SOURCES, SINKS, AND FLUXES OF DISSOLVED ORGANIC CARBON IN SUBARCTIC FEN CATCHMENTS

by

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ABSTRACT

The sources, sinks, fluxes, spatial distributions, and temporal variations of dissolved organic carbon (DOC) in subarctic fen catchments as well as the temporal patterns of DOC in streams draining subarctic fen catchments in the region of Schefferville, Québec were investigated.

In June to August sampling, DOC concentrations averaged 17 mg/L in peat water, 2 - 16 mg/L in stream water, 49 - 56 mg/L in canopy throughfall, 14 - 19 mg/L in understory throughfall, 122 - 187 mg/L in stemflow, 25 - 39 mg/L in lichen and moss mat water, and 35 - 42 mg/L in soil A horizon water.

Precipitation and canopy and understory throughfall were all significant DOC sources with seasonal DOC fluxes to the forest floor of 0.1 - 0.4, 0.5 - 1.3, and 0.8 - 1.7 g DOC/m^2 of forest, respectively. The lichen and moss mats and the A soil horizon were also found to be DOC sources, whereas the B soil horizon was a DOC sink. The soil column was estimated to export 0.4 - 0.5 g DOC/m^2. Peat, also a DOC source, released 1.2 - 2.1 g DOC/m^2.

DOC concentrations in streams draining ten fen catchments were found to be positively correlated with the percentage of fen area in the catchments.

RESUME

Les sources, diminutions, flux, distributions spatiales, et variations dans le temps du carbone organique dissous (COD) dans des bassins marais subarctiques et les variations dans le temps des concentrations du COD dans les ruisseaux écoulant des bassins de marais subarctiques dans la région de Schefferville, Québec ont été étudies.

Entre juin et août, les concentrations en COD atteignent une moyenne de 17 mg/L dans l'eau de tourbe, 2 - 16 mg/L dans l'eau de ruisseau, 49 - 56 mg/L et 14 - 19 mg/L dans l'égouttement du feuillage, 122 - 187 mg/L dans l'écoulement le long du tronc, 25 - 39 mg/L dans l'eau de percolation à travers le tapis de lichens et de mousses, et 35 - 42 mg/l dans l'eau traversant l'horizon A du sol.

La précipitation et l'égouttement du feuillage ont été des sources importantes du COD avec des flux saisonnièrs au sol de la forêt de 0.1 - 0.4, 0.5 - 1.3, et 0.8 - 1.7 g COD/m^2 de forêt, respectivement. Le tapis de lichens et de mousses et l'horizon A du sol étaient aussi des sources du COD, mais l'horizon B du sol baissait la concentration du COD. Il est éstimé que la colonne du sol exporte 0.4 - 0.5 g COD/m^2. La tourbe, aussi une source de COD, a exporté 1.2 - 2.1 g COD/m^2.

Les concentrations de COD dans les ruisseaux écoulant de dix bassins marais ont été en corrélation avec le pourcentage de marais composant les bassins.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1 INTRODUCTION

Dissolved organic matter (DOM) is the organic matter which, by definition, passes through a 0.45 μm silver or glass fiber filter (Thurman 1985, p.10) and the carbon of DOM is known as dissolved organic carbon (DOC). DOC represents part of the organic carbon spectrum which includes suspended, particulate, fine particulate, coarse particulate, and volatile organic carbon. Since DOM is difficult to measure, DOC serves as a surrogate measure of organic matter in water from various sources (Thurman 1985, p.12).

DOC is the predominant type of organic carbon found in natural waters (McDowell and Fisher 1976; Wetzel 1983, p.667). It displays a wide range of properties due to its varied chemistry which includes compounds known as humic, fulvic, and hydrophilic acids. Fatty acids, sugars, amino acids, and hydrocarbons are examples of DOC compounds.

The organic matter found in lakes and streams is from two sources: allochthonous (i.e. external sources - the watershed) and autochthonous (i.e. internal sources - the pelagic and littoral zones of lakes and streams). It has been found that allochthonous sources of detrital DOM are a major source of material and energy to stream ecosystems

(Larson 1978, Wetzel 1983, p.671) and that DOC transport represents a major flux of carbon through the metabolism of lakes (Wetzel 1983). In some cases, peatlands represent a significant allochthonous source of detrital DOM thereby having a significant influence on the biology and chemistry of the lakes and streams into which they drain.

DOC is an important parameter of water quality since it can contribute to its acidity through organic acids, affect nutrient availability by forming organic complexes, reduce biological activities by absorbing light, affect metal solubility, mobility, and toxicity by forming chelates, and can act as a buffer to changes in the chemistry of peatlands (McKnight et al. 1985; Thurman 1985; Moore 1987b).

Since DOC affects water quality, it should be considered when decisions are being made regarding water management and land development for agriculture, urbanization and leisure activity. There is much interest in knowing more about organic carbon, specifically the global carbon cycles, their biogeochemical controls, and how these relate to air and water pollution and the possibility of global warming.

The importance of DOC to water quality underlines the necessity to learn more about its composition, biogeochemistry, sources, sinks, fluxes, and interactions with other compounds especially metals since DOC is believed to be responsible for the translocation of metals. Such research is currently being carried out on several levels. A considerable amount of research has been done on the sources and fluxes of DOC in temperate lakes and rivers (Thurman 1985 provides a review) but few studies have concentrated on peatlands as sources and repositories of DOC (e.g. Mulholland 1981a; Grieve 1984a, 1984b; McKnight et al. 1985; Moore 1987b) as well as the spatial and temporal distributions of DOC in peatlands (e.g. Marin et al. 1990). Little is known about the variability and seasonality of DOC export from peatlands (Urban et al. 1989). It is estimated that there are more than 2 million km^2 of peatlands in the world (Moore and Bellamy 1974) including 1.1 million km^2, or 12% of the land surface, in Canada (National Wetlands Working Group 1988). This represents a massive accumulation of organic material, the disturbance of which may cause drastic changes in the chemistry of the water downstream, affecting the structure and function of lakes and streams (Wetzel 1983, p.668), and have ecological implications on the flora and fauna of the affected region.

The purpose of this thesis is to:

(a) Identify the sources and sinks and quantify the fluxes of DOC in a fen catchment in the region of Schefferville, Québec;

(b) Determine the spatial and temporal variations of DOC in the same fen and relate these to changes in other properties of the water (e.g. pH, conductivity, ratio of absorbance at

465 and 665 nm); to determine the factors responsible for the spatial and temporal variations in DOC;

(c) Gain a better understanding of the underlying processes controlling DOC movement and concentration in the catchment;

(d) Compare relationships between DOC and absorbance at 330 nm for several types of water in an attempt to use absorbance as a surrogate for the labor-intensive and expensive DOC measurements normally used;

(e) Compare some of the results of (a) through (d) to similar studies done in other biomes. DOC concentrations in throughfall, stemflow, and soil water are of interest;

(f) Investigate the relationship between DOC concentration in stream water and % peatland area for several catchments in the subarctic region of Schefferville, Québec;

(g) Investigate the stream DOC concentration:stage height relationships for these catchments.

2 LITERATURE REVIEW

2.1 PEATLANDS: AN IMPORTANT DOC SOURCE

As DOC is important to water quality, peatlands should be studied to better understand their sources, fluxes and export of DOC. There are an estimated 2 million km^2 of peatlands in the world (Moore and Bellamy 1974) some of which represent a significant allochthonous source of DOC to the streams and lakes into which they drain, influencing their biology and chemistry. Since peat can concentrate metals (Bonnett and Cousins 1987; Weber 1988) water movement through peatlands will affect the concentration of metals in streams and lakes.

It has been reported that the amount and chemistry of inflowing water (including ground water) and the rate of water flow are important in determining the chemistry of interstitial water which in turn determines the type and biomass of the plant community inhabiting the peatland (Sparling 1966; Marin et al. 1990). In any given location the hydrology, topography, and climate will determine the plant and animal communities of a wetland (National Wetlands Working Group 1988). These factors will interact to determine the type of wetland formed which includes bogs, fens, marshes, and swamps. In Canada, peatlands are defined as wetlands which have at least 40 cm of accumulated peat (National Wetlands Working Group 1988). Bogs have little ground water inflow so that organic acids released by organic matter decomposition will not be diluted thereby maintaining acidic conditions and consequently lowering the rate of decomposition. In fens, ground water inflow brings in ions (e.g. bicarbonate and Ca^{2+}) which dilute the organic acids, raising pH and decomposition rates and providing nutrients to the plant community. As the peatland thickens the influence of ground water decreases, inputs of bicarbonate decrease, and H^+ concentrations increase since they are no longer diluted (Moore and Bellamy 1974; Urban et al. 1989).

DOC concentrations in streams draining wetlands and catchments with wetlands range from 10 - 40 mg/L which is generally larger than in streams draining forested watersheds (e.g. Mulholland and Kuenzler 1979; Mulholland 1981a; Schlesinger and Melack 1981; Grieve 1984a; Moore 1987b; Moore and Jackson 1989; Eckhardt and Moore 1990). Wetland water has the largest DOC concentrations of any natural water due to slow decomposition and slow water movement resulting in the build up of organic matter (Thurman 1985, p.65).

DOC concentrations in streams reflect the sources of the water and the response of these sources to rain events i.e., is DOC diluted or is more DOC entering the stream to offset the dilution effect. This will determine the DOC:discharge relationship of the stream. Varying correlations between stream DOC concentration and discharge have been reported, some positive (e.g. Schlesinger and Melack 1981; Grieve 1984b), some negative (e.g. Mulholland

and Kuenzler 1979; Mulholland 1981a; Clair and Freedman 1986), some both positive and negative (e.g. Collier et al. 1989), and some reported very weak or no correlation (e.g. Moore 1987b; Moore and Jackson 1989; Eckhardt and Moore 1990).

It appears that physical conditions such as height of the water table, storage capacity of the peatland, and hydraulic conductivity of the peat (Bay 1969) are important determinants of DOC export. To the author's knowledge only one attempt has been made to correlate percentage wetland in catchments to DOC concentrations in stream water draining the catchments. Eckhardt and Moore (1990) reported significant correlations ($R^2 = 0.26 - 0.67$; $p < 0.01$) between these parameters.

2.2 SOURCES, SINKS, AND FLUXES OF DOC

Numerous studies have looked at the sources, sinks, and fluxes of DOM or DOC in catchments (e.g. Foster and Grieve 1982; Cronan and Aiken 1985; McDowell and Likens 1988; Moore 1989; Moore and Jackson 1989; Dalva 1990). These studies have shown that organic matter concentrations in water increase as precipitation passes through the forest canopy, forest floor, and organic soil horizon but decreases when passing through the mineral soil horizon, remaining fairly constant thereafter as the water seeps into the streams. The changes in DOC concentrations will differ from one catchment to another due to differences in vegetation, topography, climate, and geology. It is important to note that the DOC entering in precipitation and the DOC entering the streams through seeps are not the same due to the time it takes the DOC to make its way through the system. McDowell and Likens (1988) found that the mean age of organic matter in soil is hundreds to thousands of years old and tens of thousands of years old in trees. It may also be concluded from this that the disturbance of a catchment (e.g. logging) may result in long term changes in DOC movement within and leaving a catchment (Collier et al. 1989; Moore 1989).

During the winter months, however, DOC movement is halted. With spring snowmelt the accumulated DOC from snow begins to flow over land towards streams and lakes and the DOC accumulated during the fall months (e.g. in leaves) will also be flushed out of the catchment due to the increased channels of water movement during the spring.

The terrestrial origin of humic substances is through the chemical and biological degradation of plant (including roots) and animal residues in addition to the synthetic activities of micro-organisms (Schnitzer 1978, pp.1-2; Wetzel 1983, p. 677; Shotyk 1984, p.45; Kumada 1987, p.65). In most streams and small rivers, terrestrial DOM is the main source of DOC whereas in larger lakes autochthonous sources of DOC are predominant (Wetzel 1983, p.681; Thurman 1985, pp.284-285) the main sources being plankton and the littoral community including macrophytes and epiphytic/epipelic algae (Wetzel 1983, p.679; Thurman 1985, pp. 80-81). Humic substances appearing in aquatic environments are derived from rainfall, the leaching of plant organic matter directly (e.g. tree canopy leachate), leaching of soil organic matter, decomposition of algae and phytoplankton, UV oxidation of organic matter near the surface of water bodies, and polymerization reactions among the organic matter functional groups. For larger bodies of water, the latter three processes will be important whereas for most streams and rivers the first three processes will be important. It is expected that during low streamflow conditions, most organic matter will come from ground water (Larson 1978; Thurman 1985, pp.358-359).

