UC Irvine
UC Irvine Previously Published Works

Title

Precambrian Shield Wetlands: Hydrologic Control of the Sources and Export of Dissolved Organic Matter

Permalink

https://escholarship.org/uc/item/0f85z43t

Journal

Climatic Change, 40(2)

ISSN

0165-0009

Authors

Schiff, Sherry
Aravena, Ramon
Mewhinney, Eric
et al.

Publication Date

1998-10-01

DOI

10.1023/a:1005496331593

Copyright Information

Peer reviewed

PRECAMBRIAN SHIELD WETLANDS: HYDROLOGIC CONTROL OF THE SOURCES AND EXPORT OF DISSOLVED ORGANIC MATTER

SHERRY SCHIFF[1], RAMON ARAVENA[1], ERIC MEWHINNEY[1], RICHARD ELGOOD[1], BARRY WARNER[1], PETER DILLON[2], SUSAN TRUMBORE[3]

1. Department of Earth Sciences, University of Waterloo, Waterloo, ON N2L 3G1 Canada
2. Dorset Research Centre, Ontario Ministry of Environment, Dorset, ON P0A 1E0 Canada
3. Department of Earth System Science, University of California-Irvine, Irvine, CA 92717 USA

Abstract. Most Precambrian Shield forested catchments have some wetland component. Even small riparian wetlands are important modifiers of stream chemistry. Dissolved organic matter (DOM) is one of the most important products exported by wetlands in streams. Stratigraphic control of hydraulic conductivity generally leads to decreasing conductivity with depth. Thus important flowpaths occur in the uppermost organic rich layers and are reflected in chemical profiles of dissolved organic carbon (DOC). Accumulation of DOC in peat porewaters is the net effect of production, consumption and transport. DOC profiles vary with degree of interaction with the surrounding upland catchment and distance from the edge of the wetland as well as internal processes within the wetland. In wetlands, DOM production is offset by flushing resulting in decreasing DOC concentrations with increasing flows. Despite old carbon (2,000 to 3,000 years) at relatively shallow depths, ^{14}C activity in DOC exported from wetlands is mostly modern (recent carbon), consistent with shallow flowpaths and export of DOM from shallow organic rich horizons. In contrast, the source area for DOM in upland catchments with developed B horizon soils increases with antecedent soil moisture conditions resulting in increasing DOC concentrations with higher stream flows. Activity of ^{14}C in stream DOC from upland catchments span a range from low activities (older carbon) similar to B horizon soil water during dry moisture conditions to values slightly less than modern (more recent carbon) during high moisture conditions. The more modern carbon activities reflect the increased contribution of the organic rich litter and A horizon soil layers in the area immediately bordering the stream under wet antecedent moisture conditions. Reduced hydrologic export or loss of wetlands under drier climatic conditions may result in in larger fluctuations in stream DOC concentrations and reduced DOM loads to lakes.

keywords: wetlands, forested catchments, dissolved organic carbon, carbon cycling

1. Introduction

Few forested catchments on the Precambrian Shield do not contain wetlands. Typical wetland characteristics include hydric soils, hydrophilic vegetation and water tables near the surface for a large portion of the year. These wetlands can range from large expanses covering areas of km^2 to small wet riparian areas bordering streams. Because of the undulating nature of the Precambrian Shield and moderate hydraulic conductivity of the glacial tills, wetlands in this setting are often topographically controlled (Devito, 1995).

The presence of wetlands in forested catchments greatly modifies the chemical export in surface streams. Precambrian Shield wetlands increase the retention of sulfate (LaZerte, 1993, Devito, 1995) and nitrate (Devito and Dillon, 1993), thus mitigating the effects of acid atmospheric deposition. Wetlands can also function as a natural source of contaminants such as methyl mercury by enhancing mercury methylation (St. Louis et al., 1995, Branfireun et al., 1996).

One of most important products of wetlands is dissolved organic matter (DOM). Export of DOM increases with the proportion of catchment covered by wetlands (Mulholland and Kuenzler, 1979, Urban et al., 1988, Clair et al., 1994, Dillon and Molot, 1997). In aquatic systems, DOM is an important component in the food web (Hobbie and Wetzel, 1992) and the acid-base balance of softwaters (Eshelman and Hemond, 1985), has a major role in the transport and toxicity of trace metals and other contaminants (Thurman, 1985, Driscoll et al., 1995), affects light penetration (Fee et al., 1998) and protects aquatic organisms from the effects of UV radiation (Skully and Lean, 1994). In addition, export of DON (dissolved organic nitrogen) constitutes the main loss of N from pristine forested catchments (Hedin et al., 1995). Wetlands increase the export of both total organic nitrogen and total phosphorus (Devito et al., 1989)

Global climate change accompanying the rising atmospheric levels of CO_2 and CH_4 will affect the hydrologic balance on the Precambrian Shield and, consequently, wetland geochemistry. In northwestern and central Ontario Canada, predicted climate change scenarios are for warmer and slightly drier conditions with an important emphasis on drier late summers and warmer winters (Mortsch and Quinn, 1996). Our approach is to examine the current relationships between hydrology and the export of DOM in forested catchments, both with and without wetlands, in order to speculate on the effect of this climate change scenario on downstream surface waters. Three aspects will examined in this paper:

a) the role of hydrology on DOM in porewaters of peatlands

b) the contrast between uplands and wetlands in small forested catchments in central Ontario in the sources and export of DOM

c) the changes in DOC (dissolved organic carbon) stream concentrations and export in these small forested catchments during wet and dry hydrological conditions.

2. Methods

Data discussed in this paper were collected from two field areas: the Experimental Lakes Area (ELA) near Kenora, Ontario, and the Harp Lake

and Plastic Lake Watersheds near Huntsville Ontario (Fig.1). Two sphagnum dominated boreal forest wetlands, wetland 632 and wetland 979 were studied at the ELA. Wetland 632 is in a headwater catchment whereas wetland 979 receives inflow from several upstream lakes. Both wetlands have similar stratigraphy, ^{14}C age with depth profiles of solid peat, developmental history and hydraulic conductivity distribution with depth (Poschadel et al., 1997).

Harp Lake watershed is in the temperate forest region of the Precambrian Shield. A forest dominated by maple and birch overlies glacial till covered bedrock of biotite and horneblende gneiss and amphibolite schist. The watershed has been divided into a series of subcatchments most of which contain some wetland area (Fig. 1). Plastic Lake watershed has thinner soils and a predominantly coniferous forest cover. The two wetlands studied, Harp 4 and Plastic swamps have similar peat stratigraphy and peat age versus depth profiles.
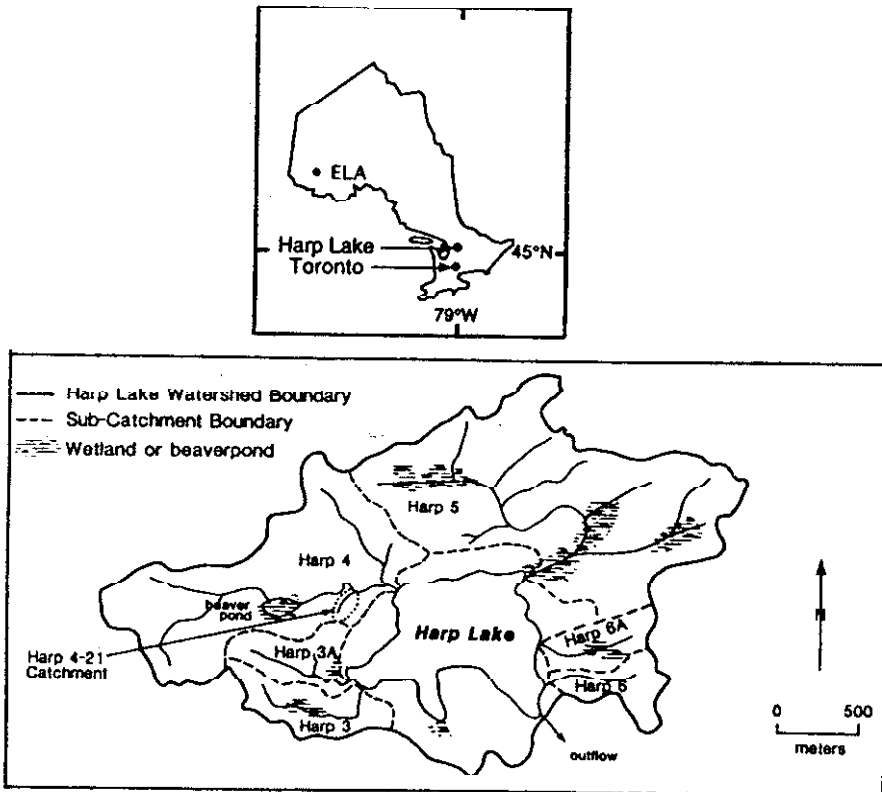

Figure 1: Location of the Harp Lake Basin and the Experimental Lakes Area. Map of Harp watershed shows subbasins with shading in the wetland areas. The areas of the entire Harp Lake catchment and the subbasins are: Harp Basin (506 ha), Harp 3 (26.0), Harp 3A (19.7), Harp 4 (119.5), Harp 5 (190.5), Harp 6 (10.0) and Harp 6A (15.3).

