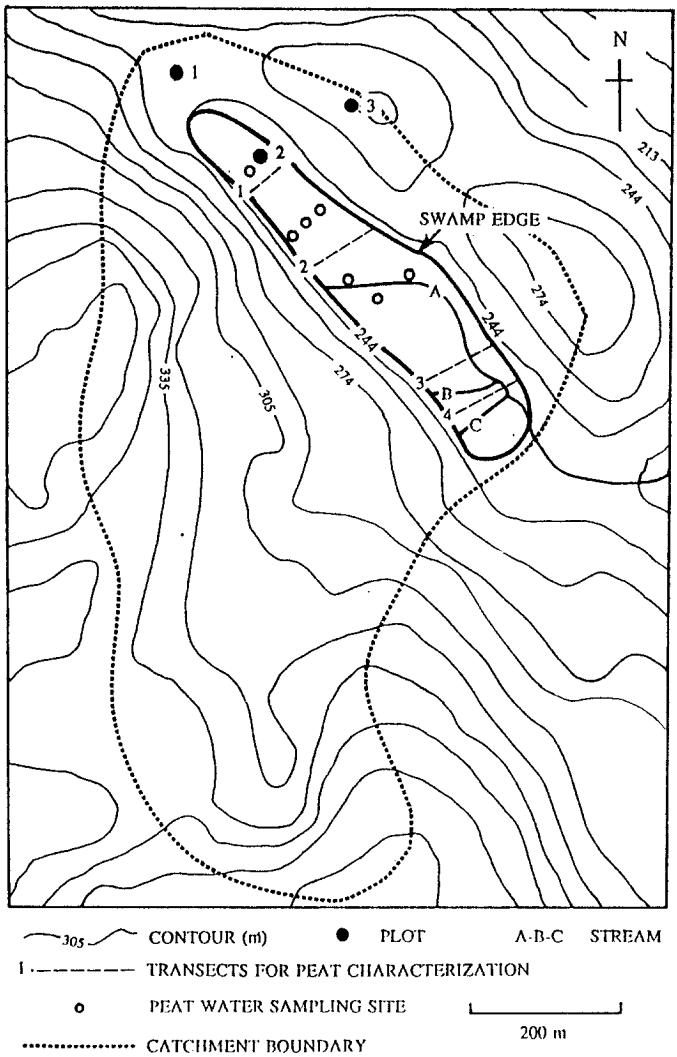

Fig. 1. The catchment, showing the location of the three plots and the sampling sites and transects within the swamp.

tinental (mean annual temperature 5.5 °C) with a mean annual precipitation of 988 mm, of which 262 mm falls as snow. Water seeps out of the foot of the western slope, mainly as three springs, which then cut across the swamp and represent the major surface runoff from the catchment (streams A, B and C, Fig. 1).

Vegetation in the swamp is primarily yellow birch (*Betula allenghaniensis*), eastern hemlock (*Tsuga canadensis*) and red maple (*Acer rubrum*), with some eastern white cedar (*Thuja occidentalis*) and black ash (*Fraxinus*

nigra). The understory is dominated by ferns (e.g. *Onoclea sensibilis* and *Dryopteris spinulosa*) and mosses (e.g. *Lycopodium lucidulum*). The swamp soil is a Mesisol (Canadian Soil Survey Committee 1978), varying in thickness from 75 cm at the edges to over 200 cm in the centre.

The northeastern slope is covered by mixed forest, comprised mainly of eastern hemlock (*T. canadensis*), red pine (*Pinus resinosa*), American beech (*Fagus grandifolia*) and red oak (*Quercus rubra*). The soils are shallow, with hornfels exposures common and are generally Dystric Brunisols or Humo-Ferric Podzols.

The western and northwestern slopes are dominated by sugar maple (*Acer saccharum*) and American beech (*F. grandifolia*), with red oak (*Q. rubus*) on the upper slopes. The soils are shallow Dystric Brunisols on the steep portions, becoming thicker on the gentler northwestern slope. Thin Melanic and Eutric Brunisols occur on the limestone at the foot of the western slope.

Three sites (15 × 15 m), representing the major vegetation and soil associations in the catchment, were chosen to monitor sources and sinks of DOC (Fig. 1). Plot 1, representing the deciduous forest on the western and northwestern slopes, had a tree stem basal area of 36 m^2 ha^{-1}, and was dominated by sugar maple (77%, 578 stems ha^{-1}), with white ash (15%, 89 stems ha^{-1}) and beech (8%, 44 stems ha^{-1}). Plot 2, located in the swamp, was dominated by yellow birch (67%, 311 stems ha^{-1}), hemlock (31%, 177 stems ha^{-1}) and red maple (8%, 44 stems ha^{-1}) and had a tree basal area of 21 m^2 ha^{-1}. Plot 3, located on the northeastern slope with a tree basal area of 54 m^2 ha^{-1}, contained hemlock (50%, 356 stems ha^{-1}), beech (25 %, 177 stems ha^{-1}), red pine (12%, 89 stems ha^{-1}) and red oak (12%, 89 stems ha^{-1}). These vegetation assemblages and densities are typical of those reported for Mont St. Hilaire by Phillips (1972).