Chemical and biological decomposition of plant and animal residues resulting in the production of terrestrial humic substances is ultimately controlled by conditions such as pH, nutrient status, temperature, and water content of the soils (Kumada 1987, p.11). In acidic soils the activities of decomposers such as bacteria and fungi will be inhibited, thereby slowing down the degradation process. Extreme temperature and anaerobic conditions have the same results. Soil type will also have an effect on organic matter content such that finer textured soils with an adequate supply of water and nutrients will favor the production and accumulation of organic matter. Soils with high clay contents will tend to adsorb and thus inactivate decomposing enzymes (Foth 1984).

In a study of subarctic spruce-lichen woodland soils Moore (1981) found that low temperature was the major factor inhibiting decomposition. Acidity, low N content, lack of readily available C, and low mesofaunal populations were also found to be contributing factors. However, micro-organisms, water content, and other macro-nutrients (Ca, Mg, P, K) were found to be relatively unimportant.

In wetlands, the amount of organic matter far exceeds that present in other ecosystems. Peat accumulates due to water-logging, anaerobic conditions and thus slow rates of decomposition. Hydrologic, thermal, and nutrient regimes are the controlling factors of decomposition in wetlands (Moore 1988).

DOM losses from wetland catchments may be expected to be greater than that from forested catchments. Schlesinger and Melack (1981) analyzed data from the literature on the rate of organic carbon loss from different types of watersheds and found that wetland watersheds have the highest rate of loss ranging from 2 - 53 g C/m^2/yr. In the Schefferville region, Moore (1987b) reported export values from four peatland catchments ranging from 1 - 5 g DOC/m^2 for June to September sampling seasons. Other studies have reported export values all of which are in the range of 2 - 53 g C/m^2/yr (e.g. Day et al. 1977; Mulholland and Kuenzler 1979; McKnight et al. 1985; Clair and Freedman 1986; Collier et al. 1989; Urban et al. 1989; Eckhardt and Moore 1990).

How do these DOC fluxes in wetland streams compare to gas fluxes in wetlands? Carbon inputs to a wetland are from plants photosynthesizing atmospheric CO_2 into compounds necessary for their existence, organic carbon being deposited by rainfall, and inflowing water (including ground water). Carbon outputs include bacteria respiring CO_2 and CH_4 and organic carbon exported in stream and ground water. In a study of 4 fens in the Schefferville area, Moore and Knowles (1987) reported estimated annual emissions of 0.1 - 0.6 g CH_4-C/m^2 and 10 - 20 g CO_2-C/m^2 which is equal to and often surpasses the organic carbon exported in streams indicating that the major flux of carbon in wetlands occurs as CH_4 and CO_2 emissions (Moore 1987b).

2.3 MOVEMENT AND ADSORPTION OF DOM IN SOIL

Organic matter in soil is subject to movement by water percolating through soil and precipitation through binding with clays and metals. In the process DOM will translocate metals and metal oxides from soils to streams and lakes. Presumably, the DOM-metal complex will remain soluble until it has bound a critical amount of metal, rendering the complex insoluble (Dawson et al. 1978).

The translocation of DOM from the forest floor and the upper organic soil horizon mobilizes Fe, Al, trace metals, and hydrophobic organic compounds to a Podzolic (Spodic) horizon (McDowell and Likens 1988). The resultant Podzol soils have a characteristic grayish eluviated upper horizon and a reddish or brownish lower (B) illuvial horizon.

Presumably, the precipitation of the chelates is due to the fact that they become more and more insoluble as they bind Fe and Al.

Podzol formation will generally occur under coniferous vegetation because the rate of decomposition of coniferous vegetation is less than that for deciduous vegetation thus allowing time for chelating agents (i.e. DOM) to percolate down the soil profile. Numerous studies have been carried out on DOC translocation in Podzols (e.g. Schnitzer and Desjardins 1969, Ugolini et al. 1977, Dawson et al. 1978, Herbauts 1980, McDowell and Wood 1984) and adsorption reactions involving Fe and Al (e.g. Ponomareva 1964, Schnitzer 1969, McDowell and Wood 1984). Results from McDowell and Wood (1984) indicate that the mechanism of DOC adsorption is abiotic.

Work done by Moore (1987b) in subarctic peatlands indicates that $CaCO_3$ and $MgCO_3$ may be important in adsorbing DOC compounds. This agrees with work done by Kovalev and Generalova (1967) who found that precipitation of Fe may occur with the flocculation of humic acids through the influence of Ca and Mg cations that form insoluble compounds with humic acids. Similar processes of DOM flocculation by carbonate compounds have been found to take place in lakes (e.g. Otsuki and Wetzel 1973; Wetzel and Otsuki 1974).

DOC-metal interactions in soils have been studied extensively by Soviet scientists (Kovalev and Generalova 1967 provide a review) and others (e.g. Broadbent and Ott

1957; Chao et al. 1962; Schnitzer and Skinner 1963; Levesque and Schnitzer 1967; Sequi et al. 1975; Goodman and Cheshire 1976; Saar and Weber 1979 and 1980; Saar 1980; Abdul-Halim et al. 1981; Perdue and Lytle 1983; Pohlman and McColl 1988). Schnitzer (1978) also provides a review.

2.4 FATE OF ORGANIC MATTER

Autochthonous and allochthonous aquatic organic matter undergo processes which dictate their distribution and fate. These are sorption/partition (including hydrophobic sorption, hydrogen bonding, ligand exchange, cation and anion exchange), precipitation (flocculation), volatilization (evaporation), oxidation/reduction reactions (metals are reduced and organic matter is oxidized), complexation of metal ions, and biotic uptake (Thurman 1985, p.365-407; Meyer et al. 1988).

Terrestrial organic matter is affected by the same processes except that the type of organic matter is different. Terrestrial organic matter is generally labile whereas aquatic organic matter is generally refractory. Labile terrestrial organic matter is eliminated before it finds its way to water bodies leaving only refractory compounds (Wetzel 1983, chap. 22). Some terrestrial organic matter will enter into the ground water and in some cases will represent a significant input of organic matter to the streams draining a catchment (e.g. Wallis et al. 1981).

2.5 MEASUREMENT OF DOC

There are several methods used to measure DOC concentrations in water. The potassium dichromate ($K_2Cr_2O_7$) wet oxidation method uses an excess of $K_2Cr_2O_7$ to oxidize the organic matter, releasing CO_2. The remaining unreduced $Cr_2O_7^{2-}$ is titrated to determine the original DOC concentration in the sample. Since the oxidation procedure is not 100% effective a conversion factor of 1.28 is required (Moore 1988). For organic carbon compounds with a simpler structure, the oxidation procedure is complete. The two major drawbacks of this method are the incomplete oxidation of organic matter and cost.

A second method uses potassium persulfate ($K_2S_2O_8$) (Menzel and Vaccaro 1964) and has been modified by Stainton (1973) and McDowell et al. (1987). In a sealed ampoule $K_2S_2O_8$ oxidizes the organic matter to CO_2 which is then quantified by gas chromatography or by an infrared detector.

In the past few years, automated machines employing the potassium persulfate method (e.g. Dohrmann DC-80) or high temperature combustion of the organic matter and detection of the resultant CO_2 by a non-dispersive infrared analyzer (e.g. Beckman 915B, Shimadzu TOC-500) have gained importance due to their superior efficiency. Whether they are completely efficient is still debated as Sugimura and Suzuki (1988) claim that all previous measurements of organic carbon in seawater have been underestimated by two to three times. Their machine uses a lower combustion temperature

(550°C) and an improved catalyst. These automated machines are fast and efficient, but expensive.

The fastest and least expensive method is UV-visible spectrophotometry. Several studies have used water color as an indication of DOM and DOC concentrations by measuring color as an absorbance at wavelengths < 400 nm and have found significant correlations (e.g. Grieve 1985; Edwards and Cresser 1987 for TOC; Moore 1985 and 1987a). This technique works best for samples containing humic matter of similar absorptivity i.e., with organic compounds having a similar absorbance per mass of organic carbon (Lewis and Tyburczy 1974), on samples with little colored inorganic compounds such as Fe (Moore 1985, 1987a), and on samples of similar pH (usually 7) which may be achieved using a phosphate buffer (Thurman 1985, p.315). The major drawback of this technique is that it works effectively only for certain types of water.

2.6 CHARACTERIZATION OF HUMIC MATTER

Humic matter can be characterized by spectroscopy (IR, UV-visual, nuclear magnetic resonance, fluorescence, and mass spectrometry), chromatography, X-ray analysis, electron microscopy, electron diffraction analysis, surface tension measurements, molecular weight measurements, and electrometric titrations (Schnitzer 1978, p.11; Thurman 1985, pp. 312-325 and 334-343).

The E4/E6 ratio (the ratio of absorbance at 465 and 665 nm or 400 and 600 nm) is used as an estimate of the relative concentrations of high molecular weight humic and low molecular weight fulvic acids in a sample. Chen et al. (1977) have determined that the particle sizes and weights of both humic and fulvic acids determine the magnitude of the E4/E6 ratio. Low molecular weight fractions will produce a high ratio whereas relatively high molecular weight fractions will produce a low ratio which is supposedly due to the reddish color of humic acids resulting in a greater absorbance at 660 nm (Thurman 1985, p.314). Chen et al. (1977) also found that pH will significantly affect molecular weight and, as such, the E4/E6 ratio.

CHAPTER 2

STUDY SITES AND METHODOLOGY

1 STUDY SITES

The Schefferville area of Québec-Labrador (55°N, 67°W) is in the transitional zone between the subarctic and the tundra of Ungava. This area consists of a wide range of vegetation patterns including lichen-heath tundra, birch-willow scrub, spruce lichen woodland, spruce feather-moss forest, muskeg, sedge meadow, and string bogs (Wright 1981, pp. 26-28). Generally, alpine tundra with discontinuous permafrost is to be found on the ridge tops, spruce-lichen woodlands in well drained areas, and spruce-moss forests in poorly drained areas (Waterway et al. 1984). Peatlands, located in valleys and occupying between 5 and 25% of the land surface (Moore 1988), are classified as low subarctic wetland by Zoltai and Pollet (1983) and range, in terms of vegetation and water chemistry, from poor fens to rich fens.

Schefferville receives an average annual precipitation of 793 mm (272 mm for June, July, and August), has average temperatures of -23°C in January and 13°C in July, and is snow covered from mid-October through to mid-May. Peatlands and soils are frozen from late October to mid-May. The iron-rich soils in the area are mainly shallow brunisols, podzols, gleysols, and deep organic soils (Nicholson and Moore 1977).

Two fens in the Schefferville area were studied. Iron

Arm fen catchment (Figure 2.1) is located 20 km east of Schefferville covering an area of 5 ha, of which 3.2 ha is a mixture of spruce-lichen woodland and spruce-moss forest. The woodland and forest both have black spruce (Picea mariana) intermixed with tamarack (Larix laricina) and soils that are generally shallow and rocky. A ground cover of fruticose lichens (genus Cladonia) dominates in the woodland. The spruce-moss forest has a greater tree density (2500 stems/ha where a stem is > 1 cm in diameter) and a more closed canopy than the woodland (2000 stems/ha) with an extensive understory of shrubs dominated by Labrador tea (Ledum groenlandicum) and a ground cover dominated by mosses such as Dicranum fuscescens. The woodland and forest drain into the fen area, comprising the remaining 1.8 ha, which is drained by three small converging streams. The open fen area is covered extensively by Carex spp., whereas the margins have a more diverse vegetation of various mosses and shrubs along with Carex spp. The margins of the open fen area blend into the forested fen area which has P. mariana and L. laricina with a ground cover of Sphagnum spp.