Instrumentation and methods to characterize the hydrology and geochemistry were similar at all sites. Hydrogeological instrumentation includes both water table wells and piezometers slotted over discrete depth intervals (further details are contained in Mewhinney, 1996, Devito et al., 1996, Hinton et al., 1997, Poschadel, 1997). Stream flow at Harp watershed is measured continuously and stream chemistry has been analyzed on a daily to biweekly basis (e.g. Dillon and Molot, 1997). DOC was analyzed by high temperature combustion at the University of Waterloo or by persulfate oxidation by the Ontario Ministry of Environment (1983). DOM samples for C:N ratios were obtained by freezedrying filtered (0.2 μm) water samples if NO_3 concentrations were insignificant or by ultrafiltering with a Minitan ultrafiltration system equipped with a 1000 Dalton molecular weight cutoff filter. C:N ratios were measured on a Carlo Erba Elemental Analyzer. Methods used for ^{14}C analysis followed Schiff et al. (1997). Analytical precision for ^{14}C was $\pm$ 10 $^0/_{00}$.

3. Results and Discussion

3.1. ROLE OF HYDROLOGY ON DOC CONCENTRATIONS IN PEATLANDS

Dissolved organic matter is an intermediary in the decomposition process and is both produced and consumed during the diagenesis of organic matter to form the peat sediments in wetlands. The net DOC production reflects the balance between these two competing processes. Accumulation of peat can range from tens of cms to over ten metres (Warner, 1996) and represents a large store of organic material that is continuously available for microbial decomposition. The highest rates of decomposition however are found closest to the surface where there is a higher input of fresh litter and recently synthesized labile organic matter, the carbon has been exposed to less decomposition and where there is a larger abundance of alternate electron acceptors to complete the redox couple (e.g. Poschadel et al., 1997, Brigham et al., 1995). Rates of both production and consumption are highly temperature dependant.

Peatland hydrology affects the concentrations of dissolved carbon observed in peat porewater profiles. The importance of hydrology on CH_4 and CO_2 fluxes from peatlands is well documented (Moore et al. 1990, Romanowicz et al., 1994). Within the peat, stratigraphy plays a major role in carbon transport by groundwaters. In general, hydraulic conductivities decrease with depth (e.g. Fig. 2), creating conditions for higher groundwater

flow rates through the uppermost part of the peat column. However, the groundwater flow regime in wetlands is quite dynamic and complex.

Different conceptual models have been postulated for groundwater flow in peatlands. The static model (Ingram, 1983) assumes that the near surface is the only active hydrological zone and that the water below is basically stagnant. This model also assumes that the wetland is isolated from the underlying groundwater flow system and that raised bogs only occur in recharge areas. Limited empirical evidence obtained mainly from raised bogs in Britain lends support to this model.

A second model postulated by Siegel and Glaser (1987) recognizes that in the raised portion of a peatland, a groundwater mound exists, creating the conditions for a vertical gradient in the hydraulic head. The significantly lower hydraulic conductivities of the lower layers produces a significant lateral groundwater flow in the near surface layers towards the edge of the raised bog. This second model predicts that there will be groundwater exchange between adjacent peatlands and between underlying substrates and the peatland. This dynamic model has been supported by data collected in peatland complexes in the USA (Siegel and Glaser, 1987, Glaser et al., 1997) and Europe (Waddington and Roulet, 1997).

A third model applies to wetlands located in groundwater discharge zones with hydrological flow conditions that range from very stable conditions associated with regional groundwater aquifers (Roulet et al 1990) to highly variable flow conditions associated with local scale groundwater flow systems (Devito et al., 1996). In these wetlands, decreases in hydraulic conductivity with depth in the peat also confine the important lateral flowpaths to the uppermost layers.

Recently Siegel et al. (1995) and Devito et al. (1997) have shown that groundwater flow directions can change over timescales of weeks to years depending on the size of the peatland and the changes in the boundary conditions. Drier conditions cause differential decreases in the water table and changes in the hydraulic head differences between peatlands and the surrounding landscape. Conditions for flow reversal are created and recharge areas can become discharge areas. These flow reversals can have a significant effect on the biogeochemistry of a peatland (Siegel et al., 1995, Glaser et al., 1997, Waddington and Roulet, 1997).

Despite the complexity of the flow systems in peatlands, all of the models and supporting data show that the flowpaths in the uppermost peat layers dominate the hydrogeologic flow in peatlands. Transport of dissolved carbon species along flowpath within the peat also affects the observed concentrations in peat porewaters. Production, consumption and transport are competing processes. The net effect is the accumulation observed in the porewater profiles. Even though production of dissolved carbon generally

decreases with depth, the maximum in the porewater concentrations profiles of DOC, CO_2 and CH_4 in a small boreal forested peatland at ELA occurs significantly below the water table (Fig 2). Above the maximum, hydrologic flow is rapid enough to flush dissolved carbon produced in the surface layers. Below the maximum, production may also be occurring at lower rates as evident in incubation studies of peat from these depths (Poschadel et al., 1997) but groundwater flow is slower allowing accumulation. The concentration maximum therefore likely does not represent a maximum in production in most cases but the depth of highest accumulation.
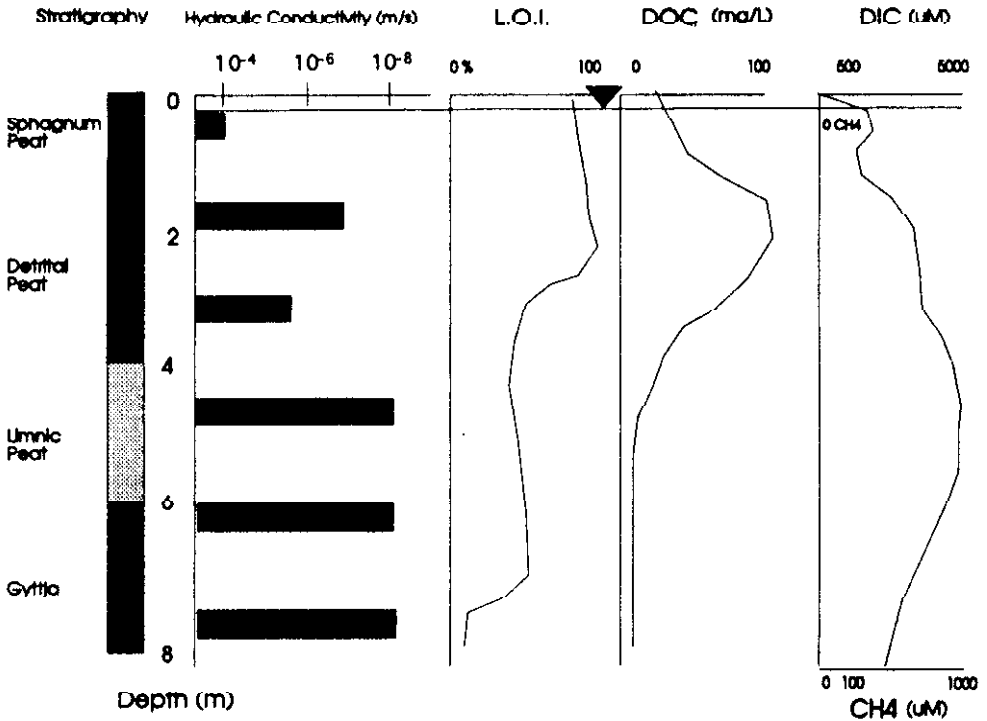

Figure 2: Peat stratigraphy, average hydraulic conductivity, loss on ignition (LOI) and average dissolved carbon profiles from 3 sites located in the central depression at distances of 1, 10 and 20 metres from the central pond in the wetland 632 at the Experimental Lakes Area. Because the DIC and CH_4 profiles are similar in shape, only one line is drawn for both. Water table location is indicated by the line with the solid triangle. In the unsaturated zone above the water table, DIC declines to levels in equilibrium with atmospheric CO_2, whereas CH_4 concentrations are quickly reduced to zero by methanotrophs. See Mewhinney (1996) for additional information on physical, chemical and hydrogeologic characteristics of these sites.