Precipitation was collected in rain gauges in a clearing about 3 km south of the catchment. Throughfall in each of the three plots was collected in 5 polyethylene funnels, 21 cm in diameter, placed 45 cm above the soil surface, and draining into closed 5 L buckets. A plug of glass wool was inserted into the neck of the funnel to prevent particles falling into the bucket and a 1 mm fiberglass mesh was placed over the funnel from September onwards to prevent leaves falling into the funnel. Stemflow was collected by wrapping a plastic collar twice around each tree in the three plots; the tube drained through a glass wool plug into a covered bucked ranging in capacity from 5 to 60 L.

Soil leachates were collected in zero tension lysimeters (Jordan 1968), 15 × 23 cm in size and covered with 1 mm fibreglass mesh, with a tube at the base leading into a bottle. Five lysimeters were installed at the base of

each of the A and B horizons at plots 1 and 3 and from late September, three lysimeters per plot were placed beneath the litter layer at plots 1, 2 and 3.

Replicate throughfall, stemflow and soil water samples at each site were bulked in the field and the volume noted. On three dates (17 August, 14 September and 25 October, 1987), samples were kept separate and analysed to provide an assessment of within-site variability.

Peat water was extracted from depths of 30, 60 and 90 cm at 8 locations in the swamp (Fig. 1). Perforated 250 mL bottles, with 1 mm mesh over the perforations, were attached to a stake which was inserted into the peat to the appropriate depth. Water was extracted through the bottle into a plastic tube leading to the surface, with vacuum provided by a hand pump.

Water table depth in the peat was measured in 2 cm diameter PVC tubes driven to a depth of 1 m. The temperature profile of the peat at plot 2 was recorded with a thermistor cable to a depth of 2 m. Two 45° V-notch weirs were installed in the stream draining the upper portion of the swamp, one at the foot of the western slope, where the stream emerged and the other about 180 m downstream (Figs 1 and 5). Stream water was sampled and discharge measured at these two locations.

Sampling was conducted at approximately weekly intervals from July 1 to November 15, 1987. In addition, stream and peat water samples were collected weekly from April 2 to May 3, 1988, during and after snowmelt. After collection, samples were filtered through Whatman GF/C paper, stored at 4 °C and analysed as follows: pH with an Accumet model 210 meter and specific conductance at 25 °C with a YSI model 32 conductivity meter, within 24 h of collection; and DOC by the dichromate wet oxidation method, using a correction factor of 1.28 (Moore 1985), within a week of collection. Analyses of samples in triplicate revealed coefficients of variation in DOC averaging 3%. We have found that, compared to high-temperature, catalytic oxidation methods (Beckman and Ionics TOC analyzers), the dichromate method gives similar DOC concentrations (95—100%), as do the persulfate and Dohrmann methods, for extract of soils and plant tissues. However, the latter 3 methods all underestimate (by about 20%) DOC concentrations determined by the catalytic methods in samples of peat, river and ground waters (Koprivnjak et al., pers. comm.).

The capacity of subsoil horizons to adsorb DOC was determined on 11 samples, 10 mineral and 1 organic. After air-drying and grinding to pass through a 2 mm sieve, 5 g of the sample was placed in 100 mL flasks. A DOC-rich solution was produced by soaking beech and maple leaves in distilled water for 10 days, filtering the suspension through Whatman

GF/C paper and then diluting to give solutions containing 0, 10, 19, 32, 50 and 61 mg DOC L^{-1}. 50 mL of these working solutions were added to the soil samples in the flasks, shaken for 3 h, left overnight and then filtered through Whatman GF/C paper. The DOC concentration was then determined on the filtrate. From the observed change in DOC concentration, linear regression of DOC sorption on initial DOC concentration was used to predict the equilibrium DOC concentration, at which there is zero net DOC sorption (Nodvin et al. 1986).

The 11 soil samples were analysed for pH in 0.01 M $CaCl_2$, organic carbon by Walkley-Black digestion, loss in ignition between 420 and 850 °C for $CaCO_3$ content, and oxalate-soluble iron and aluminum content (McKeague 1978).

Results

Forest canopy and mineral soils

During the sampling period July 1—November 15, 1987, 253 mm of precipitation fell, representing 75% of the long-term mean. For this period, interception of precipitation by the forest canopy at the three sites was 18, 33 and 43% at plots 1, 2 and 3, respectively; stemflow was insignificant compared to throughfall, amounting to about 1% of the precipitation (Table 1). Associated with this change in the volume of water passing through the canopy was a substantial increase in both pH and specific conductance: the tree canopy at all three plots neutralised over 90% of the acidity imported in the precipitation, which has an average pH of 4.3 (Moore & Dubreuil 1987).