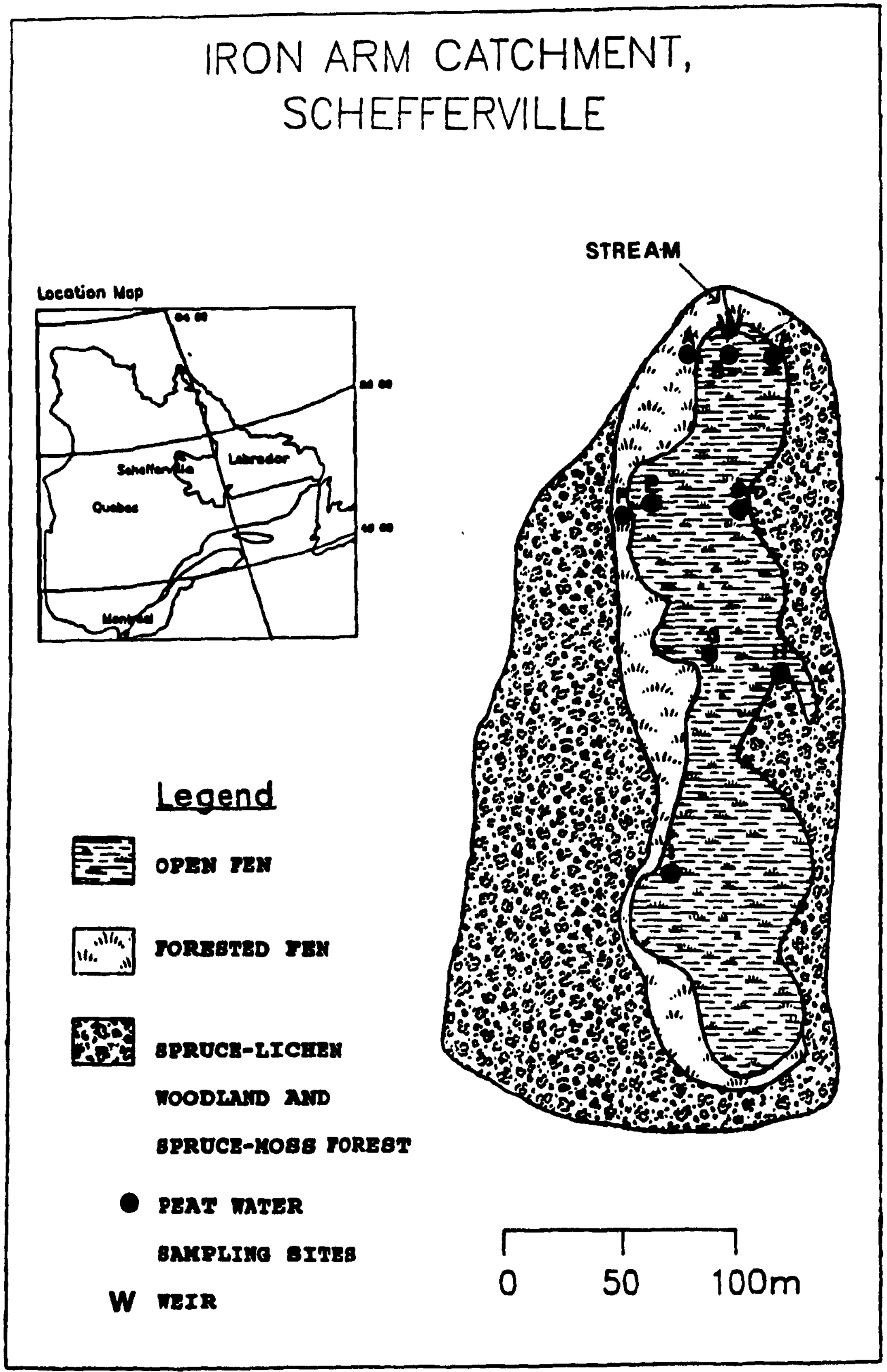
IRON ARM CATCHMENT,
SCHEFFERVILLE
STREAM
Location Map
Schefferville
Labrador
Quebec
Montreal
Legend
OPEN FEN
FORESTED FEN
SPRUCE-LICHEN WOODLAND AND SPRUCE-MOSS FOREST
● PEAT WATER SAMPLING SITES
W WEIR
0
50
100m

FIGURE 2.1

Pelletier fen (Figure 2.2) is part of a 10 ha-drainage basin located about 8 km north of Schefferville. The open fen has an area of 2.6 ha and is drained by one stream which was almost dry during the sampling season. Unlike Iron Arm fen, it is a patterned fen dominated by *Carex* spp. and *Sphagnum* spp. Strings are dominated by *Carex* spp., *Chamaedaphne calyculata*, *Salix* spp., and dwarf birch (*Betula glandulosa*) and pools by *Carex* spp. and *Menyantheses*.

The streams draining eight other catchments in the area were also investigated. They ranged in area from 0.4 - 20.1 km^2 with 11 - 59% of the catchment area being open and forested fen (Table 2.1).

Table 2.1: Characteristics of the 10 catchments in the Schefferville area. Catchments 9 and 10 are Iron Arm and Pelletier, respectively.

CATCHMENT	AREA (km^2)	(.............% OF CATCHMENT.............)				
		FEN	TUNDRA	LAKES	LICHEN WOODLAND	SPRUCE-MOSS FOREST
1	0.4	23	0	0	63	14
2	0.6	47	0	2	40	11
3	0.6	13	22	2	33	30
4	1.9	11	26	0	17	47
5	7.5	26	6	4	41	24
6	7.3	48	0	4	34	15
7	20.1	20	0	10	44	26
8	0.2	59	0	0	9	32
9	0.05	36	0	0	30	34
10	0.1	36	0	0	30	34

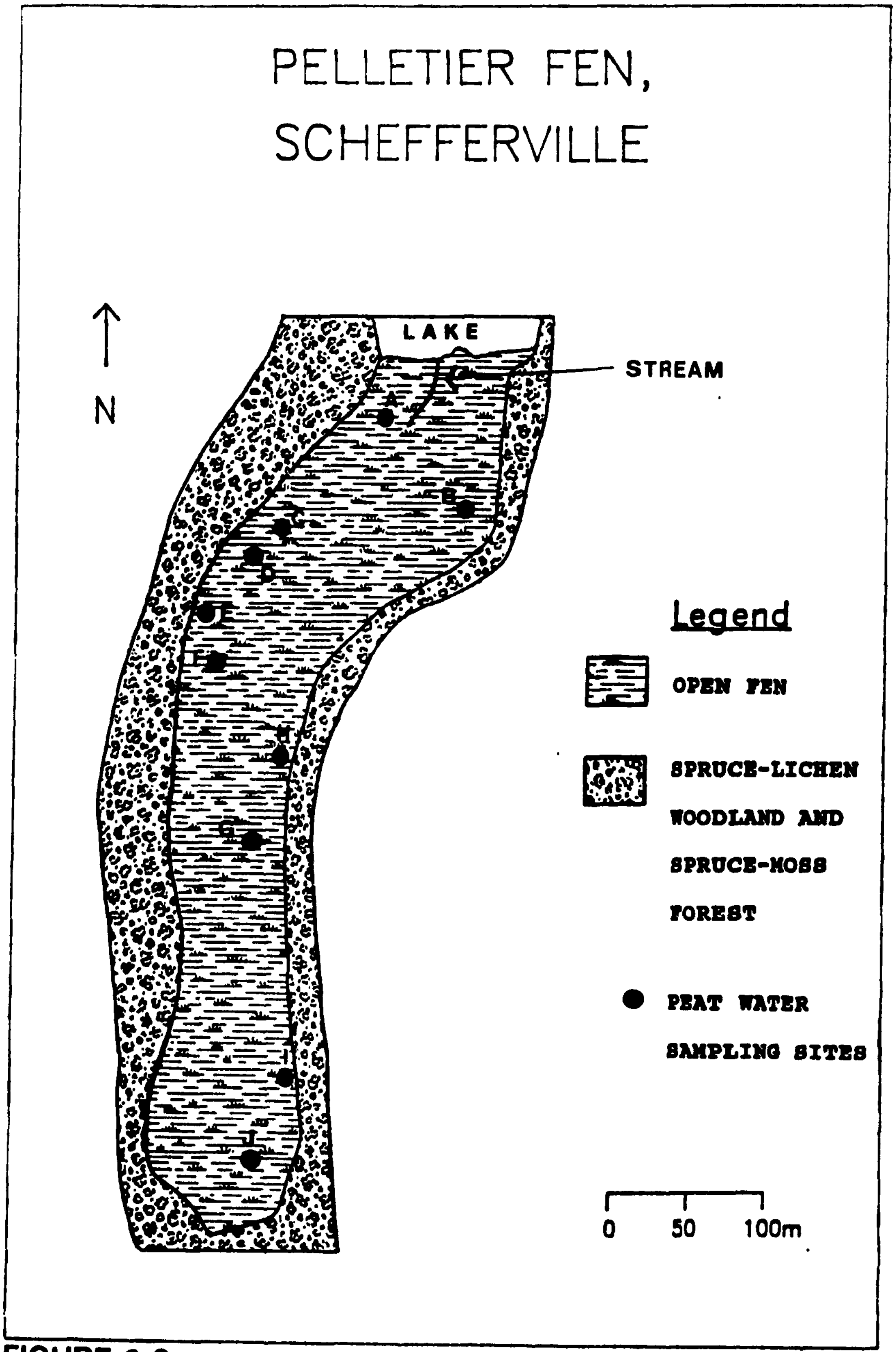
PELLETIER FEN,
SCHEFFERVILLE
N
LAKE
STREAM
A
B
C
D
E
F
G
H
I
J
Legend
OPEN FEN
SPRUCE-LICHEN WOODLAND AND SPRUCE-MOSS FOREST
● PEAT WATER SAMPLING SITES
0
50
100m

FIGURE 2.2

2 METHODS

2.1 SAMPLE COLLECTION

Samples of stream and peat water were collected weekly at both fens from mid-June to late-August 1988. In addition, precipitation, stemflow, throughfall, and soil water samples were collected at Iron Arm. Precipitation was collected in an open area away from trees, using funnels as described below and depth of precipitation was measured by a rain gauge installed near the funnel.

Stemflow, throughfall, and soil water samples were collected from the spruce-moss forest and the spruce-lichen woodland on the slope draining into Iron Arm fen. Seventeen trees were sampled for stemflow and throughfall; 11 trees (8 spruce and 3 larch) in the lichen woodland and 6 trees (4 spruce and 2 larch) in the spruce-moss forest. These were randomly chosen and represent the different species, sizes and shapes present in both the forest and woodland. Stemflow was collected by a collar wrapped two and a half times around the lower part of a tree stem, channelling water into a plastic bottle. A wad of glass wool in the collar neck prevented particulate matter from entering the bottle.

Throughfall was collected under the canopy of trees by funnels emptying into plastic collection bottles. The funnels were covered by a mesh to prevent clogging of the neck and glass wool was used in the neck to prevent contamination by particulate matter.

Water from the lichen and moss mat and soil was collected by five replicate lysimeters installed under the mat and the soil A horizon and within the soil B horizon in the woodland and forest. Lysimeters used were plastic rectangular trays with an area of 333 cm^2 and were covered with mesh to prevent clogging. They were inserted into trenches dug into the soil. At the bottom of the tray a hole with a tube attached to it led to a plastic collection bottle.

At Iron Arm, peat water was collected weekly from four depths (10, 25, 50, and 100 cm) at nine sites. A thin, hollow metal rod with small holes at its base, was inserted to the desired depth, a vacuum created with a hand pump, and the water drawn up the rod into a collection bottle. At Pelletier fen, the depths for peat water sampling varied from 10 cm to 150 cm for the ten sites which were sampled weekly. Samples were collected by the above method or from previously installed piezometers.

From mid-June to late August 1989, stream, stemflow, throughfall, and soil water was collected weekly from Iron Arm fen only. Streams draining 8 other catchments in the area were sampled weekly during 1989 and 1990 (mid-May to late August). Samples were refrigerated and analyzed for pH, conductivity at 25°C, absorbance at 330 or 400 nm, and the ratio of absorbance at 465 and 665 nm (E4/E6 ratio) within two days and DOC within a week.

2.2 MONITORING OF DISCHARGE

At Iron Arm fen, stream water discharge was monitored using a Belfort continuous water level recorder. A 30° v-notch weir was constructed to control the discharge and a measuring tape was attached to the weir so that at every sampling date the height of the water flowing through the weir was recorded. Using the height value (h), discharge (Q) was calculated by the equation

$$Q = 0.3708\ (h_e)^{5/2}$$

where 0.3708 is a constant for 30° v-notch weirs, $h_e = h + 0.0021$ m, and Q is measured in m^3/s (Shen 1981). The amount of water seeping around the weir and at other sites in the catchment is not known.

Discharge was calculated for each sampling date and was used as an average until the next sampling date. Discharge was multiplied by the DOC concentration for that date giving L/s x mg/L x s = mg DOC exported. These values were summed to estimate DOC export (in grams) for the season and divided by the catchment area to give export in g/m^2.

The continuous record of water level fluctuations can also be used to calculate discharge. This involves determining the baseline (zero discharge) and dividing the chart into areas of roughly equal discharges which are then summed. It was found that for the entire sampling season the difference between this cumbersome method and using average weekly values was negligible. Only on sampling dates when the water level was below the v-notch was the above method used as the condition of zero discharge did not last until the next sampling date.

2.3 EVAPOTRANSPIRATION

Evapotranspiration from the open fen area was estimated using available data of daily air temperatures, net radiation, and ground heat flux in the Priestley-Taylor model (Stewart and Rouse 1976) as follows:

$$E_T = \frac{\alpha\ (S/S+\tau)\ (Q^*-G)}{L_v} = \frac{\alpha\ (0.434+0.012T_a)\ (Q^*-G)}{(2499.1-2.343T_a)}$$

where $\alpha = 1$, T_a = air temperature (°C), Q^* = net radiation, G = ground heat flux, L_v = latent heat of vaporization of water, S = slope of the saturation vapor pressure-temperature curve, and τ = psychometric constant (Wright 1981).