The degree of interaction with the surrounding upland catchment and distance from the edge of the wetland also affects the dissolved carbon profiles. Transport of nutrients, O_2, and other electron acceptors such as SO_4^{2-} as well as labile DOC in surface or ground waters draining the upland terrestrial catchment will affect the rates and pathways of organic matter decomposition. This can be seen in the porewater profiles of CH_4 (Mewhinney, 1996) and also in the CH_4 flux rates but not in the DOC profiles because of the effects of flushing in the shallow part of the peat. The competing roles of production, consumption and flushing is clearly observed in DOC profiles collected in a series of piezometers nests located in a transect from near upland areas towards the central pond at 632 wetland (Fig. 3). These profiles show no significant increase of DOC along the flowpath from upland areas towards the pond (from NAD to NAA) in the surficial peat. The DOC maximum associated with accumulation corresponds well with low hydraulic conductivity layers determined both by piezometer tests and stratigraphic coring (Mewhinney, 1996).
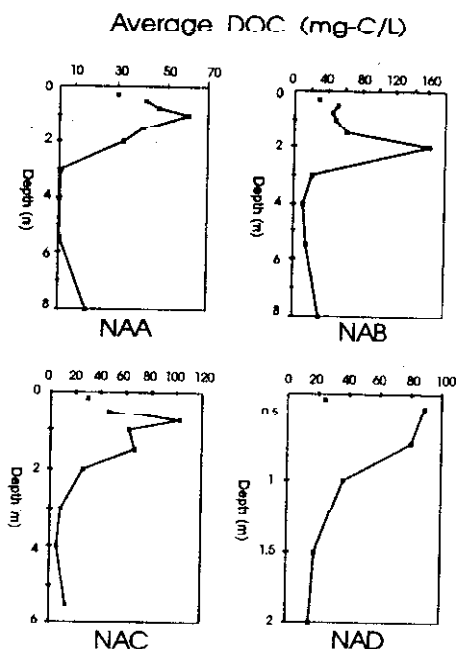
Average DOC (mg-C/L)

Figure 3: Peat porewater profiles of DOC in the wetland 632 at the Experimental Lakes Area on 15 July, 30 July and 29 August 1996. Locations are on the north side a) 1 metres from the central pond, b) 10 metre from the central pond, c) 20 metres from the central pond and d) 10 metres from the edge of the wetland. Piezometers screen lengths are 20 to 30 cm centred on the depth indicated by the symbol. The uppermost symbol is the DOC concentration at the water table. See Mewhinney (1996) for additional information on physical, chemical and hydrogeologic characteristics of these sites.

Hydrology also plays a role in the seasonal changes observed in DOC concentrations in wetlands. The higher concentrations observed during dry summer and early fall periods is a result of lower flushing and higher decomposition rates under lower water tables and warmer conditions compared to spring and winter (McKnight et al.,1984, Marin et al., 1990, Dalva and Moore, 1991). However, not all wetlands show this seasonal DOC pattern. Two of our study sites, Plastic and Harp 4 wetlands with similar stratigraphy show DOC concentrations in the range of 20 to 30 and 6 to 9 mg·l^{-1} respectively. The lower DOC concentrations observed at Harp 4 is related to the continuous flushing of this wetland during the entire non-frozen season. The high water table at this wetland is maintained by a continuous input of groundwater associated with a thicker overburden than at the Plastic wetland (Devito et al., 1996). The higher DOC concentration at Plastic is due to accumulation of DOC as a result of less flushing especially during times of lowered water table. This wetland is hydrologically disconnected from the upland groundwater flow system during the summer (Devito et al., 1996).

In summary, the hydrology governs the appearance of the porewater profiles in peatlands through controlling both the position of the water table and the velocity of water movement along flowpaths. The flow system affects the supply of labile organic substrates, the supply of redox sensitive species including the depth of penetration of oxygen and the flushing of reactants and products. The dominant flowpaths are confined to the shallow peat layers. Consequently, the stream export of chemical species from wetlands will be governed by the processes affecting the uppermost peat despite the large inventory of carbon held in northern peatlands.

3. 2. SOURCES OF DOM EXPORTED FROM WETLAND AND UPLAND CATCHMENTS

Elevated DOC concentrations are observed in catchments with wetlands compared to upland catchments under all conditions including baseflow and springmelt (Marin et al., 1990, Dalva and Moore, 1991, Mann and Wetzel, 1995). Even small valley bottom wetlands and wet riparian areas are important modifiers of stream chemistry and catchment export (Hemond 1990). Harp 4 wetland is a small mixed coniferous/deciduous swamp covering less than 1.2 ha and is topographically constrained to the valley bottom (Devito, 1995). The wetland comprises only 5% of the basin of 22.7 ha. The hydrology is controlled by the input of both surface and groundwater. During high flow conditions the majority of the flow is routed through the surface of the wetland in the form of a lagg. Despite the anticipation that the effect of the wetland on catchment export may be limited by the high ratio of upstream catchment area to wetland area and the surface flowthrough, the

DOC concentrations are high and show a marked rise over the 150 metre section of the stream bounded by the wetland (Fig. 4).
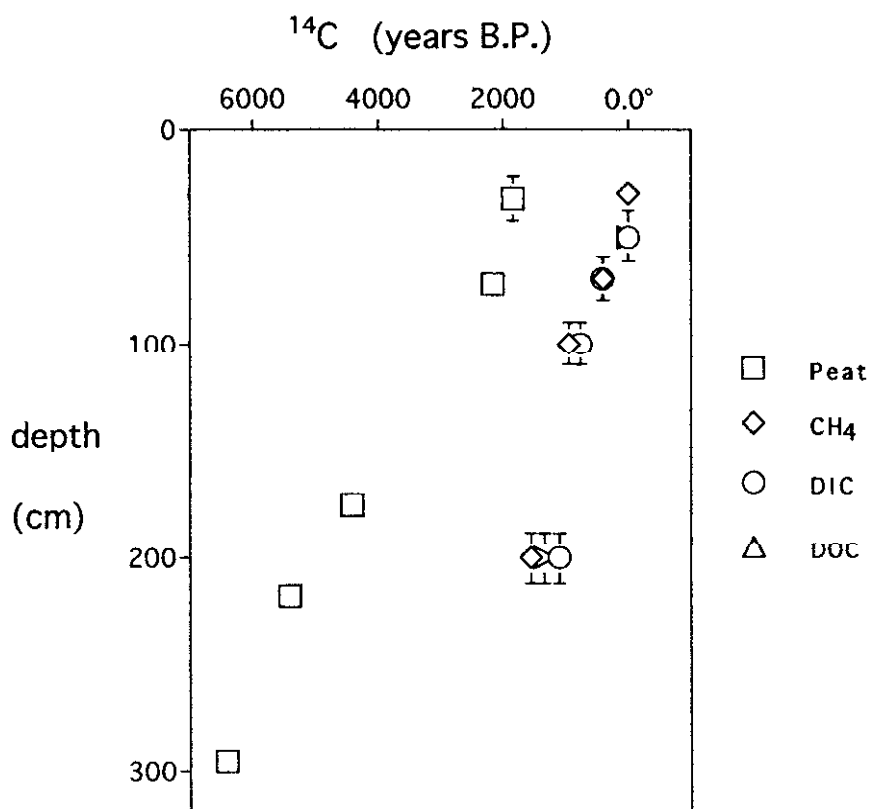

Figure 4: ^{14}C ages of peat porewater DOC, CH_4 and CO_2, and solid peat in wetland 979 at the Experimental Lakes Area. .