DOC concentrations were low in precipitation (volume-weighted mean of 2.0 mg L^{-1}) and increased in throughfall and stemflow, with weighted means of 9.1 to 14.6 and 23.1 to 67.6 mg L^{-1}, respectively (Table 1). For the sampling period, DOC flux in precipitation amounted to 0.49 g m^{-2} and increased to 1.96 to 2.29 g m^{-2} in combined throughfall and stemflow. Weekly sampling showed that there was a strong seasonal pattern, with DOC concentrations in throughfall and stemflow in all plots being an average of 86% greater in the summer period (July and August) than the fall (mid-October to November 15), as indicated by the Mann-Whitney U test ($p < 0.05$). Throughfall DOC concentrations were highest in plots 2 and 3, which had multi-layered canopies and were of mixed composition, and lowest in the more open, deciduous plot 1.

When replicate samples of throughfall, stemflow and soil water were analysed separately, throughfall DOC concentrations revealed a high

Table 1. Flux of water, volume-weighted mean DOC concentration, DOC flux, pH and specific conductance at the three plots for precipitation, throughfall (TF) and stemflow (SF) and the mean concentration of DOC in samples collected from beneath the A and B horizons of the soil in plots 1 and 3, from July 1—November 15, 1987.

Plot	Water flux (mm)	DOC concentration (mg L^{-1})	DOC flux (g m^{-1})	pH	Sp. conduct. (μS cm^{-1} at 25 °C)
Precipitation	253	2.0	0.49	4.3	26
1 TF	204	9.1	1.86	5.4	47
SF	3	30.1	0.10	5.7	125
A	—	46.0	—	5.4	119
B	—	16.6	—	5.3	35
2 TF	170	13.2	2.24	5.7	73
SF	2	23.1	0.05	5.8	109
3 TF	140	14.6	2.05	5.3	112
SF	3	67.6	0.17	4.5	181
A	—	49.2	—	4.8	128
B	—	19.4	—	5.4	115

spatial variability, with an average coefficient of variation of 0.47, based on 5 throughfall collectors in each plot. Major differences were also noted in stemflow concentrations: concentrations were highest in pine, hemlock and oak (means of 61 to 109 mg DOC L^{-1}) and lowest in beech, birch and maple (means of 16 to 40 mg DOC L^{-1}). Tree size also affected stemflow DOC concentrations: there was a significant correlation (Spearman Rank correlation, $r = 0.50$ and 0.70, $p < 0.05$) between stemflow DOC concentration and diameter at breast height for maple and hemlock, respectively ($n = 12$ and 14).

DOC concentrations were high in water collected from the organic horizons at plots 1 and 3, with mean values of 46.0 and 49.2 mg L^{-1}, respectively (Table 1). The underlying B horizon water samples contained smaller DOC concentrations of 16.6 and 19.4 mg L^{-1}. The volumes of water collected in the lysimeters were erratic, suggesting that in these stony soils and during a dry summer, water collection was inefficient. Consequently, DOC flux calculations have not been attempted for water moving through the organic and B horizons.

The results of the laboratory sorption experiment with a deciduous leaf leachate and subsoils from a Dystric Burnisol (plot 1), a Humo-Ferric Podzol (plot 3) and a Eutric Brunisol (at the foot of the western slope) give an indication of the relative ability of the soil materials to adsorb

DOC. In all soil samples, the regression between DOC sorbed and initial DOC concentration in the solution was significant at the $p < 0.01$ level (Table 2). For the soil profile samples collected at plots 1 and 3, the equilibrium DOC concentration (at which there is no net retention or release of DOC from the soil), predicted from the sorption regression, decreased with depth in the soil, from 48 and 69 mg L^{-1} in the upper mineral horizons to 3 to 10 mg L^{-1} in the C horizons at about 50 cm depth. Horizons collected from a Eutric Brunsiol developed on limestone parent material at the foot of the western slope also showed decreasing equilibrium DOC concentrations, from 14 to 10 mg L^{-1}. A sample of the peat, collected from a depth of 50 to 55 cm at plot 2, revealed an equilibrium DOC concentration of 66 mg L^{-1}. These equilibrium DOC concentrations are in general accordance with the concentrations recorded in the soil water samples from plots 1 and 3 (Table 1), and suggest that there are further decreases in DOC concentration as water percolates through the mineral soil in the catchment.

After $\log_{10}$ transformation of the soil properties, equilibrium DOC concentration was positively associated ($p < 0.05$) with the organic carbon content of the soil, when the eluvial Ae horizon and peat samples were excluded (Fig. 2). There was also a positive association between equilibrium DOC concentration and oxalate-extractable Fe content ($p < 0.01$), but no relationship with oxalate-extractable A1 content ($p = 0.40$). The multiple regression of equilibrium DOC concentration against organic carbon, and oxalate-extractable Fe and Al contents was very significant ($r^2 = 0.92, p = 0.004$).