2.4 DETERMINATION OF DOC FLUXES

The areas of the forested and fen parts of Iron Arm catchment were determined from a 1:2100 scale air photo. The area under canopy cover was determined by marking off four 10 x 10 m quadrats in both the spruce-lichen woodland and spruce-moss forest, counting the number of stems, measuring canopy widths and diameter at breast height. Only stems greater than 1 cm in diameter and trees taller than 1.7 m were included.

DOC flux (g DOC/m^2) in throughfall, for example, was calculated by multiplying the average throughfall DOC concentration (mg/L = g/m^3) by throughfall depth (mm). The amount of DOC in grams was determined by multiplying the flux (g/m^2) by the area under canopy cover (m^2). Note that as an alternative, volume weighted DOC concentrations could have been used but were not found to alter the results significantly.

2.5 LABORATORY ANALYSES

2.5.1 WATER SAMPLES

Water samples were filtered through Whatman GF/C glass fiber filters. Dissolved organic matter (DOM) is defined as the organic matter which passes through a 0.45 um silver or glass-fiber filter and the carbon of DOM is known as DOC. The GF/C glass-fiber filters commonly used for DOC studies (this one included) have a retention capacity of 1.2 um diameter, however, Moeller et al. (1979) have found that filtering through a 0.45 um filter does not produce any detectable differences in the results.

Samples were analyzed for the following properties:

(1) pH with a glass electrode,

(2) conductivity at 25°C,

(3) absorbance at 330 nm using a Bausch and Lomb Spectronic 20 spectrophotometer with 2.5 cm diameter tubes or absorbance at 400 nm using a Bausch and Lomb Spectronic 100 with 10 cm cells,

(4) the ratio of absorbance at 465 and 665 nm (E4/E6 ratio) using a Bausch and Lomb Spectronic 100 spectrophotometer with 10 cm cells,

(5) DOC using the potassium dichromate wet oxidation method or the potassium persulphate/CO_2 gas chromatography method (Appendix I).

2.5.2 SOIL SAMPLES

Soil profiles including the lichen and moss mats were sampled from the spruce-lichen woodland and spruce-moss forest in the upland part of Iron Arm catchment and used in two sets of experiments. Soil samples were air dried and passed through a 2 mm sieve to remove stones, gravel, and twigs.

Pieces of mat or eighty grams of individual soil horizons were spread out onto 13.1 cm-diameter Buchner funnels with a Whatman 42 filter paper at the bottom. The soils formed a layer approximately 1 to 2 cm thick. Varying amounts of water (50 - 200 ml) of known DOC concentrations (3 - 122 mg/L) were poured onto the soils or mats at varying intervals over a period of 20 to 45 minutes. Residence time of the water varied with the moisture conditions of the soil or the mats and the pouring rates. One hour after the last water was poured was the maximum amount of time needed for any water to percolate through and be collected for DOC determination.

In a second experiment, the DOC adsorption/desorption abilities of B horizon soil samples were investigated. Five grams of soil were measured into each of 6 plastic cups to which 50 ml of water of 0, 5.6, 11.7, 16.8, 22.4, and 28 mg

DOC/L was added. The mixture was stirred and allowed to stand for 24 hours after which the supernatant was filtered through GF/C paper and analyzed for DOC.

CHAPTER 3

SOURCES, SINKS, AND FLUXES OF DOC IN IRON ARM CATCHMENT

1 DOC CONCENTRATIONS AND FLUXES IN THE FORESTED AREAS

1.1 DOC IN STEMFLOW, THROUGHFALL, AND SOIL WATER

In 1988 DOC concentrations in stemflow, woodland canopy throughfall, forest canopy throughfall, and forest understory throughfall averaged 187, 59, 53, and 14 mg/L, respectively, whereas in 1989 they averaged 122, 55, 45, and 19 mg/L. DOC concentrations in water percolating through the lichen mat, moss mat, and woodland and forest soil A horizons averaged 36, 39, 40, and 41 mg/L, respectively, in 1988 whereas in 1989 they averaged 26, 25, 35, and 42 mg/L (Table 3.1). The differences in DOC concentrations between 1988 and 1989 are not statistically significant (based on the standard deviations of the means) due to their variability from one sampling day to the next.

Comparison of these DOC values to selected literature values (Tables 3.2 and 3.3) indicate that the average DOC concentrations in stemflow (187 and 122 mg/L in 1988 and 1989, respectively) were larger than all other studies presented except Moore (1989), probably because coniferous bark produces more sugar-containing residues than other types of trees resulting in relatively larger DOC values. Moore (1989) reported a high average stemflow value of 336 mg DOC/L in a New Zealand forest, related to the presence of certain scale insects on the stems which exuded honeydew,

Table 3.1: DOC concentrations and fluxes in Iron Arm catchment based on sampling from June 8 to August 23, 1988 and June 11 to August 28, 1989. DOC concentrations in stemflow, canopy and understory throughfall water are weighted for the proportion of spruce and larch trees in the area. Fluxes for mat and soil water are not available due to problems with the lysimeters. Values of DOC released by canopy and understory are in g/m^2 of canopy and understory, respectively. Values in { } are in g/m^2 of forest.

	Depth (mm)		Weighted avg. DOC (range) (mg/L)		DOC released (g/m^2)	
	1988	1989	1988	1989	1988	1989
Precipitation	145	209	1-2	1-2	0.1-0.3	0.2-0.4
Stemflow	<1	<1	187 (54-381)	122 (42-255)	-	-
Canopy Throughfall	34	106	56 (32-92)	49 (17-112)	1.9 {0.5}	5.2 {1.3}
In:						
Spruce-lichen woodland	46	97	59 (32-110)	55 (24-112)	2.7	5.3
Spruce-moss forest	24	114	53 (31-75)	45 (17-97)	1.3	5.1
Understory Throughfall (Spruce-moss forest)	76	116	14 (9-22)	19 (6-38)	1.1 {0.8}	2.2 {1.7}
Lichen Mat	-	-	36 (31-43)	26 (17-36)	-	-
Moss mat	-	-	39 (23-49)	25 (14-39)	-	-
Soil Water						
A horizon in:						
Spruce-lichen woodland	-	-	40 (28-49)	35 (14-54)	-	-
Spruce-moss forest	-	-	41 (17-68)	42 (19-55)	-	-
B horizon in:						
Spruce-lichen woodland	-	-	-	17 (10-23)		

Table 3.2: Selected literature values of DOC (mg/L) in stemflow (SF), throughfall (TF), and precipitation (Ppt).

Study	Site Vegetation	DOC Range (mean) SF	TF	Ppt
Collier et al.	Larry R., N.Z.			0.5-2
(1989)	pines	2-20	3-16	(1)
		(8)	(7)	
	manuka	17-153	5-55	
		(46)	(18)	
	scrub		6-32	
			(13)	
Dalva (1990)	Mt. St. Hilaire, Que.			2
	maple, beech, ash	10-78	4-22	
		(30)	(9)	
	hemlock, yellow	10-61	5-3[illegible]	
	birch	(23)	(1[illegible])	
	hemlock, red pine,	34-150	7-32	
	beech, red oak	(68)	(15)	
Foster and Grieve	Bentley Park Wood,		20-	2
(1982)	Warwickshire		325	
	deciduous, grassland,			
	coniferous plantation			
Hoffman et al.	Tennessee		6(leaves)	1-2
(1980)	deciduous forest		3 (no leaves)	
Likens et al.	Ithaca, NY			0.3-3
(1983)	forest, farmland			(2)
	Hubbard Brook, N.H.			0.07-3
	northern hardwood			(1)
McDowell and	Hubbard Brook, N.H.		(12)	(1)
Likens (1988)	deciduous forest		(34)	
Moore (1987c)	Schefferville, Que.		60	2
	black spruce		78	2
Moore (1989)	Maimai, New Zealand	(356)	(16)	(1)
	beech, podocarps,			
	broadleaf hardwoods			
Moore and Dubreuil	Mt. St Hilaire, Que.			(2)
(1987)	beech	(21)	(12)	
	maple	(27)	(9)	
	ash	(33)		
Moore and Jackson	Larry R. New Zealand	(47)	(21)	(1)
(1989)	moss/fern/scrub			
	dominated by manuka			
Mulholland (1981a)	Creeping Swamp, N.C.	<7-	<18	
	red maple, ash,	<120		
	black and tupelo gum	(29)		
Wallis et al.	Mount Allen, Alberta		2-6	1-3
(1981)	coniferous, deciduous	(4)	(2)	

Table 3.3: Selected literature values of DOC (mg/L) in soil water.

Study	Site and Soil Type	Horizon	DOC (mean)
Collier et al. (1989)	Larry R., N.Z. podsolized, gleyed	A	18-57
		A,G	(31-36)
Cronan and Aiken (1985)	Adirondacks, NY Spodosols	O/A	20-32
		B	5-8
Dalva (1990)	Mt. St. Hilaire, Que. Podzol, Brunisol	O/A	17-80
		B/C	(17-19)
McDowell and Likens (1988)	Hubbard Brook Valley, N.H. Spodosol	E	(28-38)
		upper B	(6)
		B (30cm)	(3)
McDowell and Wood (1984)	Hubbard Brook Valley, N.H. Spodosol	A2	13-86
		B2ir	(6)
		B (30cm)	(3)
Moore (1989)	Maimai, New Zealand Dystrochrepts and Humults	surface	(56)
		sub-surface	(12)
Moore and Jackson (1989)	Larry R., N.Z. Aquic Spodosols and Histosols	surface	(46)
		sub-surface	(46)
Wallis et al. (1981)	Mount Allen, Alberta Podzols	upper 50cm	3-35 (11)
		saturated zone	(3)

thus allowing for the growth of sooty mold fungi. The upper range of stemflow values in studies by Mulholland (1981a), Collier et al. (1989), and Dalva (1990) fall within this study's range of 54 - 381 mg DOC/L.

Except for the study by Moore (1987a), which was also done in the Schefferville region, literature values for throughfall are all lower than for this study's average values of 56 mg DOC/L in 1988 and 49 mg DOC/L in 1989, including Wallis et al. (1981) where coniferous species were involved. The coniferous species in the study by Wallis et al. (1981) were Lodgepole pine (Pinus contorta), Engleman spruce (Picea englemannii), and Fir (Abies lasiocarpa) whereas in this study the main conifer was black spruce (Picea mariana). Thus, DOC concentration in throughfall is a function of tree species and climate.

Soil water DOC concentrations for this study (35 - 42 mg/L for the A horizon; 17 mg/L for the B horizon) are within the literature value ranges of 13 - 86 mg/L for O and A horizons and 3 - 46 mg/L for subsurface horizons (Table 3.3). There is a large range of DOC values in soil water since factors such as soil type, depth, and incident moisture conditions are all important in determining the amount of DOC released.

Dry fallout is the non-volatile organic dust which can accumulate in the collectors thus elevating the DOC concentrations of the samples (Thurman 1985, p.22). Throughfall collectors used in this study were not designed to prevent the collection of dry fallout and thus DOC values for precipitation were thought to be high. To compensate, values of 1-2 mg DOC/L were arbitrarily used since this is the range found in other studies (Thurman 1985, p. 22; Table 3.2). Similarly, canopy and understory throughfall values may be larger than they should be but this error is very small considering the large DOC concentrations found in throughfall.

1.2 LEACHING OF DOC BY PRECIPITATION

Precipitation for the sampling seasons (June 8 to August 23, 1988 and June 11 to August 28, 1989) was 145 mm and 209 mm, respectively, representing the second driest on record and slightly below average. The difference in precipitation affected the depth of stemflow, canopy throughfall and soil water in the woodland and forest sites (Table 3.1). Canopy throughfall amounted to 17 and 32% of incident precipitation on the canopy in the forest and woodland sites, respectively, in 1988, and increased to 55 and 46% in 1989. The amount of precipitation percolating through the woodland lichen mat, forest moss mat, and woodland soil A and B horizons increased from 1988 to 1989. The exact amounts are not known due to problems with the lysimeters. Except for understory throughfall (52% of incident precipitation in 1988; 56% in 1989), the percentage increase from 1988 to 1989 is significant and is due to the 44% increase in rainfall in 1989 compared to 1988.

In 1988, DOC fluxes in woodland canopy throughfall, forest canopy throughfall, and forest understory throughfall were 2.7, 1.3, and 1.1 g DOC/m^2 of canopy, respectively, and increased to 5.3, 5.1, and 2.2 g DOC/m^2 in 1989 (Table 3.1), indicating that the amount of precipitation is important in determining the amount of DOC released by the vegetation. Figure 3.1 however, indicates a weak correlation between DOC concentration and rainfall amount, based on weekly sampling. R^2 values range from 0.003 to 0.283. This suggests that in addition to the amount of precipitation, other factors such as rainfall intensity, time elapsed between precipitation events, and temperature may determine the rate of DOC leaching. Collier et al. (1989) reported that season, rainfall intensity and duration were important in determining DOC concentrations in stemflow and throughfall water.