The DOC exported from these small wetlands is derived from the near surface. This is a direct consequence of the dominant hydrological flowpaths being located at and immediately below the water table and is evident in the ^{14}C activities of the DOC. Despite ^{14}C ages of solid peat of 1000 to 2000 years at a depth of 50 cm below the surface, ^{14}C activities of DOC exported from wetlands are predominantly modern (Fig. 5). Near modern ^{14}C activities indicate that the majority of the organic carbon in the DOC was derived from atmospheric CO_2 that was fixed as organic matter and subsequently solubilized within the last 45 years (Schiff et al., 1990). Because of the lack of solid phase physical mixing processes in wetlands and the confinement of living roots to very shallow layers, recent organic carbon is only found in the near surface of the wetland. Activities of ^{14}C in DOC from the hydrologically active surface peat zone are all modern (Mewhinney, 1996).
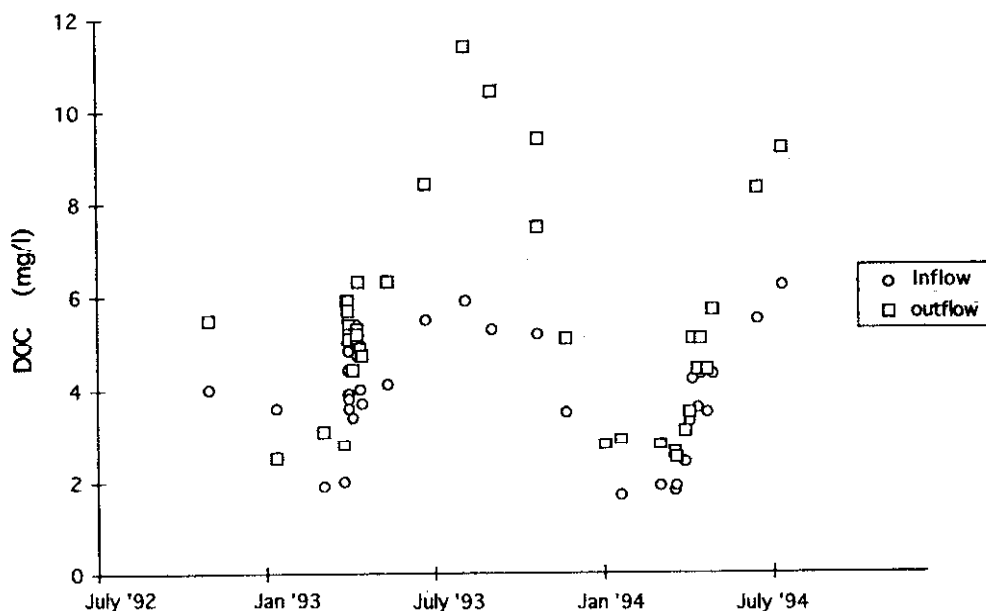
Figure 5: DOC in the inflow and outflow streams of Harp 4 wetland.

At depth in the peatland the water is not stagnant. The offset of the ^{14}C ages of the DOC, CO_2 and CH_4 from the age of the solid peat at depths between 0.5 and 3.0 metres in a small sphagnum dominated peatland (Fig. 6) shows that more recent dissolved carbon is being transported within the peat profile. This pattern has also been observed in other northern peatlands (Aravena et al., 1993, Charman et al., 1993, Chanton et al., 1995). However, the confinement of the ^{14}C activities to near modern values in the DOC exported from peatlands confirms the dominance of the shallow hydrogeologic flowpaths.

The near modern ^{14}C activities in DOC exported from wetlands is in contrast to stream DOC in upland catchments such as Harp 4-21 which have developed B horizon podzolic soils. In Harp 4-21, the DOC exported in the stream can vary from values substantially less than 0 $^{o}/_{oo}$ to modern values depending on the antecedent moisture conditions (Fig. 5). Values less than 0 $^{o}/_{oo}$ are observed in soil waters within or below the soil B horizon and correspond to DOC that has been substantially altered by sorption and microbial decomposition processes within the soil (Schiff et al. 1997). Ratios of C:N indicate that the exported DOC may be chemically different in upland and wetland catchments corresponding to differences in ^{14}C activity (Schiff, unpublished data).
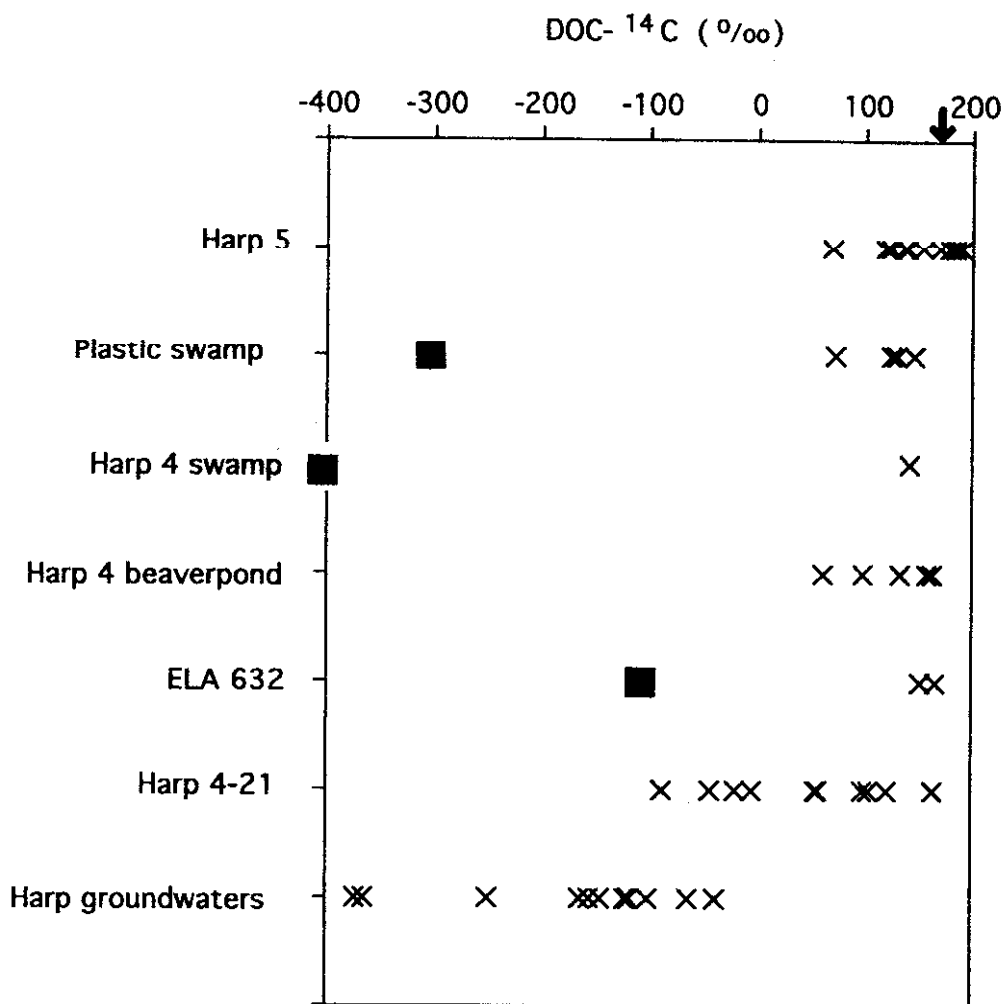
Figure 6: [14]C activity in outlet streams (X) from wetlands Harp 5, Plastic swamp, Harp 4, Harp 4 beaverpond (see Fig.1), ELA wetland 632, the stream from upland catchment Harp 4-21 and the groundwaters in Harp 4-21. Solid squares mark the ^{14}C activity in the solid peat at 50 cm below the surface of the peat. The ^{14}C ages corresponding to these ^{14}C activities are: Plastic swamp (2910 yrs b.p.), Harp 4 swamp (4060 yrs b.p.) and ELA 632 (1010 yrs b.p.). The arrow on the top axis shows the ^{14}C activity measured in leaves at Harp 4-21 in 1990.