Swamp soil

The concentration of DOC in peat water extracted from depths of 30, 60 and 90 cm at the 8 sites ranged widely; however, average concentrations for the three depths at each site from July to November ranged from 41 to 81 mg DOC L^{-1}, with an overall mean of 59 mg L^{-1}. In general, seasonal mean DOC concentrations were greater at the 90 cm depth than higher in the peat profile, although differences were relatively small and inconsistent. The sites exhibited similar temporal variations in DOC concentration with that at plot 2, and DOC concentration and peat temperature, specific conductance and water table position are presented in Fig. 3. DOC concentrations reached their highest values in the summer (100 to 225 mg L^{-1}) and decreased during the late summer and autumn to 20 and 60 mg L^{-1}, a concentration range which was also observed just after the spring snowmelt. This pronounced seasonal pattern appears to be associated with both the thermal and hydrologic regimes. At five sites in the

Table 2. Properties of the 11 soil samples, sorption isotherm for DOC and predicted equilibrium DOC concentration.

Soil	Depth (cm)	pH	Org. C (%)	Fe_o[1] (%)	Al_o[1] (%)	$CaCO_3$ (%)	Sorption isotherm[2]	r^2	Equilibrium DOC (mg L^{-1})
1 Bhf	15–18	3.7	5.8	4.03	1.08	0	$Y = 0.56x - 27.0$	0.858	48.2
Bm	25–28	4.2	1.2	1.04	0.64	0	$Y = 0.63x - 6.2$	0.987	10.0
C	43–46	4.5	1.4	1.00	1.23	0	$Y = 0.73x - 7.1$	0.995	9.6
3 Ae	3–6	3.1	1.4	0.31	0.09	0	$Y = 0.34x - 23.6$	0.778	69.1
Bf	12–15	3.9	3.4	1.18	1.81	0	$Y = 0.71x - 12.6$	0.982	18.6
Bm	30–33	4.2	0.7	0.66	0.65	0	$Y = 0.73x - 4.6$	0.999	6.3
C	55–60	4.3	0.3	0.85	0.39	0	$Y = 0.70x - 2.0$	0.996	2.9
4 Bf	12–15	6.7	3.6	1.06	0.65	0	$Y = 0.73x - 10.8$	0.994	14.8
Bmk	28–30	6.9	1.0	0.87	0.32	22	$Y = 0.69x - 9.5$	0.988	13.6
Ck	85–88	7.0	0.2	0.38	0.04	32	$Y = 0.51x - 4.9$	0.970	9.8
2 Om	50–55	5.3	54.0	0.20	0.10	0	$Y = 0.61x - 40.0$	0.943	66.2

Soils 1, 2 and 3 were sampled from plots 1, 2 and 3 and soil 4 from the limestone exposure at the foot of the western slope.

[1] oxalate-extractable Al (Al_o) and Fe (Fe_o)

[2] Y is sorption of DOC (mg g^{-1} soil)
x is initial concentration of DOC in solution (mg L^{-1})
r^2 is coefficient of determination, all regressions are significant at the $p < 0.01$ level

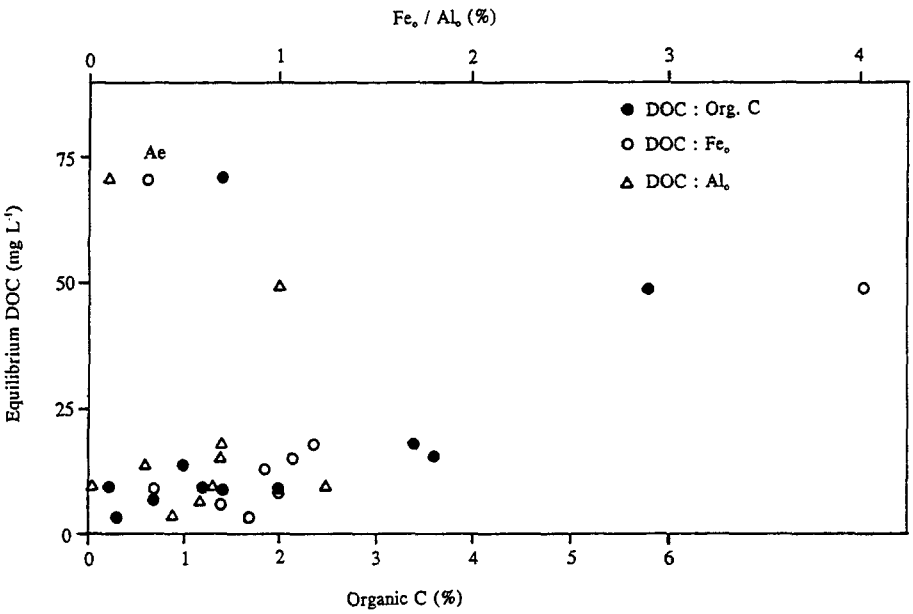

Fig. 2. Relationship between equilibrium DOC concentration (DOC_{eq}) and organic carbon (OC) and oxalate-extractable iron and aluminum (Fe_o and Al_o) for the 10 mineral samples. Regressions have been calculated excluding the eluvial Ae sample:

$DOC_{eq} = 19.3\log_{10}OC + 13.4$ $\quad r^2 = 0.51, p = 0.032$
$DOC_{eq} = 42.3\log_{10}Fe_o + 14.9$ $\quad r^2 = 0.74, p = 0.003$
$DOC_{eq} = 8.91\log_{10}Al_o + 17.3$ $\quad r^2 = 0.10, p = 0.398$
$DOC_{eq} = 12.6\log_{10}OC + 45.5\log_{10}Fe_o - 18.2\log_{10}Al_o + 8.9$ $\quad r^2 = 0.92, p = 0.004$

swamp, there was a significant (Spearman Rank Correlation, $p < 0.05$) positive relationship between temperature and DOC concentration at 60 cm. Peat temperatures were 10 to 15 °C at 60 to 90 cm during the summer, but fell to <6 °C during the winter. From a depth of 15 cm in early July at plot 2, the water table fell to 80 cm in early September and rose to a depth of 20 cm by mid-November. During and shortly after snowmelt, water remained above or at the peat surface. Specific conductance showed a less pronounced seasonal pattern, ranging between 75 and 225 μS cm^{-1}, as did pH (6.5 to 7.4)

Streams

Because of the low precipitation during the summer and fall, water rarely flowed in stream channel A, though there was usually flow in tributaries B and C (Fig. 4). Samples along the main channel (A) and the two tributaries (B and C) were collected at 8 dates after major rainfall events and during

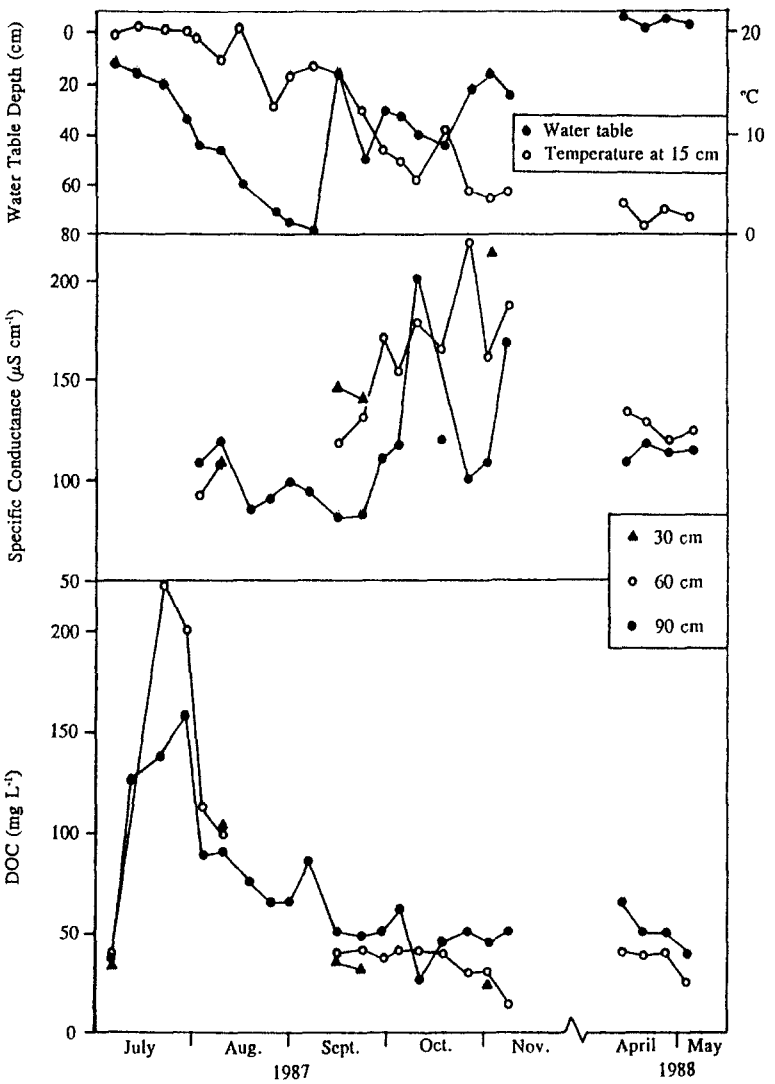

Fig. 3. Temporal pattern of DOC concentration, specific conductance at depths of 30, 60 and 90 cm and temperature at 15 and 60 cm and water table position at plot 2.

and after snowmelt. Data collected at three sampling dates, two in the fall and one soon after snowmelt, revealed strong longitudinal variations in DOC concentrations along the main channel (Fig. 5). Concentrations were low in the stream A headwaters, fed by a spring emerging from the western slope (<3 mg L^{-1}), but increased rapidly to 20 mg L^{-1} as the stream passed through the swamp. Concentrations decreased towards the outlet (6—10 mg L^{-1}), through the diluting effect of the two tributaries (B and C), which contained <3 mg DOC L^{-1} and whose channels pass