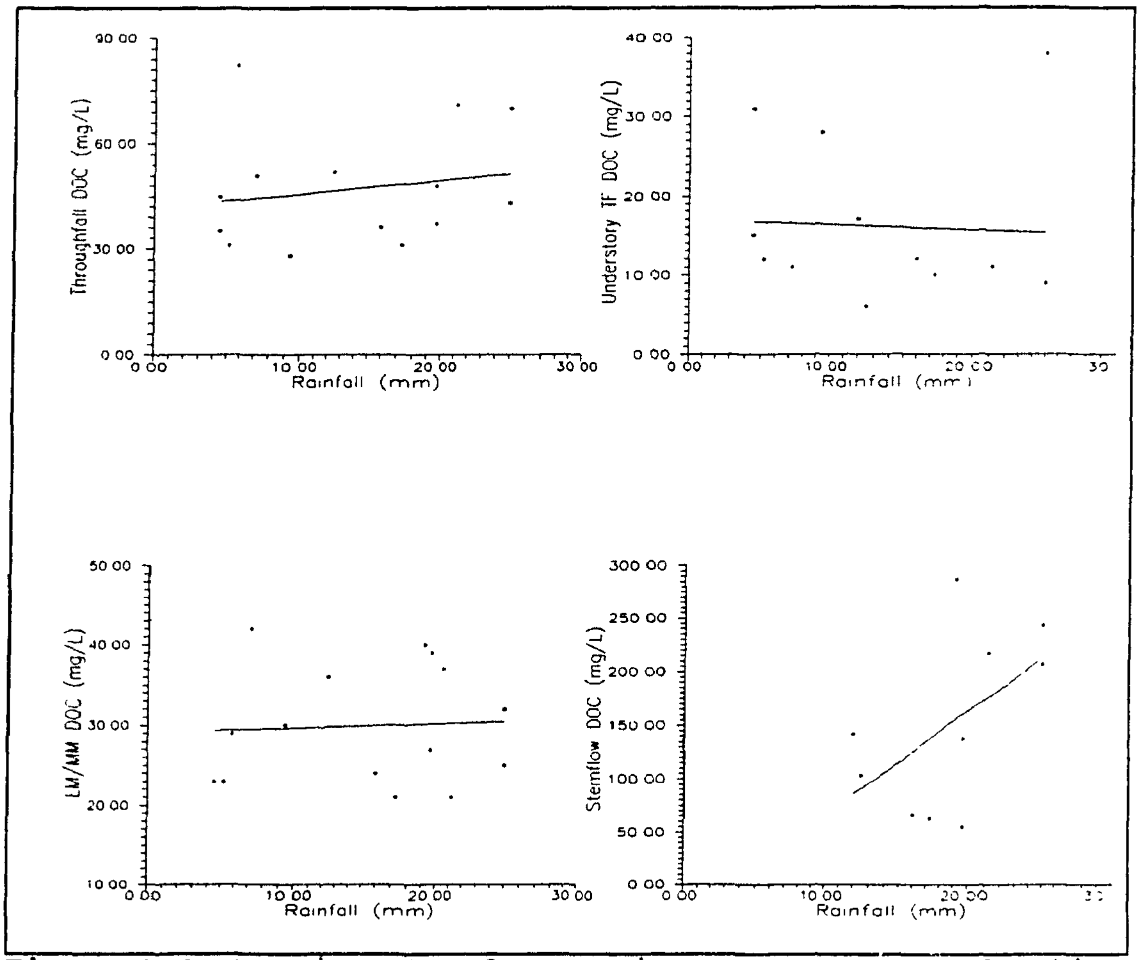

Figure 3.1: DOC in water from various sources as a function of rainfall at Iron Arm for the 1988 and 1989 sampling seasons. TF = throughfall; LM/MM = lichen mat/moss mat. R^2 values range from 0.003 for LM/MM to 0.283 (p = 0.11) for stemflow.

1.3 SOURCES AND SINKS OF DOC

Canopy throughfall, understory throughfall, and precipitation were all sources of DOC, with average DOC concentrations of 49 - 56, 14 - 19, and 1 - 2 mg/L, respectively. Stemflow was a negligible DOC source due to its small volume.

The DOC input from precipitation was relatively small on an areal basis for both seasons, ranging from 0.1 - 0.4 g DOC/m^2 but is a substantial component of the overall source of DOC to the catchment. DOC in precipitation is thought to be volatile organic matter and organic dust in the air above a forest canopy (Thurman 1985, p.21). Normally, the DOC concentration is about 1-2 mg/L in incident rainfall (Thurman 1985, p. 22; Table 3.2).

In the spruce-lichen woodland, lysimeters were located away from tree canopies and thus throughfall water did not fall on the forest floor areas where the lysimeters were located. Thus, the DOC concentrations in lichen mat and soil water are representative of the open areas of the woodland, which represents 80% of the woodland area, and not where canopies have an influence. No such problem was encountered in the spruce-moss forest.

During 1989, the average DOC concentrations of lichen mat and woodland soil A and B horizon water were 26, 35, and 17 mg/L respectively, indicating that water does become enriched with DOC as it percolates through the lichen mat and soil A horizon. The soil B horizon appears to be a DOC sink probably due to its iron-rich nature (Nicholson and Moore 1977).

Similarly, in the spruce-moss forest in 1989, moss-mat water had 25 mg DOC/L whereas soil A horizon water had 42 mg DOC/L. No data are available for the soil B horizon, however, it would be expected that due to the iron-rich nature of the B horizon, water percolating through would have < 42 mg DOC/L.

1.4 DOC SOURCES AND SINKS BASED ON LABORATORY ANALYSES

The field data presented in the previous section suggest that the lichen and moss mats and the soil A horizon were DOC sources whereas the woodland soil B horizon was a DOC sink.

These findings were checked in the lab using several soil, lichen, and moss samples from the field sites. Soils were air dried and passed through 2 mm sieves to remove stones, gravel, and twigs. In one experiment either a piece of mat or eighty grams of soil was spread out onto Buchner funnels with a filter paper at the bottom. Varying amounts of water of known DOC concentrations were poured onto the soils or mats and water percolating through was analyzed for DOC.

The results (Table 3.4) indicate that the lichen and moss mats are either sources or sinks of DOC depending on the DOC concentration of the added water and whether the mat was dry or already wet to begin with. For example, the lichen mat was a DOC sink when water of 112 mg DOC/L was added to the dry mat, but with a second application of 112 mg DOC/L water, the mat was a DOC source. The soil A horizon was a source of DOC, except when 112 mg DOC/L water was poured onto a lichen woodland soil A horizon. The fact that DOC was adsorbed may be due to a function of the experiment. A large amount of the DOC may have been trapped in the soil due to an insufficient amount of water to flush it out. A second application of 112 mg/L water may have resulted in a net release of DOC.

The soil B horizon was a sink of DOC when the initial concentration of water poured onto it was > 36 mg/L whereas at concentrations of 3 - 8 mg DOC/L, DOC was released. When DOC percolates through the soil B horizon some of it gets adsorbed, due to the soil's iron-rich nature, while some of the organic matter already present in the soil, approximately 1% in this case, is flushed out.

Table 3.4: Results of leaching experiments, showing the DOC concentrations and amounts in water percolating through soils. Water (50 - 200 ml) of 3 - 122 mg DOC/L was poured onto samples of soils or mats at varying intervals over a period of 20 to 45 minutes. Water percolating through within an hour was analyzed for DOC. For most samples there is more than one application of water. Data in mg was calculated using the volumes of water poured and collected. In the last column, + indicates that the soil or mat was a DOC source and - indicates a sink.

		DOC (mg/L)		DOC (mg)		Out - In
Soil Horizon	Sample	in	out	in	out	(mg)
Lichen Woodland						
Lichen Mat	1	112	176	11.2	9.7	-1.5
		112	169	8.4	8.8	+0.4
	2	8	18	1.3	1.5	+0.2
	3	36	44	4.5	2.8	-1.7
		36	33	3.6	1.3	-2.3
A horizon	1	3	131	0.4	4.9	+4.5
		3	126	0.2	5.8	+5.6
	2	112	184	17.9	11.8	-6.1
B horizon	1	3	21	0.3	1.3	+1.0
		3	7	0.2	0.5	+0.3
		8	9	0.9	0.6	-0.3
	2	112	47	11.2	2.6	-8.6
		112	34	5.6	1.5	-4.1
	3	112	78	11.2	4.2	-7.0
		112	74	5.6	3.6	-2.0
	4	3	18	0.3	1.0	+0.7
	5	36	45	2.7	1.5	-1.2
Spruce-Moss Forest						
Moss mat	1	36	72	5.5	3.5	-2.0
		36	78	2.7	3.3	+0.6
	2	8	46	1.5	2.0	+0.5
	3	112	82	19.6	3.0	-16.6
		112	67	5.6	1.9	-3.7
A horizon	1	3	300	0.4	11.7	+11.3
		3	226	0.2	11.1	+10.9
	2	82	561	16.4	29.1	+12.7
B horizon	1	3	37	0.3	2.0	+1.7
		3	19	0.2	1.4	+1.2
		8	23	0.8	1.6	+0.8
	2	82	102	8.2	5.1	-3.1
		82	70	4.1	3.1	-1.0

Another experiment of DOC adsorption/desorption by B horizon samples was also conducted. Five grams of soil were measured into each of 6 plastic cups to which 50 ml of water of 0, 5.6, 11.7, 16.8, 22.4, and 28 mg DOC/L was added. The mixture was stirred and allowed to stand for 24 hours after which the supernatant was filtered through GF/C paper and analyzed for DOC by the potassium persulphate/CO_2 gas chromatography method (Figure 3.2).

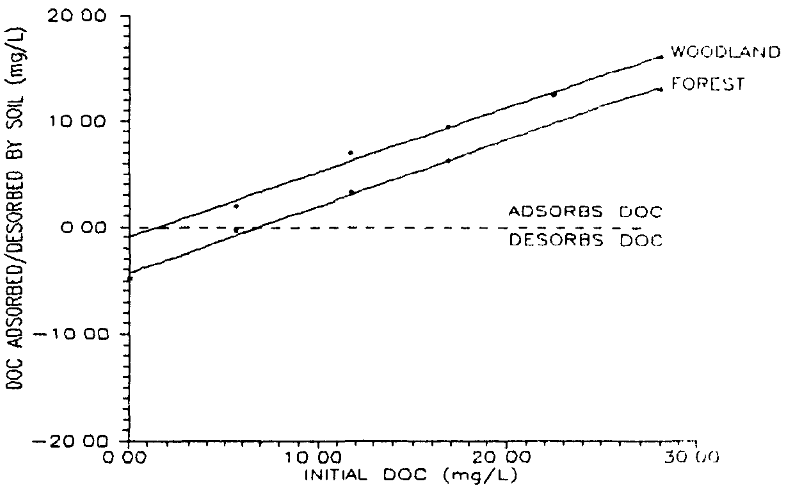

Figure 3.2: Results of DOC adsorption/desorption experiment on woodland and forest soil B horizons.

The equilibrium DOC value (i.e., the DOC concentration in the added water at which no DOC will be adsorbed or desorbed by the soil) is 1.4 mg/L for the lichen woodland soil B horizon and 6.8 mg/L for the spruce-moss forest soil B horizon (Figure 3.2). These results are in agreement with the previous lab experiment (Table 3.4) indicating that the

B horizon is a sink of DOC except if water of low initial DOC concentrations (< 8 mg/L) is incident on it.

These experiments show that the lichen and moss mats and soil B horizons are either sources or sinks of DOC depending on the DOC concentration of the incident water. Soil A horizons are DOC sources.

These laboratory experiments should be interpreted cautiously since lab conditions did not mimic field conditions. Soils were air dried and passed through 2 mm sieves to remove stones, gravel, and twigs thus changing the compaction and drainage properties of the soils, resulting in a homogenous organic layer which does not exist in the field. Temperature and moisture conditions prevalent in the field were not duplicated in the lab. Finally, the physical disturbance of the soil may have resulted in increased DOC reactivity. Due to these changes the natural DOC adsorption and release mechanisms had been altered.

2 DOC EXPORT

Iron Arm fen was drained by 3 small streams which converged and at which point a weir was installed to control and monitor discharge throughout both sampling seasons. DOC concentrations in stream water averaged 10 mg/L (range 7-12 mg/L in 1988 and 7-13 mg/L in 1989) during both sampling seasons indicating that the unusually dry conditions in 1988 had little effect on stream DOC concentrations despite a large difference in discharge between the two seasons. Estimated runoff during the 1988 and 1989 sampling seasons was 73 and 111 mm, respectively (Table 3.5). Thus, runoff during 1988 was 34% less than during 1989 whereas precipitation was 31% less in 1988 than in 1989.