The shapes of the concentration-discharge relationships for DOC also differ between upland and wetland catchments. DOC increases with increasing flow in Harp 4-21, an upland catchment (Fig. 7a), with the result that 50% of the stream export occurs in the upper 10% of the flow values (Hinton et al., 1997). Routine sampling programs may consistently underestimate DOC

export from upland catchments. In contrast, in Harp 5 which contains a large
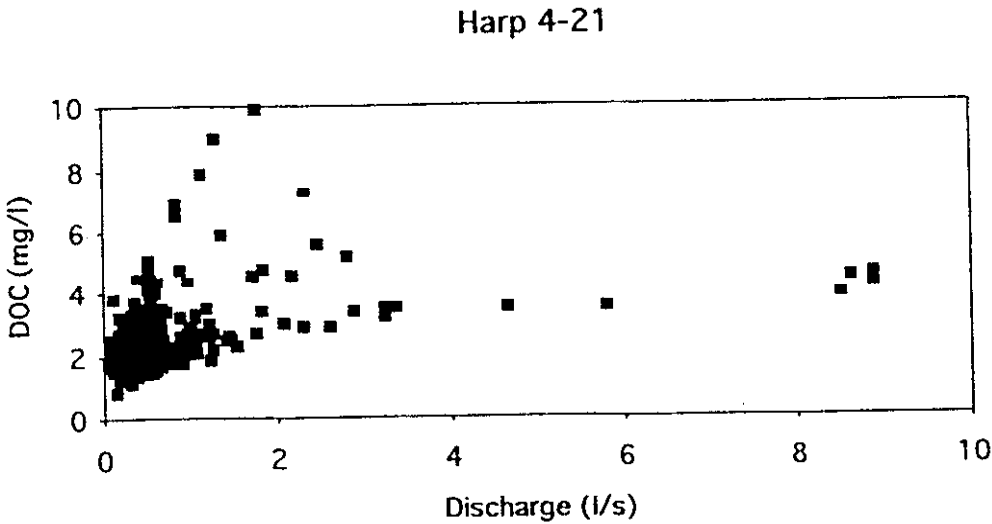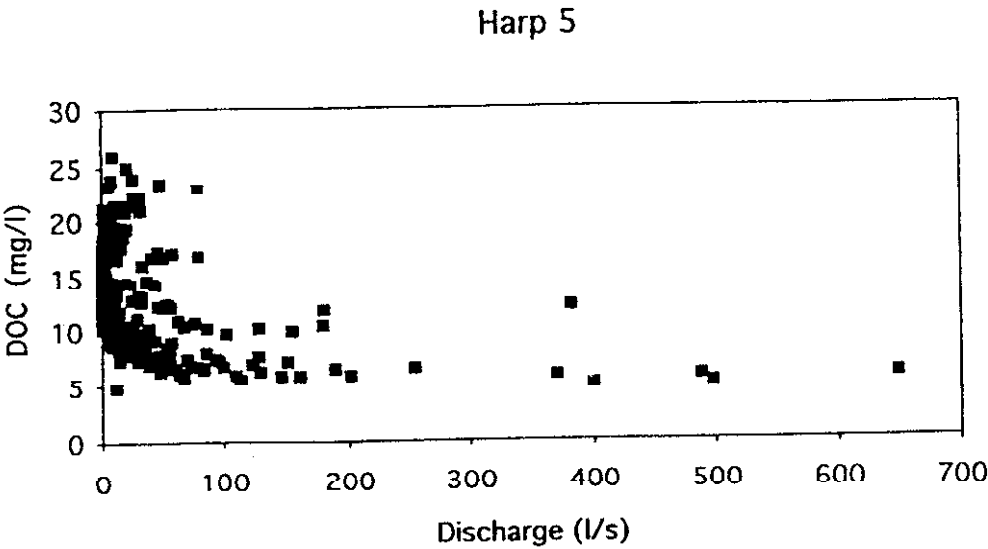wetland (Fig. 1), DOC decreases with discharge (Fig. 7b).

Harp 5

Harp 4-21

Figure 7:   DOC versus discharge in a) Harp 4-21 and b) Harp 5.

The difference in concentration-discharge relationships between wetlands and uplands is a direct consequence of the differences in the hydrology in the source area for the DOC. In wetlands, because the water table remains close to the surface, additional water from precipitation events does not greatly increase the contact with organic rich surface horizons. Precipitation events can however serve to link formerly isolated wetland pools together and allow flushing of the accumulated DOC. After this initial flush, precipitation and shallow discharging groundwaters tend to dilute the remaining DOC in the surface zone. Because the pockets of accumulated DOC are not all flushed simultaneously, the overall pattern is a decrease in DOC with increasing flow. In contrast, groundwaters residing in soils below the A horizon in upland catchments have low DOC concentrations (1-3 mg/l). In these catchments, streamflow even during storms consists mostly (typically 70-80% in storms, Hinton et al., 1994) of pre-event soil and groundwaters. Thus, at low soil moisture conditions, streamwater is low in DOC concentration and low in ^{14}C activity of the DOC reflecting the input of older carbon from the soil column. Rising water levels permit flowpaths to intersect shallow organic rich soil horizons near the stream with DOC characterized by near modern ^{14}C activity. Increased discharge allows export of near surface DOC of more modern activity in the stream (Schiff et al., 1997).

Because of the continuous contact of water with shallow organic rich soils in wetlands, a higher proportion of the carbon decomposition in the annual carbon cycle can be exported as DOC in wetlands compared to upland systems containing B horizon soils. In uplands most of the carbon cycling activity is decoupled from the stream with the balance between fixation and decomposition being stored in biomass and the soil column. Consequently, in upland catchments with thicker tills, the source of the majority of the exported DOC is the narrow band close to the stream (Hinton et al., 1998). In wetlands, a greater proportion of the decomposed carbon is exported as DOC due to the increased hydrologic flushing of shallow organic rich horizons. However, the annual DOC export remains small (10-400 kgC·ha^{-1}·yr^{-1}; Urban et al., 1988, Dillon and Molot, 1997) relative to the annual carbon fixation/respiration fluxes (500-2650 kgC·ha^{-1}·yr^{-1}; Dillon and Molot, 1997). The majority of the decomposed carbon is exported as CO_2 with a small contribution from CH_4.

The presence of open water in the form of shallow ponds (including beaver ponds) can decrease the export of DOC relative to wetlands with no open water. In boreal catchments at ELA, uplands can have little or no B horizon soil development and consequently, intermittent upland streams have high levels of DOC. However, peatlands surrounding open wetland ponds are even stronger sources of DOC than uplands due to shallow flowpaths (Mewhinney, 1996). Significant consumption of DOC occurs within the

central pond possibly due to photolytically enhanced decomposition of DOC. However, the net effect of both peat and pond is that the wetland functions as a source of DOC (Kelly et al., 1997).

Confinement of the important hydrologic flowpaths in wetlands to shallow organic rich horizons with high DOM production rates is responsible for the observed importance of wetlands in increasing the export of DOM in streams draining forested catchments.

3.3.   INFLUENCE OF WET AND DRY YEARS ON CONCENTRATION AND EXPORT OF DOM

Because the water table limits O_2 penetration into the peat profile, the geochemical pathways and rates of decomposition are dependant on water table position. Dry conditions can drastically alter the physical location of the dominant geochemical redox processes within the peat profile. LaZerte (1993) observed that under wet antecedent conditions, Plastic wetland, a small coniferous swamp, stores sulfate, mitigating the effects of atmospheric deposition of sulfur. However, under dry conditions a large portion of the stored sulfur is exported as sulfate, presumably due to oxidation under lower water table conditions and subsequent remobilization once moisture levels are increased. This release of sulfate following dry summer/early fall conditions has been noted in other wetlands (Bayley et al., 1986, Devito, 1995) and also for nitrogen and phosphorus (Devito and Dillon, 1993).

Unlike sulfate, export of DOC from Plastic swamp does not increase in dry years (Fig. 8, LaZerte, 1993) as might be expected from an associated increase in the decomposition of organic matter. The additional oxidized carbon is likely exhaled as CO_2.

In both upland and wetland catchments, the amount of DOC exported is controlled by the quantity of water exported. In Harp Lake catchment, DOC export from the subcatchments is driven by the precipitation input over the 14 year monitoring period (Fig. 9). Even though DOC concentration decreases with increasing discharge in wetland catchments and increases with increasing discharge in upland catchments, catchments dominated by wetlands near the outflow show a similar pattern to upland dominated catchments in their response to precipitation.

Changes in the export of DOC to lakes also affects the delivery and biogeochemical cycling of other components associated with DOC. Dissolved organic matter contains a significant amount of nitrogen. Typical C:N ratios for upland and temperate forested catchments range from 20 to 40 with higher values (C:N of 35 to 60) observed for boreal forest catchments at ELA (Lamontagne and Schiff, unpublished data). Dissolved organic nitrogen (DON) is the main form of N exported from these catchments (Table I).