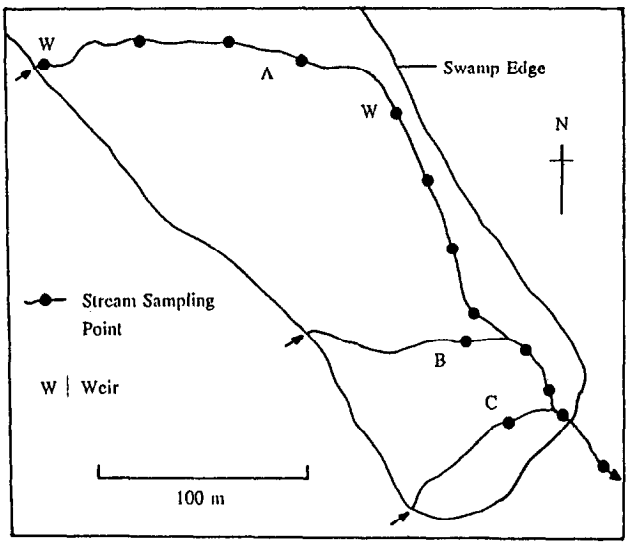

Fig. 4. Sampling points along the stream A in the southern section of the swamp.

through a much shorter swamp section. The pattern was best developed for the September and October sampling dates (for which the preceding week's precipitation was 88 and 30 mm, respectively), but the change in concentration was less pronounced for the spring sampling, when DOC concentrations in the mid-section of stream A remained <10 mg L^{-1}. Accompanying the change in DOC concentrations were higher pH values in the headwaters (7.0—7.5) and lower values in the mid-section (pH 6.5—6.9).

These patterns reveal the influence of groundwater seepage low in DOC from the western slope to the stream water. Stream water becomes progressively enriched with DOC as it cuts across the swamp, through the input of peat groundwater rich in DOC. Measurements of discharge at two weirs on the main stream channel at the western and eastern edges of the swamp (Fig. 4) gave an indication of the relative contribution of the two sources to DOC export in the stream, although this analysis was limited by the infrequent occurrence of significant flow in the stream: weekly precipitation needed to exceed 30 mm for there to be significant flow. For example, on September 14, 1987, DOC load at the upper weir was 12 g d^{-1}, whereas at the lower weir it was 397 g d^{-1}, representing a net contribution of 385 g DOC from the swamp. We calculate that water entering the stream should have contained 32 mg DOC L^{-1}, similar to the DOC concentrations observed in the swamp.

DOC export from this catchment appears to be strongly dependent on

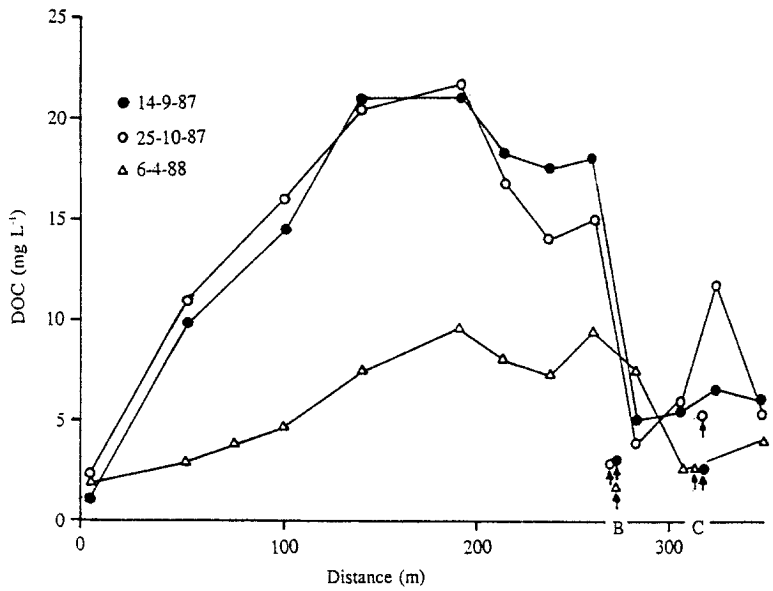

Fig. 5. DOC concentrations in stream A on 14 September, 1987, 25 October, 1987 and 6 April, 1988. Arrows indicate the DOC concentration in tributaries B and C (Fig. 1).

precipitation and runoff. In dry periods, DOC export will be very small, as most of the runoff will be groundwater with low DOC concentration derived from the catchment's slopes. The stream channels are incised 20 to 100 cm beneath the swamp surface and hydraulic gradients are low. In mesic or hemic peats, hydraulic conductivities can also be expected to be low, especially in the subsurface layers (5×10^{-5} to 5×10^{-6} cm s^{-1}, Boelter 1965). In wet periods, however, the input of DOC-rich groundwater from the swamp will contribute to a much larger DOC export. For this reason, an estimate of DOC export from the catchment is not attempted.