The seasonal DOC export in stream water was estimated to be 0.75 and 1.2 g/m^2 of catchment area in 1988 and 1989, respectively. These amounts do not account for the DOC exported in water draining from the fen at sites other than the streams. The magnitude of this export is not known.

Table 3.5: Runoff and DOC export in the stream draining Iron Arm during both sampling seasons. Runoff and export values are based on the whole catchment (5 ha).

Year	Runoff (mm)	Mean DOC mg/L (range)	DOC exported (g/m^2)	(kg)
1988	73	10 (7-12)	0.75	37.7
1989	111	10 (7-13)	1.2	62.4

The export values of 0.75 and 1.2 g DOC/m^2 are, respectively, below and within the range reported for subarctic fens by Moore (1987; 1.1 - 4.9 g DOC/m^2), and less than the literature values reported for wetlands in other regions (Table 3.6). One possible reason for this is that the literature values in Table 3.6 are annual values whereas those for this study only represent the summer season and do not take into account the spring and fall flush, when large amounts of DOC are exported. Values reported by Moore (1987) include the month of September which is a month of increased rain and, probably, movement of DOC.

Table 3.6: Selected literature values of annual organic carbon export in streams draining non-subarctic wetlands.

Study	Organic Carbon Export
Clair and Freedman 1986	5 - 14 g DOC/m^2
Day et al. 1977	10 g C/m^2
Collier et al. 1989	29 - 38 g DOC/m^2
Eckhardt and Moore 1990	6 - 18 g DOC/m^2
McKnight et al. 1985	8 g DOC/m^2
Mulholland and Kuenzler 1979	2 - 8 g C/m^2
Schlesinger and Melack 1981	2 - 53 g C/m^2
Urban et al. 1989	8 - 40 g DOC/m^2

Some studies have reported significant correlations between stream water DOC concentration and discharge for streams draining catchments with wetlands, some positive (e.g. Schlesinger and Melack 1981; Grieve 1984b), some negative (e.g. Mulholland and Kuenzler 1979; Mulholland 1981a; Clair and Freedman 1986), and some both positive and negative (e.g. Collier et al. 1989). There are many factors that control discharge from peatlands such as height of the water table, storage capacity of the peatland, and hydraulic conductivity of the peat (Bay 1969) and therefore peatlands will behave differently. At Iron Arm only weak correlations between DOC and log discharge were found (Figure 3.3). The determination of the DOC:discharge relationship during storms was not done.

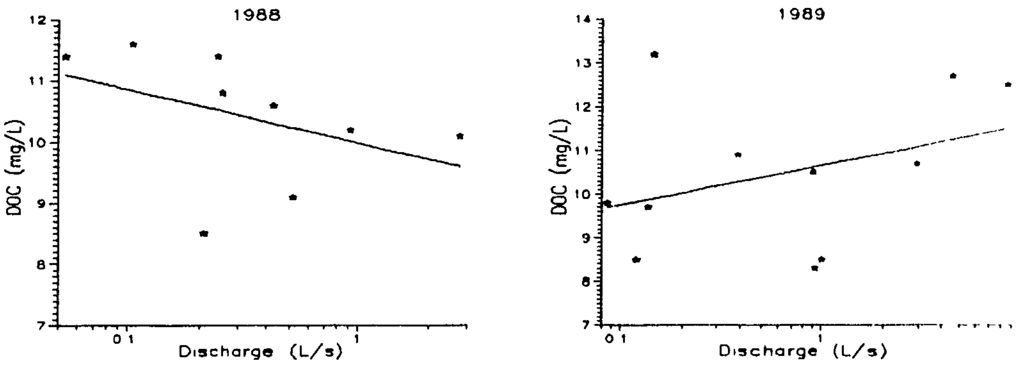

Figure 3.3: Stream DOC concentration versus log discharge at Iron Arm fen for the 1988 and 1989 sampling seasons. For 1988, $R^2 = 0.17$, $p = 0.268$; and 1989 $R^2 = 0.13$, $p = 0.283$.

3 WATER BUDGET FOR IRON ARM CATCHMENT

A water budget for Iron Arm would consist of the following parameters.

$$S = P + G_i - G_o - E_T - Q$$

where S = change in water storage of the fen

P = precipitation

G_i = ground water inflow

G_o = ground water outflow

E_T = evapotranspiration

Q = stream discharge

Using available daily air temperature, net radiation and ground heat flux data from a nearby fen to calculate E_T and assuming that $G_o = G_i$, then for the 1989 sampling season,

$$S = P - E_T - Q$$

$$S = 209 \text{ mm} - 157 \text{ mm} - 111 \text{ mm} = -59 \text{ mm}$$

The result indicates that for the 1989 sampling season Iron Arm had an overall loss of water so that water levels in fen pools decreased and there was compression of peat. This model is an approximation which may be off by a few mm since water lost from the fen at places other than the weir could not be estimated. The value of -59 mm is representative of the sampling season only and not of the whole year. At other times of the year evapotranspiration rates are smaller and precipitation rates are larger probably resulting in an overall positive water balance for the catchment.

Evapotranspiration data for the 1988 season is not available so an estimate has to be made. For the 1989 sampling season E_T was 75% of precipitation. If it is assumed to be the same for the 1988 season then 75% of 145 mm is 109 mm of E_T. Thus,

$$S = P - E_T - Q = 145 - 109 - 73 = -37 \text{ mm}$$

which also represents a water loss.

4 DOC BUDGET FOR IRON ARM CATCHMENT

It was estimated that during the 1989 sampling season there were 0.4 g DOC/m^2 input by precipitation which means that there were 7.2 kg DOC (= 0.4 g/m^2 x 18000 m^2) input into the fen only. In the upland forested part of the catchment there were 209 mm of rain and 157 mm of ET. (Note that there should be less E_T in the forest than the fen, but 157 mm will be used as an approximation). Thus, there were 52 mm of water that made its way through the soil column and presumably, into the fen part of the catchment.

The field part of this study found DOC concentrations in B soil horizon water to be 10 - 23 mg/L (Table 3.1). This was however, for the upper B horizon. Water percolating through the whole horizon is expected to have an even lower DOC concentration. Laboratory (Figure 3.2) and literature values (Table 3.3) indicate a range of 2 - 19 mg DOC/L. Assuming an average of 10 mg/L means that the forested part of the catchment exports 16.6 kg of DOC (= 10 mg/L x 52 mm x 32000 m^2) presumably to the fen part of the catchment. The total DOC input to the fen is thus 7.2 kg + 16.6 kg = 23.8 kg. There were 62.4 kg DOC exported by the stream draining the fen. Thus the difference between export and import is 38.6 kg or 2.1 g DOC /m^2 of fen. This means that during the sampling season the peat produced at least 2.1 g DOC/m^2, all of which was exported.

Similarly, for 1988, the conclusion is that peat produced at least 1.2 g DOC/m^2 (20.8 kg), all of which was exported (Table 3.7).

Table 3.7: A DOC budget for Iron Arm catchment during the 1988 and 1989 sampling seasons. All values are in kg except for values in () which are in g/m^2 of fen. Precipitation and forest values represent DOC imported by the fen.

Year	(Precip.+	Forest =	Fen Import)	Stream Export	Exp - Imp
1988	5.4	11.5	16.9	37.7	20.8
			(0.94)	(2.1)	(1.2)
1989	7.2	16.6	23.8	62.4	38.6
			(1.3)	(3.5)	(2.1)

CHAPTER 4

DOC AND CHEMISTRY OF PEAT WATER

1 SPATIAL AND TEMPORAL VARIATIONS OF DOC IN PEAT WATER

1.1 IRON ARM FEN

Peat water was sampled during the 1988 season at Iron Arm fen (Figure 2.1) and DOC concentrations ranged from 2-40 mg/L (mean=17 mg/L). Nine sites were sampled at depths of 10 and 25 cm weekly and 50 and 100 cm less frequently. Most sites did not show distinct seasonal patterns in DOC concentrations at 10 and 25 cm depths (Figure 4.1). At depths of 50 and 100 cm, data are too sparse to see any patterns, however, seasonal patterns would not be expected at lower depths. It was expected that seasonal patterns related to increased plant decomposition and seasonal warming would be seen. None was seen probably because the sampling season did not start early enough and did not finish late enough. Previous work by Moore (1987b) in fens in the area involving a sampling period lasting until late September indicates seasonal trends in DOC concentrations with a rise in concentrations during the summer and a fall in September and October. The lack of any seasonal trends in this study could also be due to the fact that 1988 had the second driest summer on record resulting in low water levels which may have had an effect on DOC production and movement in the fen. An additional problem could be the sampling method whereby a rod was used to draw up peat

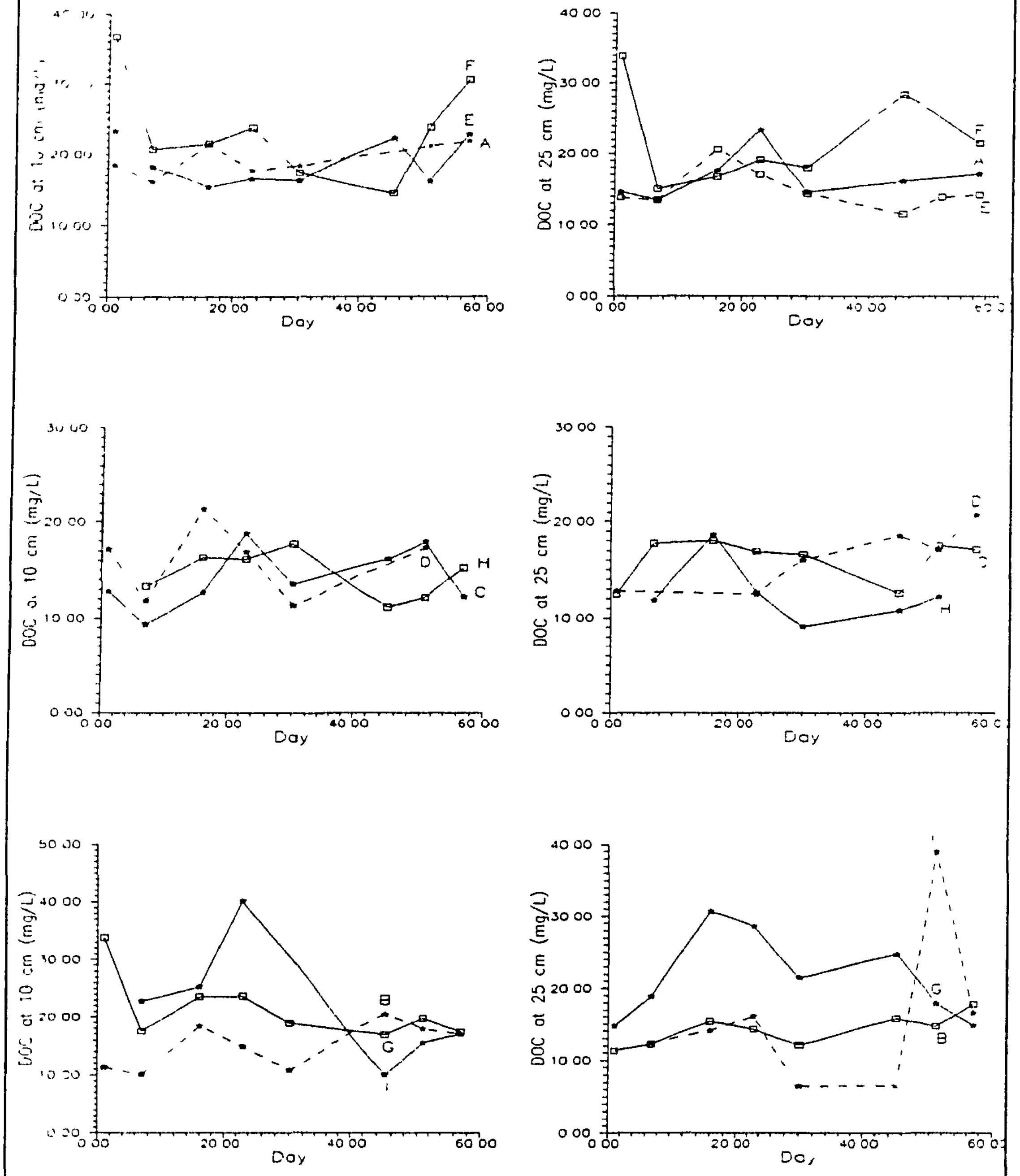

Figure 4.1: Peat water DOC concentrations at depths of 10 and 25 cm at Iron Arm fen, June to August 1988. Day 1 = first sampling day, day 57 = last sampling day. Letters refer to peat water sampling sites.

water samples instead of having permanent bottles installed at the appropriate depths. Thus, from one week to the next the "same" water was not sampled.