Table I: Export of DON, NO_3 and NH_4 as a percentage of the total nitrogen export in Harp 4-21, Harp 6 and Harp 6A. Data are the average for the years 1990 to 1994

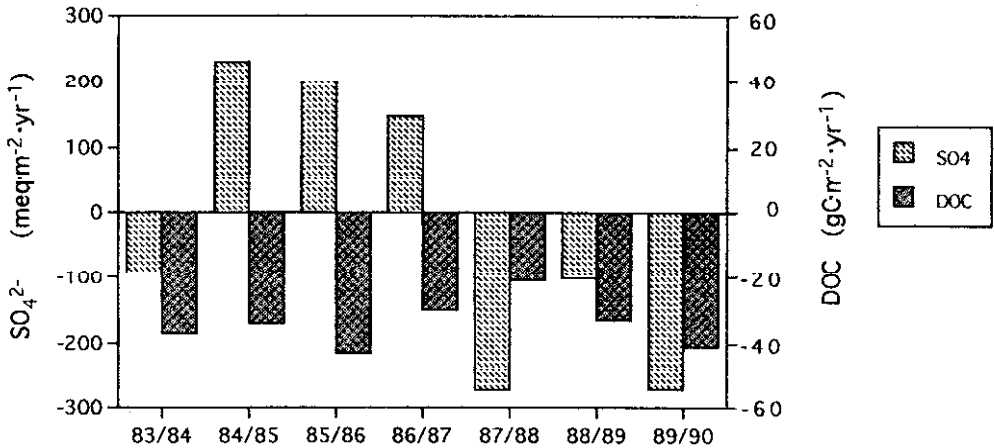|	N Export		
	% NO_3	% NH_4	%DON
Harp 4-21	26	2	71
Harp 6	46	3	51
Harp 6a	10	3	88

Figure 8 : Export of sulfate and DOC from Plastic swamp (drawn from data in LaZerte 1993).

Export of DON is not typically included in estimates of atmospheric nitrogen retention in similar forested catchments leading to a substantial overestimation of total N retention. Thus even unperturbed forested catchments leak nitrogen to streams and lakes. Export of DOM could be an important source of N (and similarly P in the form of dissolved organic phosphorus) to downstream lakes. Biogeochemical cycling and export of chemical species of interest such as Hg and other trace metals are strongly correlated with DOC export (Mierle and Ingram 1991, Driscoll et al. 1995) because of the role of DOC in increasing solubility and facilitating transport. Changes in DOC export will affect the loads of all but the major ions to lakes.

DOC is the most important control on the light penetration (Fee et al., 1998) and consequently affects the heat budget and stratification regime in lakes on the Precambrian Shield. Lake DOC concentrations will depend on both the export of DOC from the terrestrial catchments and the lake water residence time which governs the effectiveness of in situ DOC removal processes such as photo-oxidation, microbial decomposition and sedimentation. Drier conditions will decrease terrestrial DOC export and

increase water residence time suggesting that under a drier climate change scenario, lakes on the Precambrian Shield will become clearer. As a consequence, thermoclines will deepen and cold water habitat for economically important species such as lake trout will be more limited (Schindler and Curtis, 1997).
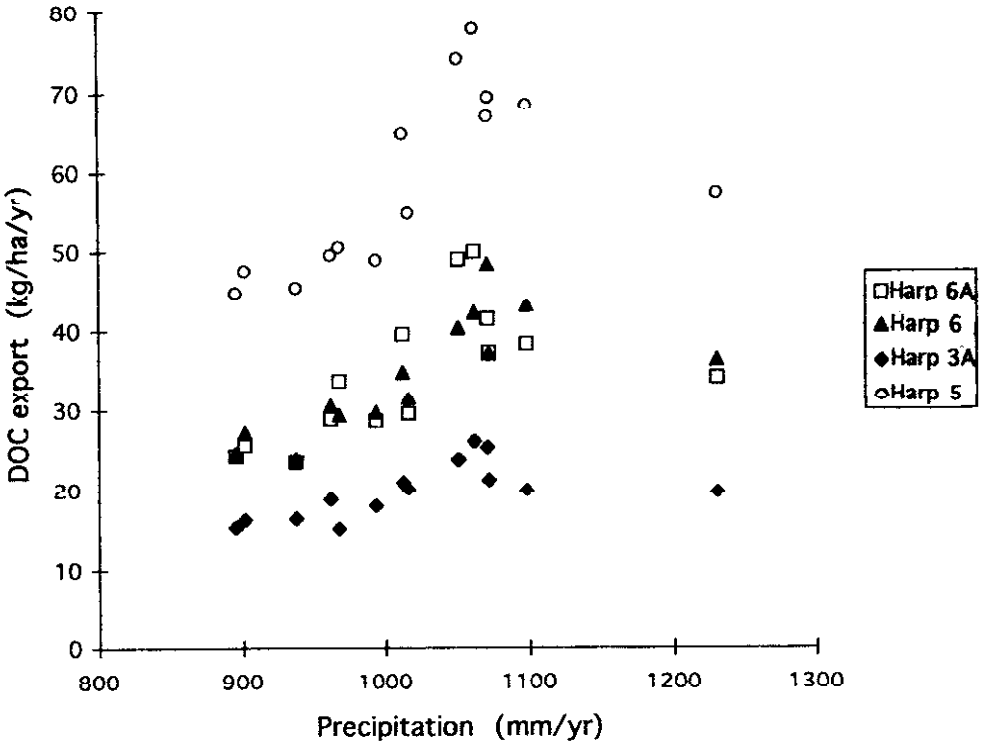

Figure 9:
    Export of DOC from subcatchments at Harp Lake versus annual precipitation measured at the Harp Lake meteorological site. All catchments have small wet riparian areas. Both Harp 6 and Harp 6A have a small wetland located near the top of the catchment. The larger of the wetlands at Harp 5 and Harp 6A are located at the terminus of the subcatchment.

Although DOC export from the catchment area is of concern for lakes with longer water residence times, seasonal fluctuations in DOC concentrations are more important for aquatic regimes in streams, wetland ponds and lakes with short water residence times. Increased penetration of UV accompanying a decrease in DOC may affect aquatic community structure (Bothwell, 1993, Schindler and Curtis, 1997). Under drier conditions during the period 1989-92, catchments at Harp Lake such as Harp 6 with limited extent of wet riparian zones along the stream show decreasing peak DOC concentrations (Fig. 10a). Peak summer values are a factor of two lower in dry summers. In contrast

neighbouring catchments such as Harp 6A show little change in seasonal DOC pattern and no marked increase in DOC in the first runoff following cessation of flow during dry summer periods (Fig. 10b). These contrasting behaviours are a direct consequence of differences in the DOC sources and the flowpaths transporting DOC to the stream in upland and wetland areas. Catchments with a significant wetland component may experience less fluctuations in stream DOC concentrations with changes in hydrologic flux. However, under dry conditions, conversion of wetland areas to upland areas or hydrologic disconnection of wetlands from exporting streams may result in larger fluctuations in DOC concentrations in streams and lakes with short water residence times.
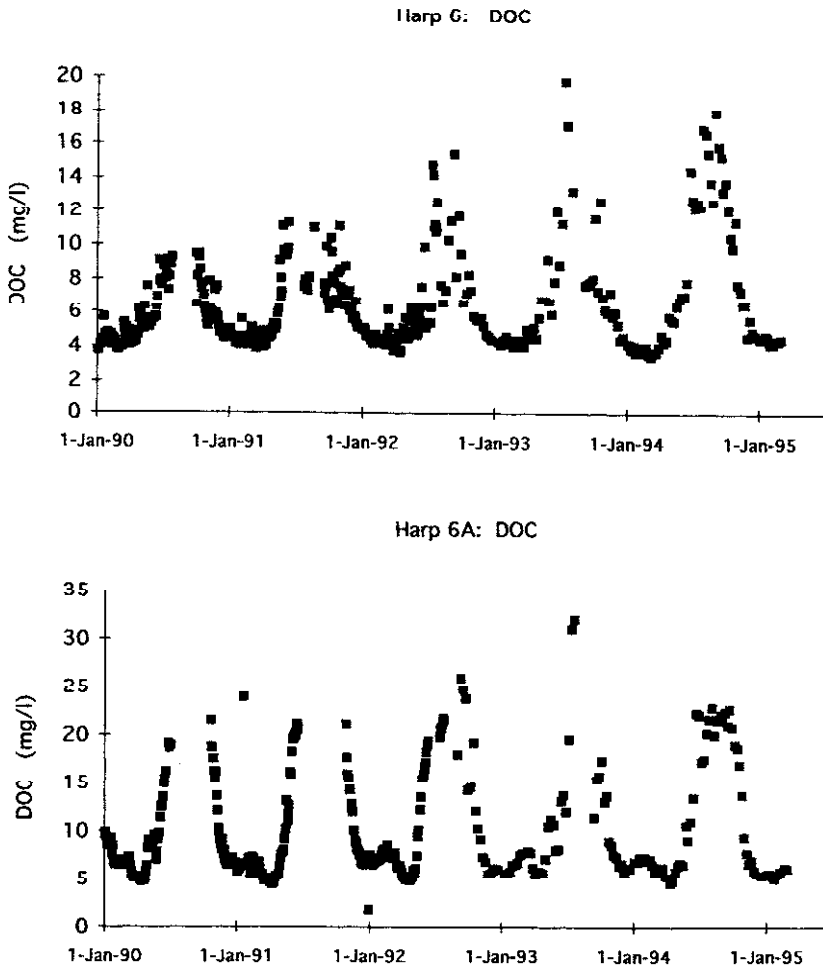