Discussion

This study has revealed some of the complex relationships that exist between the biotic and abiotic processes which regulate the production, transport and deposition of DOC, as water moves through the atmosphere-vegetation-soil-stream system. Precipitation contains low but significant concentrations of DOC (mean 2.1 mg L^{-1}, Fig. 6), which may possess relatively high proportions of low molecular mass organics (Likens et al. 1983). Water is enriched with DOC as it passes through forest canopies,

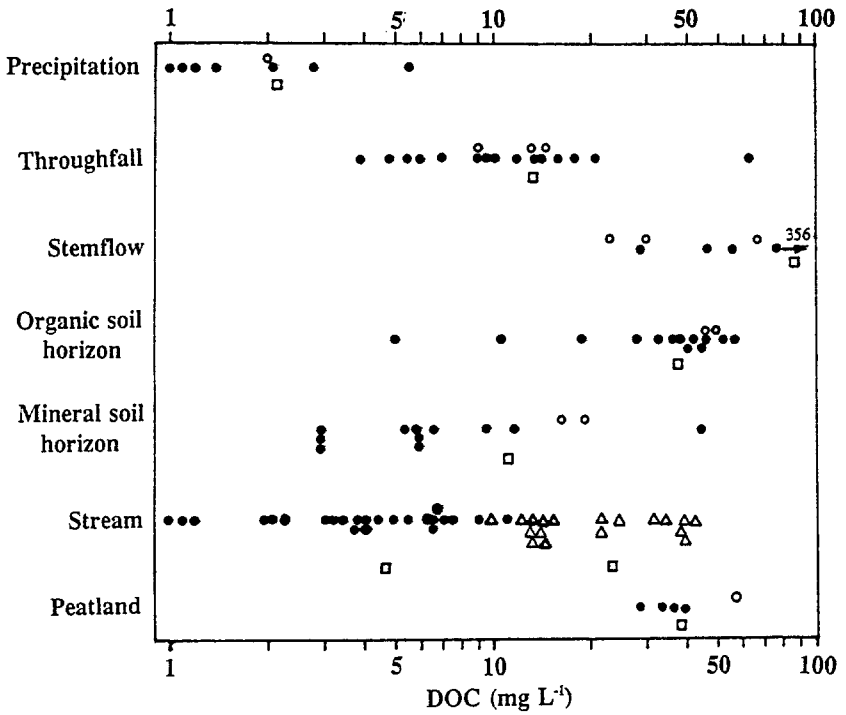

Fig. 6. Collation of literature values for DOC concentrations in temperate regions for precipitation, throughfall, stemflow, soil organic and mineral horizons and streams, mainly undisturbed forested catchments, and for peat water. Where possible, values represent the volume-weighted annual or growing season mean. Values from this study are shown as open circles. Streams draining catchments with a significant proportion (> 5%) of wetland shown as triangles. Arithmetic mean for each class is indicated by a square, with separation of wetland and non-wetland classes for streams. Literature sources are: Brinson et al. (1980); Clair & Freedman (1986); Cronan & Aiken (1985); Dahm (1980); David & Driscoll (1984); Driscoll et al. (1987); Eaton et al. (1976); Eckhardt & Moore (1990); Eshleman & Hemond (1985); Fahey et al. (1988); Foster & Grieve (1982); Gorham et al. (1984); Grieve (1984); Heikkinen (1990); Hoffman et al. (1980); Kaplan et al. (1980); Kerekes et al. (1986); Likens et al. (1983); Marin et al. (1990); McDowell & Likens (1986); McKnight et al. (1985); Moore (1987b, 1989); Moore & Jackson (1989); Mulholland (1981); Naiman (1982); Sollins & McCorison (1981); Tate & Meyer (1983); Urban et al. (1989); Velinsky et al. (1986); Wallis et al. (1981).

with a mean concentration of up to 13.0 mg L^{-1} (Fig. 6) and with annual fluxes of up to 30 g DOC m^{-2} y^{-1} (e.g. Moore & Jackson 1989). Although stemflow DOC concentrations are generally larger and more variable than those in throughfall, the small proportion of precipitation that passes through the stemflow pathway (< 2% in this study) means that stemflow forms a small portion of the DOC loading to the soil surface. However, both throughfall and stemflow can contain significant concentrations of

short-chain organics, such as carbohydrates, phenolics, aldehydes and carboxylic acids (McDowell & Likens 1988). There are frequently strong seasonal patterns in these concentrations, resulting from biological activities in the canopy and there may also be significant differences between tree species, particularly coniferous > deciduous, such as indicated by the throughfall and stemflow concentrations at the three sites in this study and by David & Driscoll (1984) and McDowell & Likens (1988). However, the high spatial variability in replicate throughfall collectors, the variable rates of interception and stemflow and the mixed nature of most tree stands precludes a more precise identification of the role of species in determining DOC flux from the forest canopy to the soil surface.

High DOC concentrations (mean 36.3 mg L^{-1}, Fig. 6) are a common feature in the organic horizons of forest soils, resulting not only from the input of DOC from the forest canopy, but also from the release of DOC by decaying soil organic matter and litter. The results show that, in general, DOC concentrations beneath coniferous stands are higher than adjacent hardwood stands (e.g. Cronan & Aiken 1985; David & Driscoll 1984) but, as noted by McDowell & Likens (1988), the causes of the variations in these concentrations are poorly understood and the release of DOC from different litter types warrants further study.