All peat sites had inconsistent DOC concentrations with depth (Figure 4.2). Some sites showed increasing DOC concentrations with depth while others showed decreasing concentrations indicating that there is little vertical mixing in the peat profile (Moore 1987b). This may also be due to the distinct anaerobic and temperature conditions and type of organic matter prevailing at the different depths of a peat profile, influencing the population and type of microbes which decompose the organic matter as well as the rate of decomposition.

It was expected that at the 10 cm depth there would be spatial patterns of DOC concentrations related to differences in vegetation between the sites: a larger plant biomass and diversity would produce a larger DOC concentration. All nine sampling sites were rated as rich, medium, or poor based on the inferred above-ground vegetational biomass and its diversity. A rating of rich means that the site had vegetation which included *Sphagnum* and other mosses, dwarf birch, black spruce, and shrubby vegetation. A rating of poor means that the site only had *Carex* spp. Based on this classification there is no relationship between mean seasonal DOC concentrations and observed vegetational biomass (Table 4.1). This is probably due to a number of factors including hydrology (water table height and drainage patterns), plant type and microbial populations at the different sites which affect production and consumption of DOC. For example, sites G and I which are rated as poor in vegetation, had relatively large DOC concentrations at the 10 cm depth. These two sites were located down slope of vegetation-rich areas from which peat water could be migrating. The anaerobic layer may have been relatively closer to the surface at these two sites resulting in decreased oxidation of organic matter, thus allowing it to accumulate.

Table 4.1: Mean seasonal DOC concentrations (mg/L), conductivity (Ec) at $25^{\circ}C$ (μS/cm), and pH of peat water at 10 and 25 cm depths at Iron Arm fen, June - August 1988. Vegetation ratings are based on inferred above-ground biomass and diversity.

		10 cm depth			25 cm depth		
Site	Vegetation	DOC	Ec	pH	DOC	Ec	pH
A	rich	19	34	6.1	16	47	6.4
E	rich	19	58	6.6	15	84	6.8
F	rich	24	41	6.2	21	52	6.3
C	medium	14	30	6.4	16	33	6.6
D	medium	16	29	6.5	16	40	6.8
H	medium	14	22	5.8	13	40	6.5
B	poor	15	32	6.4	12	32	6.4
G	poor	22	46	6.3	21	57	6.9
I	poor	22	43	6.2	16	52	6.4

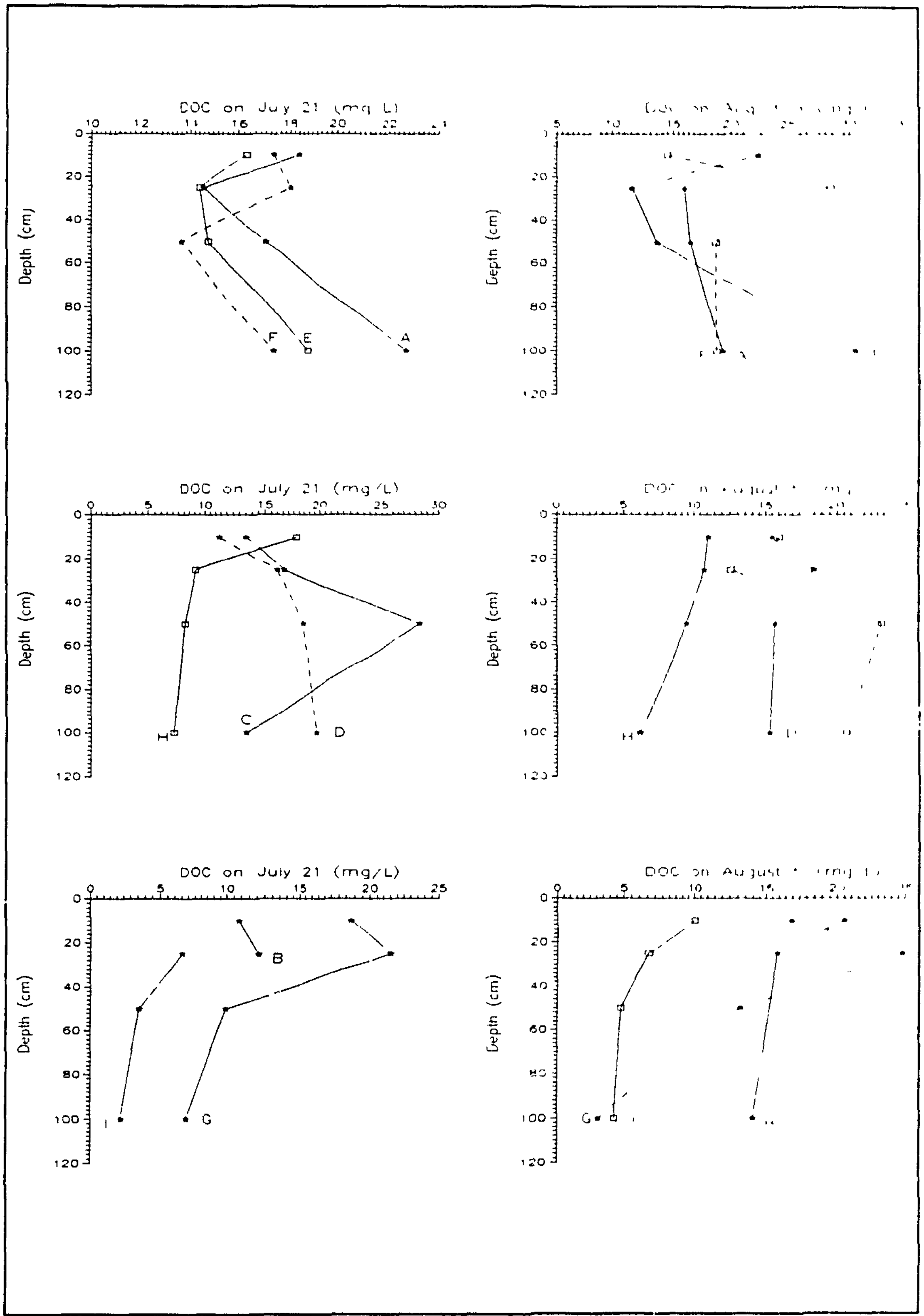

Figure 4.2: Peat water DOC concentrations at 10, 25, 50, and 100 cm depths at Iron Arm fen on July 21 and August 5, 1988.

1.2 PELLETIER FEN

Peat water was sampled during the 1988 season at Pelletier fen (Figure 2.2) and DOC concentrations ranged from 6-76 mg/L (mean=18 mg/L). Site E had the largest mean DOC concentration in surface peat water with 23 mg/L. Sites H, I, and J also had relatively large mean DOC concentrations (17 mg/L) in surface peat water whereas the remaining six sites had values in the range of 10 - 13 mg/L (Table 4.2).

Table 4.2: Mean seasonal DOC concentrations (mg/L), conductivity (Ec) at 25°C (µS/cm), and pH of surface peat water at Pelletier fen, June - August 1988.

Site	DOC	Ec	pH
A	13	13	5.6
B	12	17	5.8
C	13	11	5.5
D	10	10	5.8
E	23	23	5.1
F	12	19	5.8
G	10	12	5.5
H	17	13	5.5
I	17	24	5.9
J	17	14	5.3

The lateral distribution of mean DOC concentrations is a function of numerous factors including hydrology (water table height and drainage patterns), and the production and consumption of DOC at the various sites. As at Iron Arm, seasonal patterns in near-surface DOC concentrations were not observed due to the short and unusually dry sampling season. There was no pattern of DOC concentration with depth as some sites had increasing DOC concentrations, some decreasing, and some were erratic (Figure 4.3).

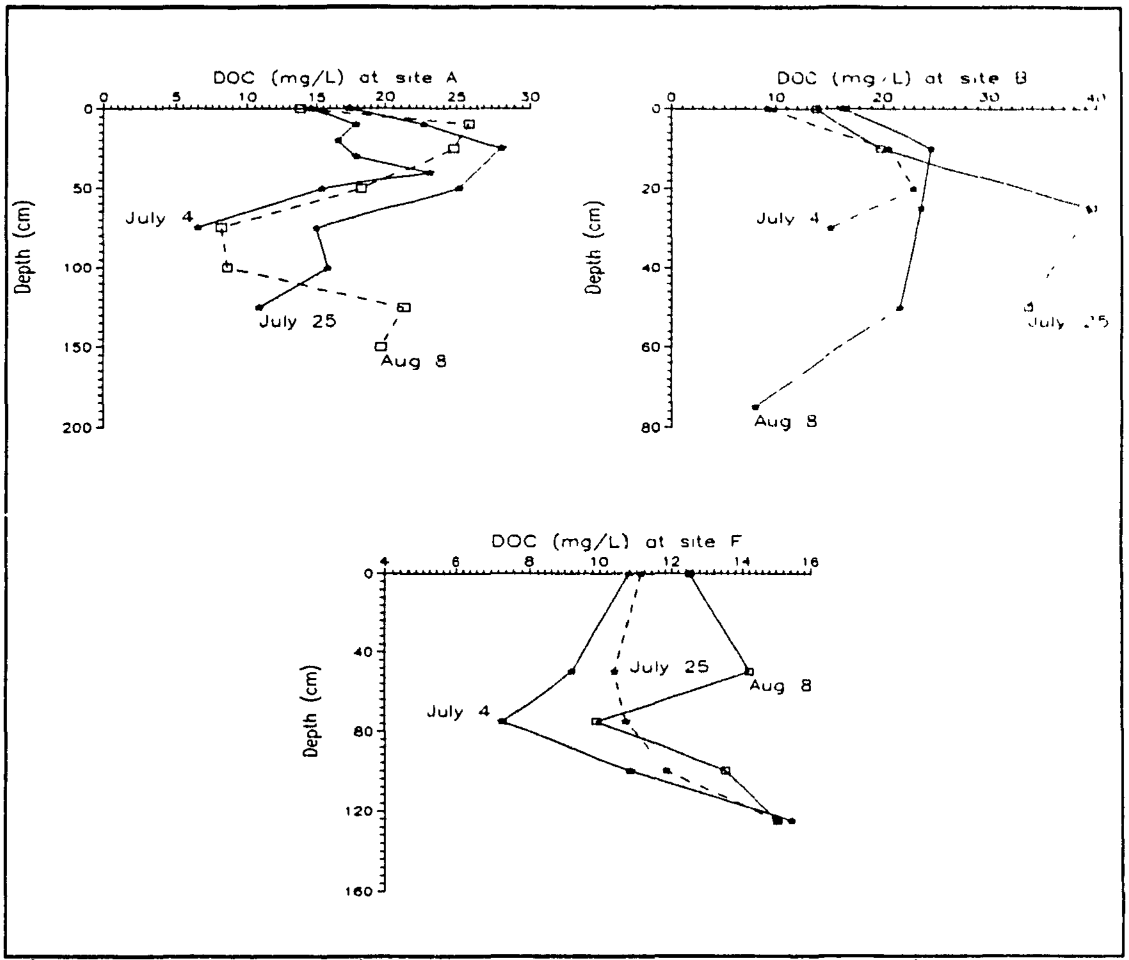

Figure 4.3: Pelletier peat water DOC concentration versus depth at three sites on three sampling days.