Figure 10: DOC concentrations in a) Harp 6 and b) Harp 6A from 1 January 1990 to 15 February 1995. Harp 6 has only limited wet areas adjacent to the stream and a small wetland in the headwaters. Harp 6A has a larger swamp located near the terminus of the catchment.

Examining catchment response to climate variability yields valuable clues as to the potential effects of various climate change scenarios. Although long term monitoring of hydrologic and chemical export of selected catchments is expensive, these long term data sets are the only way to ascertain catchment response to current climatic variability (Schindler and Curtis, 1997) and are an extremely valuable scientific resource. Analysis of long data records collected at Hubbard Brook (Likens et al., 1996) and the Experimental Lakes Area (Schindler et al. 1996) are excellent examples of the importance of long term monitoring in understanding the response of natural ecosystems to changes in atmospheric deposition and climate. A 20 year data set at ELA (Schindler et al., 1996) documents a significant decrease in DOC of lakewaters associated with a local climate warming (an increase of 1.6°C). The primary cause of this decline was the reduced export of DOC from terrestrial and wetland catchments to lakes caused by lower water tables and reduced streamflows under drier conditions.

3.4 IMPLICATIONS FOR CLIMATE CHANGE PREDICTIONS

Hydrology controls the geochemistry and export of DOM for forested catchments by affecting the internal redox biogeochemistry and by controlling the water movement along important flowpaths in organic rich horizons which are the DOM sources. Changes in DOM fluxes accompanying drier conditions could be either gradual or abrupt depending on the location of wetlands within the hydrologic flow system of the catchment. Riparian zone wetlands located near the catchment terminus will be less sensitive to alterations in catchment water yield because they receive water from the entire upslope catchment. Total export will, however, remain a function of water yield. Seasonal isolation of intermediate position wetlands from the main flow system or loss of wetland characteristics in upper parts of the catchments may result in more abrupt changes.

Prediction of catchment response to longer term climatic change, however, remains hindered by several knowledge gaps and the influence of unpredictable events. Wetland geochemistry and geochemical export from forested catchments is dominated by the hydrology. In turn, changes in vegetation and hydrology are not mutually independent. For example, an increase in the winter thaw frequency may allow increased flushing of nitrogen produced in significant quantities under the winter snowpack or promote decreased microbial nitrogen mineralization due to freezing of wetland soils under reduced snowpacks, thereby altering the nutritional status for vegetation. Thus, changes in wetland hydrology affect both water and nutrient availability and thus affect species composition. In concert, warmer and drier climates coupled with increased levels of atmospheric CO_2 may also

alter the vegetation regime. For example, a change in the species or number of trees will significantly alter evapotranspiration, the dominant control on summer wetland hydrology (Devito et al., 1996). Extension of current knowledge of climate variability to new conditions will not yield useful predictions in the event of permanent uni-directional shifts in vegetation and/or hydrology.

As an additional complication, events of a catastrophic nature may completely overwhelm the gradual adaptation to a slowly modifying climate. Tree "blow-down" as a result of high winds accompanying severe storm events alters hydrologic flowpaths and mixes or inverts stratified soil horizons. Insect infestations have been shown to completely alter the geochemistry of some catchments in unpredictable ways (Hyer et al., 1997). Finally, the current slow alteration of N-limited wetland systems by fertilization with an increased supply of atmospheric nitrogen is superimposed on climatic variability, complicating our ability to assess and predict change.

Acknowledgements

References:

Aravena, R., Warner, B.G., Charman, D.J., Belya, L.R., Mathur, S. and Dinel, H.: 1993, 'Carbon isotopic composition of deep carbon gases in an ombrogeneous mire, Northwestern Ontario', *Radiocarbon* **35**, 271-276.

Bayley, S.E., Behr, R.S., and Kelly, C.A.: 1986, 'Retention and release of Sulfur from a freshwater wetland' *Water Air Soil Poll.* **31**, 101-114.

Bothwell, M.L., Sherbot, D.M.J, and Pollock, C.M.: 1994, 'Ecosystem response to solar ultraviolet-B radiation: Influence of trophic-level interactions' *Science* **265**, 97-100.

Branfireun, B.A., Heyes, A. and Roulet, N.T.: 1996, 'The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland', *Water Resources Res.* **32**, 1785-1794.

Bridgham, S.D., Johnston, C.A., Pastor, J. and Updegraff, K.: 1995, 'Potential feedbacks of northern wetlands on climate change', *Bioscience* **45**, 262-274.

Chanton, J.P., Bauer, J.E., Glaser, P.A., Siegle, D.I., Kelley, A., Tyler, S.C., Rowanowicz, E.H., and Lazrus, A.: 1995, 'Radiocarbon evidence for the substrates supporting methane formation within northern Minnesota peatlands', *Geochim. Cosmochim. Acta* **59**, 3663-3668.

Charman, D., Aravena, R., and Warner, B.: 1993, 'Carbon dynamics in a forested peatland in north-eastern Ontario, Canada', *J. of Ecol.* **8 2**, 55-62.

Clair, T.A., Pollock, T.L., and Ehrman, J.M.: 1994, 'Exports of carbon and nitrogen from river basins in Canada's Atlantic Provinces', *Global Biogeochem. Cycles* **8**, 441-450.

Dalva, M. and Moore, T.R.: 1991, 'Sources and sinks of dissolved organic carbon in a forested swamp catchment', *Biogeochemisty* **1 5**, 1-19.

Devito, K.J.: 1995, 'Sulfate mass balances of Precambrian Shield wetlands: the influence of catchment hydrogeology', *Can. J. Fish Aquatic Sci.* **5 2**, 1750-1760.

Devito, K.J., Dillon, P.J. and LaZerte, B.D.: 1989, 'Phosphorus and nitrogen retention in five Precambrian shield wetlands', *Biogeochemistry* **8**, 185-204.

Devito, K.J. and Dillon, P.J.: 1993, 'The influence of hydrologic conditions and peat oxia on the phosphorus and nitrogen dynamics of a conifer *swamp'* *Water Resources Res.* **2 9**, 2675-2685.

Devito, K.J, Hill, A.R., and Roulet, N.: 1996, 'Groundwater-surface water interactions in headwater forested wetlands of the Canadian Shield' *J of Hydrology* **1 81**, 127-146.

Devito, K.J. and Hill, A.R.: 1997, 'Sulfate dynamics in relation to groundwater-surface water interactions in headwater wetlands of the southern Canadian Shield', *Hydrologic Processes* **1 1**

Devito, K.J., Waddington, J.M., and Branfireun, B.A.: 1997, 'Flow reversal in peatlands influenced by local groundwater systems', *Hydrol. Proc.* **1 1**, 103 110.

Dillon, P.J. and Molot, L.A.: 1997, 'Dissolved organic and inorganic carbon mass balances in central Ontario lakes' *Biogeochem.* **3 6**, 29-42.

Driscoll, C.T., Blette, V., Yan, C., Schofield, C.L., Munson, R. and Holsapple, J.: 1995, 'The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack Lakes' *Water Air Soil Poll.* **6 7**, 319-44.

Eshleman, K. N., and Hemond, H. F.: 1985, 'The role of organic acids in the acid-base status of surface waters at Bickford watershed, Massachusetts', *Water Resources Res.* **2 1**, 1503-1510.