This study has confirmed the ability of subsoil mineral horizons to adsorb and reduce DOC concentrations in water percolating through the soil profile. Most well-drained subsoils have pore water DOC concentrations in the range of 5 to 15 mg L^{-1} (mean 8.1 mg L^{-1}, Fig. 6), the exception being those soils developed in poorly drained sites and exhibiting gley features (e.g. Moore & Jackson 1989). Laboratory experiments of DOC adsorption have confirmed the ability of mineral soils to adsorb DOC. The results of McDowell & Wood (1984) with 5 subsoil samples from Hubbard Brook suggested that HCl-extractable iron and aluminum and organic carbon contents are primary controls on the equilibrium DOC concentrations, and that the association is positive for iron and aluminum and negative for organic carbon. For a different range of soils, Jardine et al. (1989) have recently shown that much of the sorption of DOC by soils may be related to iron extracted by dithionite-citrate-bicarbonate reagent. The results of our study show that, although the mechanisms for adsorption of DOC may be related to extractable iron and aluminum, the organic carbon content of the soil may play an important role in determining equilibrium DOC concentrations, particularly in the upper subsoil horizons. The range of soil samples used in this study is too small to provide a further statistical identification of the importance of soil properties on DOC adsorption and equilibrium DOC concentrations. However, Moore et al. (in press) have used partial regression analysis of data for 48 soil

samples to show that the primary control on DOC_{eq} is organic carbon content (positive association), and secondarily with oxalate-extractable Al and dithionite-extractable Fe (negative association).

Soils containing carbonates are also able to reduce DOC concentrations to low values (<10 mg L^{-1}), as shown by the laboratory experiments and the low DOC concentrations (<3 mg L^{-1}) evident in the springs draining the western slope of the Mont St. Hilaire catchment. Otsuki & Wetzel (1974) have noted the importance of carbonates in controlling DOC concentrations in lake water, presumably through the precipitation of DOC on the surface of the carbonate minerals.

Concentrations of DOC are high in water extracted from peatlands, with values ranging from 25 to 50 mg L^{-1} commonly reported (mean 39.0 mg L^{-1}, Fig. 6). The high contents of organic matter in peatland soils and the absence of significant mechanisms to reduce DOC concentrations (apart from microbial utilization of DOC and co-precipitation with iron in oxidising zones), ensure these high concentrations. However, this study, as well as those of Moore (1987a) and Marin et al. (1990) have revealed the high spatial and temporal variability of peat water DOC concentrations. Factors controlling these DOC concentrations include plant tissue and peat type, peat temperature (influencing microbial production and utilization of DOC) and hydrologic regime, more specifically the diluting and flushing effects associated with a high water table and the probable concentration of DOC as evapotranspiration lowers the water table during dry periods. Swamps in southern Canada commonly exhibit water tables well beneath the surface during the summer (National Wetlands Working Group 1988). A further factor is the chemistry of the peat water: the present study has shown a negative relationship between DOC concentrations and specific conductance in the lower (60 cm) depths of the peat profiles, and this may be associated with the precipitation of DOC in contact with carbonate-rich water, as has been observed for the well-drained sideslope soil with a calcareous subsoil and parent material. Marin et al. (1990) have recently reported a positive association between specific conductance and DOC concentration in a poor fen in Wisconsin, which they attribute to the influence of DOC on conductance in water where other ions are in low concentrations. More work is required to be able to establish the reasons for the high spatial and temporal variability of DOC concentrations in peat water.

The concentration of DOC in streams is very variable, ranging from 1 to 50 mg L^{-1} (Fig. 6) and reflects the sources and pathways of DOC and runoff within the catchment. In undisturbed, forested catchments underlain by weathered, well-drained soils, DOC concentrations in streams are usually <10 mg L^{-1} (mean 4.6 mg L^{-1}, Fig. 6), but as the proportion of

the catchment occupied by wetlands increases, or as the soils become shallower and less able to adsorb DOC, stream DOC concentration and export increase (e.g. Eckhardt & Moore 1990; Mulholland & Kuenzler 1979; Urban et al. 1989). The streams draining the lower section of the Mont St. Hilaire catchment illustrate this pattern. DOC concentrations are low in springs draining the western slope, and increase downstream through the influence of DOC-rich groundwater supplied by the swamp.

The mixture of sources of DOC, in terms of both their DOC concentration and their hydrologic importance in producing runoff, means that stream DOC concentrations may show strong temporal variability associated with seasonal and discharge variations. Export of DOC from catchments will also be variable from year to year, depending on the sources of DOC and their contribution to runoff, as illustrated by studies in which DOC export has been measured over a number of years (e.g. Tate & Meyer 1983; Urban et al. 1989). Thus, linkages of catchment components through hydrologic pathways are of paramount importance in determining DOC fluxes.

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