Fechner, E.J. and Hemond, H.F.: 1992, 'Methane transport and oxidation in the unsaturated zone of a Sphagnum peatland' *Global Biogeochem. Cycles* **6**, 33-44.

Fee, E.J., Hecky, R.J., Kasian, S.E., and Cruikshank, D.: 1998, 'Potential size-related effects of climate change on mixing depths in Canadian Shield Lakes', *Limnol. Oceanogr.* **4 1**, (in press).

Glaser, P.H., Siegle, D., Romanowicz, E.A., and Shen, Y.P.: 1997, 'Regional linkages between raised bogs and the climate, groundwater and landscape of north-western Minnesota', *J of Ecology* **8 5**, 3-16.

Hedin, L.O., Armesto, J.J., and Johnson, A.H.: 1995, 'Patterns of nutrient loss from unpolluted, old-growth temperate forests: evaluation of biogeochemical theory', *Ecology* **7 6**, 493-509.

Hemond, H.F.: 1990, 'Wetlands as sources of dissolved organic carbon to surface waters', In: Perdue, E.M. and Gjessing, E.T. (Eds). *Organic Acids in Aquatic systems*, John Wiley & Sons, New York. pp. 301-313.

Hinton, M.J., Schiff, S.L., and English, M.C.: 1994, 'Examining the contributions of glacial till water to storm runoff using two- and three-component hydrograph separations', *Water Resources Res.* **3 0**, 983-993.

Hinton, M.J., Schiff, S.L., and English, M.C.: 1997, 'The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments', *Biogeochem.* **3 6**, 67-88.

Hinton, M.J., Schiff, S.L., and English, M.C.: 1998, Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield. Biogeochemistry (in press).

Hobbie, J.E., and Wetzel, R.G.: 1992, 'Microbial control of dissolved organic carbon in lakes - Research for the future', *Hydrobiologia* **229**, 169 180.

Hyer, K.E., Galloway, J.N., and Eshleman, K.E.: 1997. Episodic nitrate and ammonium transport along a spatial gradient in a forested headwater stream in Virginia. *EOS Abstracts Spring mtg of Amer. Geophy. Union.* S168.

Ingram, H.A.P.: 1983, 'Hydrology'. In: *Mire, Swamp, Bog, Fen and Moore Vol 4A. General Studies* (Ed. A.J.P. Gore) Elsevier, Amsterdam. pp. 67-158.

Kelly, C.A., Rudd, J.W.M., Bodaly, R.A., Roulet, N.P., St. Louis, V.L., Heyes, A., Moore, T.R., Schiff, S., Aravena, R., Scott, K.J., Dyck, B., Harris, R., Warner, B., and Edwards, G.: 'Increases in Fluxes of Greenhouse Gases and Methyl Mercury following Flooding of an Experimental Reservoir', *Environ. Sci. Tech.* **31**, 1334-1344.

Lansdown, J.M., Quay, P.D. and King, S.L.: 1992, 'CH_4 production via CO_2 reduction in a temperate bog: A source of ^{13}C- depleted CH_4', *Geochim. Cosmochim. Acta* **56**, 3493 3503.

LaZerte, B.D: 1993, 'The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp', *Biogeochemistry* **18**, 153-175.

Likens, G.E., Driscoll, C.T., and Buso, D.C.: 1996, 'Long-Term Effects of Acid Rain: Response and Recovery of a Forest Ecosystem.' *Science* **272**, 244-246.

Mann, C.J., and Wetzel, R.G.: 1995, "Dissolved organic carbon and its utilization in a riverine wetland ecosystem' *Biogeochemistry* **31**, 99-120.

Marin, L.F., Kratz, T.K., and Bowser, C.J.: 1990. 'Spatial and temporal patterns in the hydrogeochemistry of a poor fen in northern Wisconsin', *Biogeochemistry* **11**, 63-76.

McKenzie, C., Schiff, S.L., Aravena, R., Kelly, C.A., and St. Louis, V.: 1998, 'Effect of temperature on Production of CH_4 and CO_2 from Peat in a Natural and Flooded Boreal Forest Wetland' *Climatic Change* 40, 247-266 (this volume)

McKnight, D.M., Thurman, L.M., Wershaw, L., and Hemond, H.: 1984. 'Biogeochemistry of aquatic humic substances in Thoreau's bog, Concord, Massachusetts. *Ecology* **66**, 1139-1352.

Mierle, G. and Ingram, R.: 1991. 'The role of humic substances in the mobilization of mercury from watersheds', *Water Air Soil Poll.* **56**, 349-357.

Mewhinney, E.: 1996, *The importance of hydrology to carbon dynamics in a small boreal forest wetland,* Unpublished M.Sc Thesis., University of Waterloo., 150 pp.

Moore, T., Roulet, N., and Knowles, R.: 1990, 'Spatial and temporal variation of methane flux from subarctic/northern boreal fens', *Global Biogeochem. Cycles* **4**, 29-46.

Mortsch, L.D. and Quinn, F.H.: 1996, 'Climate Change Scenarios for Great Lakes Basin Ecosystem Studies', *Limnol. Oceanography* **41**, 903-911.

Mulholland, P.J. and Kuenzler, E.J.: 1979, 'Organic carbon export from upland and forested wetland watersheds', *Limnol. Oceanogr.* **24**, 960-966.

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

Poschadel, C.: 1997, *Floating peat island formation at an experimentally flooded wetland: Impacts on methane and carbon dioxide production and flux rates to the atmosphere,* Unpublished M.Sc Thesis. University of Waterloo. 160 pp.

Romanowicz, E.A, Sielgel, D.I., and Glaser, P.H.: 1994, 'Hydraulic reversals and episodic methane emissions during drought cycles in mires', *Geology* **21**, 231-234.

Roulet, N.T.: 1990, 'Hydrology of a headwater basin wetland: groundwater discharge and wetlands maintenance', *Hydrol. Proc.* **4**, 387-400.

Schiff, S.I., Aravena, R., Trumbore, S.E., and Dillon. P.J.: 1990. 'Dissolved organic carbon cycling in forested watersheds: A carbon isotope *approach*' *Water Resources Res.* **26**, 2949-2957.

Schiff, S.L., Aravena, R., Trumbore, S.E., Hinton, M.J., Elgood, R., and Dillon, P.J.: 1997, 'Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ^{13}C and ^{14}C', *Biogeochem.* **36**.

Schindler, D.W. and Curtis, P.J.: 1997, 'The role of DOC in protecting freshwaters subjected to climatic warming and acidification from UV exposure', *Biogeochem.* **36**, 1-8.

Schindler, D.W., Curtis, P.J., Parker, B.R., and Stainton, M.P.: 1996, 'Consequence of climate warming and lake acidification for UV B penetration in North American boreal lakes' *Nature* **379**, 705-708.

Scully, N.M., and Lean, D.R.S.: 1994, 'The attenuation of ultraviolet light in temperate lakes'. *Arch. Hydrobiol.* **43**. 135-144.

Siegel, D.I. and Glaser, P.J.: 1987, 'Groundwater flow in a bog-fen complex, Lost River peatland, Northern Minnesota' *J of Ecology* **75**, 743-754.

Siegel, D.I., Reeve, A.S., Glaser, P.H., and Romanowicz, E.A.: 1995, 'Clinate-driven flushing of pore water in peatlands' *Nature* **374**, 531-533.

St. Louis, V.L., Rudd, J.W.M., Kelly, C.A., Beaty, K.G., Bloom, N.S. and Flett, R.J.: 1995, 'Importance of wetlands as sources of methyl mercury to boreal forest ecosystems' *Can. J Fish. Aquatic Sci.* **51**, 1065-1076.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. John Wiley & Sons. 780 pp.

Thurman, E. M.: 1985, *Organic geochemistry of natural waters*. Martinus Nijhoff/Dr W. Junk Publishers, 497p.

Urban, N.R., Bayley, S.E., and Eisenreich, S.J.: 1988, 'Export of dissolved organic carbon and acidity from peatlands' *Water Resources Res.* **25**, 1619-1628.

Waddington, J. M. and Roulet, N.T.: 1997, 'Groundwater flow and dissolved carbon movement in a boreal peatland' *J. Hydrol.* (in press).

Warner, B.J.: 1996, 'Vertical gradients in peatlands', in *Wetlands: Environmental Gradients, Boundaries and Buffers.*, Mulamoottil, G., Warner, B.G. and McBean, E.A. (eds.) CRC Press. p. 45-65