2 CHEMISTRY OF PEAT WATER

2.1 IRON ARM FEN

At some sites peat water at depths of 10 cm and 25 cm had a distinct seasonal pH pattern, increasing until a peak was reached in late July or early August and then decreasing (Figure 4.4). The pH ranged from 4.95 to 7.50 (mean=6.57). Conductivity ranged from 17.1 to 198.5 μS/cm (mean=56.8 μS/cm) and at some sites showed a pattern of

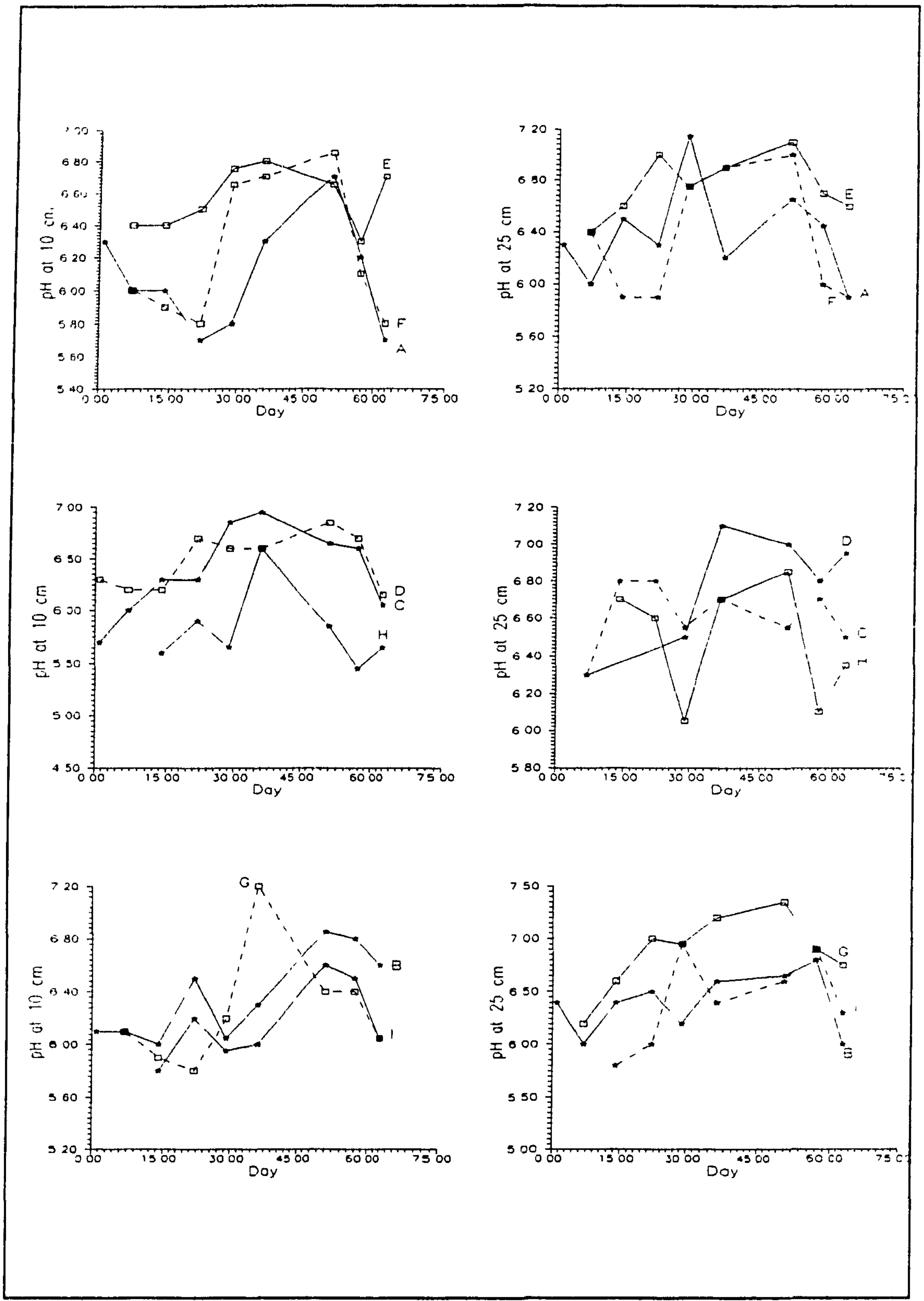

Figure 4.4: Iron Arm peat water pH at depths of 10 and 25 cm, June to August 1988. Day 1 = first sampling day, day 63 = last sampling day.

increasing conductivity throughout the sampling season and in some cases an apparent decline in early August (Figure 4.5). These patterns are probably partly due to increased plant decomposition as the season warms up thus releasing more ions such as Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+}. Height of the water table and rate of water flow are important in determining the ion concentration in the water (Sparling 1966). From the sparse data available at depths of 50 and 100 cm, the pH and conductivity patterns seen at 10 and 25 cm were not present.

It was found that both pH and conductivity increased with depth (Table 4.3) suggesting that the upper layer of the peat profile may be subject to ombrotrophic conditions so that cations of ground water origin are not able to penetrate the upper layer (Moore and Bellamy 1974). Microorganisms in the peat form organic acids which release H^{+} ions which can be flushed away by flowing water (i.e. H^{+} ions adsorbed on peat exchange sites would be released in exchange for cations in water), react with bicarbonate to form CO_2 and H_2O (Moore and Bellamy 1974), or remain present in solution or adsorbed on peat exchange sites (Sparling 1966). As the peat thickens, ground water flow is reduced nearer the surface and thus H^{+} ions are no longer flushed away but accumulate (Moore and Bellamy 1974), resulting in higher acidity and possibly lower conductivity towards the surface. With time the H^{+} ions at the lower depths will be diluted by the cations present in ground water.

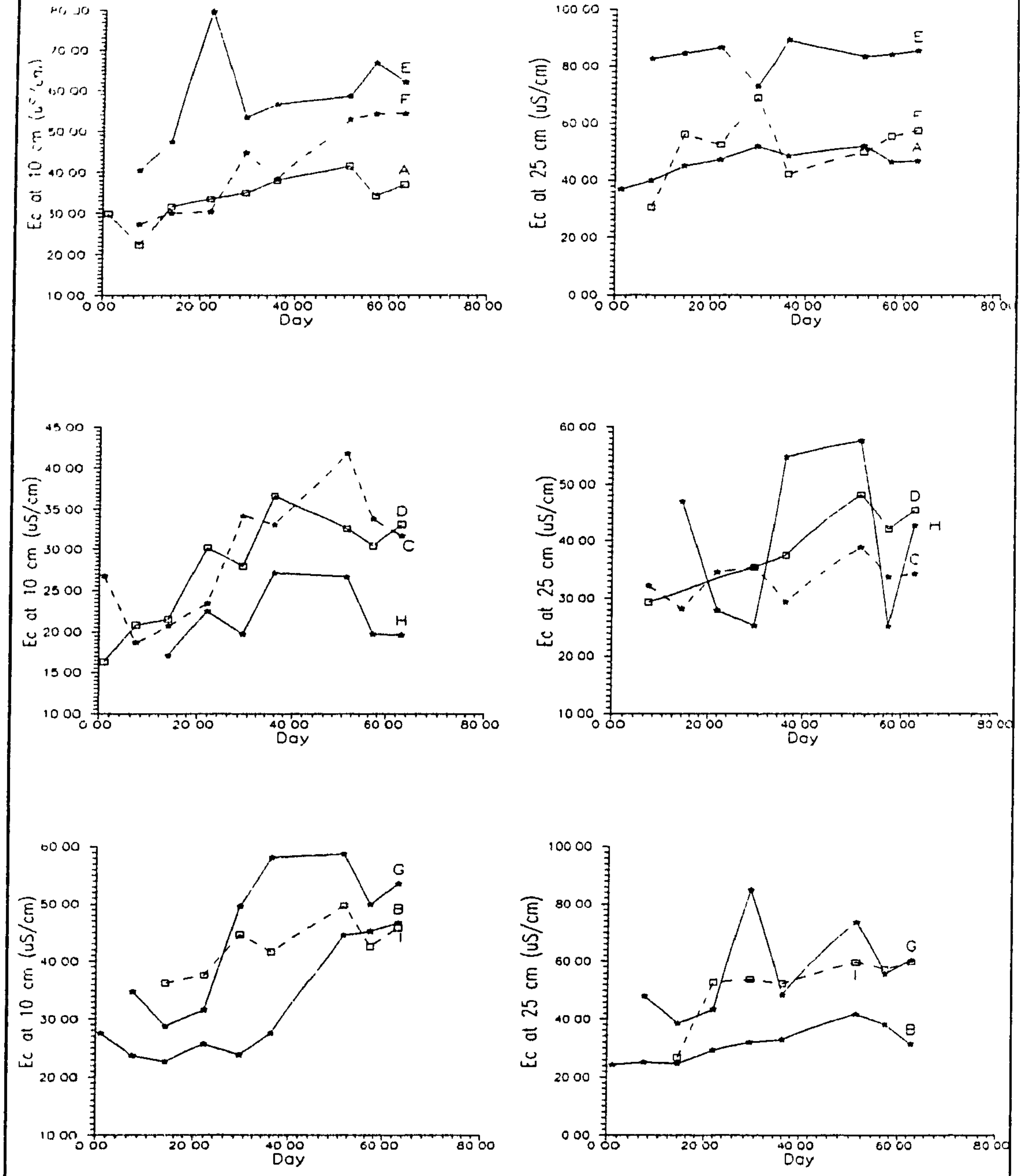

Figure 4.5: Iron Arm peat water conductivity (25°C) at depths of 10 and 25 cm, June - August 1988. Day 1 = first sampling day, day 63 = last sampling day.

Table 4.3: Mean seasonal DOC concentrations (mg/L), conductivity (Ec) at 25°C (μS/cm), and pH in peat waters at Iron Arm fen, June - August 1988.

Site	Depth (cm)	DOC	Ec	pH
A	10	19	34	6.1
	25	16	47	6.4
	50	20	45	6.9
	100	25	46	6.9
B	10	15	32	6.4
	25	12	32	6.4
	50	-	-	-
	100	16	67	6.9
C	10	14	30	6.4
	25	16	33	6.6
	50	24	57	6.2
	100	17	42	6.8
D	10	16	29	6.5
	25	16	40	6.8
	50	17	57	6.8
	100	17	66	7.2
E	10	19	58	6.6
	25	15	84	6.8
	50	14	89	7.1
	100	24	92	7.2
F	10	24	41	6.2
	25	21	52	6.3
	50	17	70	6.6
	100	18	72	7.1
G	10	22	46	6.3
	25	21	57	6.9
	50	19	107	7.0
	100	5	152	7.1
H	10	14	22	5.8
	25	13	40	6.5
	50	11	162	7.4
	100	7	188	7.4
I	10	22	43	6.2
	25	16	52	6.4
	50	9	78	6.8
	100	3	103	6.8

In this study, DOC does not fluctuate with pH and conductivity agreeing with results reported by Moore (1987b) who, using a principal components analysis, found that peat water DOC concentration was independent of cations such as

Ca^{2+}, Mg^{2+}, and K+ (which are a surrogate for conductivity) and pH of the peat water.

The E4/E6 ratio (the ratio of absorbance at 465 nm and 665 nm) is used as an estimate of the relative concentrations of high molecular weight humic and low molecular weight fulvic acids in a sample. Chen et al. (1977) found that pH will significantly affect molecular weight and as such the E4/E6 ratio. These changes however, are minimal for the pH range (4.95-7.50) of the peat water samples in the present study.

The E4/E6 ratio was found to generally decrease with depth indicating a change from the presence of predominantly low molecular weight fulvic acids at the surface of the peat profile to predominantly higher molecular weight humic acids further down the profile (Table 4.4). Such a distribution of humic and fulvic acids indicates that abiotic condensation (fulvic acids condensing to form humic acids) maybe taking place (Hedges 1988, p.47). It may be that the E4/E6 ratio is related to the state of decomposition. The more decomposed the organic matter, the smaller the E4/E6 ratio.

Table 4.4: Peat water E4/E6 ratio versus depth at Iron Arm fen on July 21 and August 5, 1988.

Site	Depth (cm)	July 21	Aug. 5
A	10	8.6	9.3
	25	7.7	9.8
	50	6.0	8.4
	100	3.9	5.4
B	10	9.7	4.6
	25	6.8	13.3
	50	-	-
	100	6.1	7.0
C	10	6.0	9.1
	25	4.5	8.6
	50	4.3	4.7
	100	5.1	-
D	10	8.4	8.0
	25	4.6	4.7
	50	4.3	4.0
	100	-	4.6
E	10	8.0	10.2
	25	9.3	9.1
	50	5.4	-
	100	5.3	11.3
F	10	9.8	10.0
	25	6.4	6.4
	50	5.1	5.2
	100	4.2	7.8
G	10	5.1	6.7
	25	3.9	-
	50	9.1	10.1
	100	9.4	-
H	10	5.9	9.5
	25	5.7	5.3
	50	5.0	3.5
I	10	7.1	-
	25	9.5	7.8

2.2 PELLETIER FEN

At some sites (A, B, C, D, F) surface peat water pH increased throughout the sampling season (Figure 4.6). The pH ranged from 4.30 to 6.60 (mean=5.8). Conductivity ranged from 5.6 to 77.4 µS/cm (mean=27.5 µS/cm) and at some sites (A, B, C) increased throughout the sampling season (Figure 4.6). Unlike at Iron Arm, pH did not consistently increase with depth but was generally erratic. Conductivity was less erratic and, at most sites sampled, increased with depth (Table 4.5). From the sparse data available, the E4/E6 ratio showed an erratic pattern with depth.

Mean conductivity and pH were both lower than at Iron Arm suggesting that Iron Arm is more minerotrophic. This could be due to more ground water input at Iron Arm, more weathering of the rocks underlying Iron Arm fen resulting in increased cation release, and height of the water table.

Hydrology (ground water inflow, amount of surface water, water table height , water flow through the peat), topography, and vegetation are probably all responsible for the differences observed between the two peatlands.

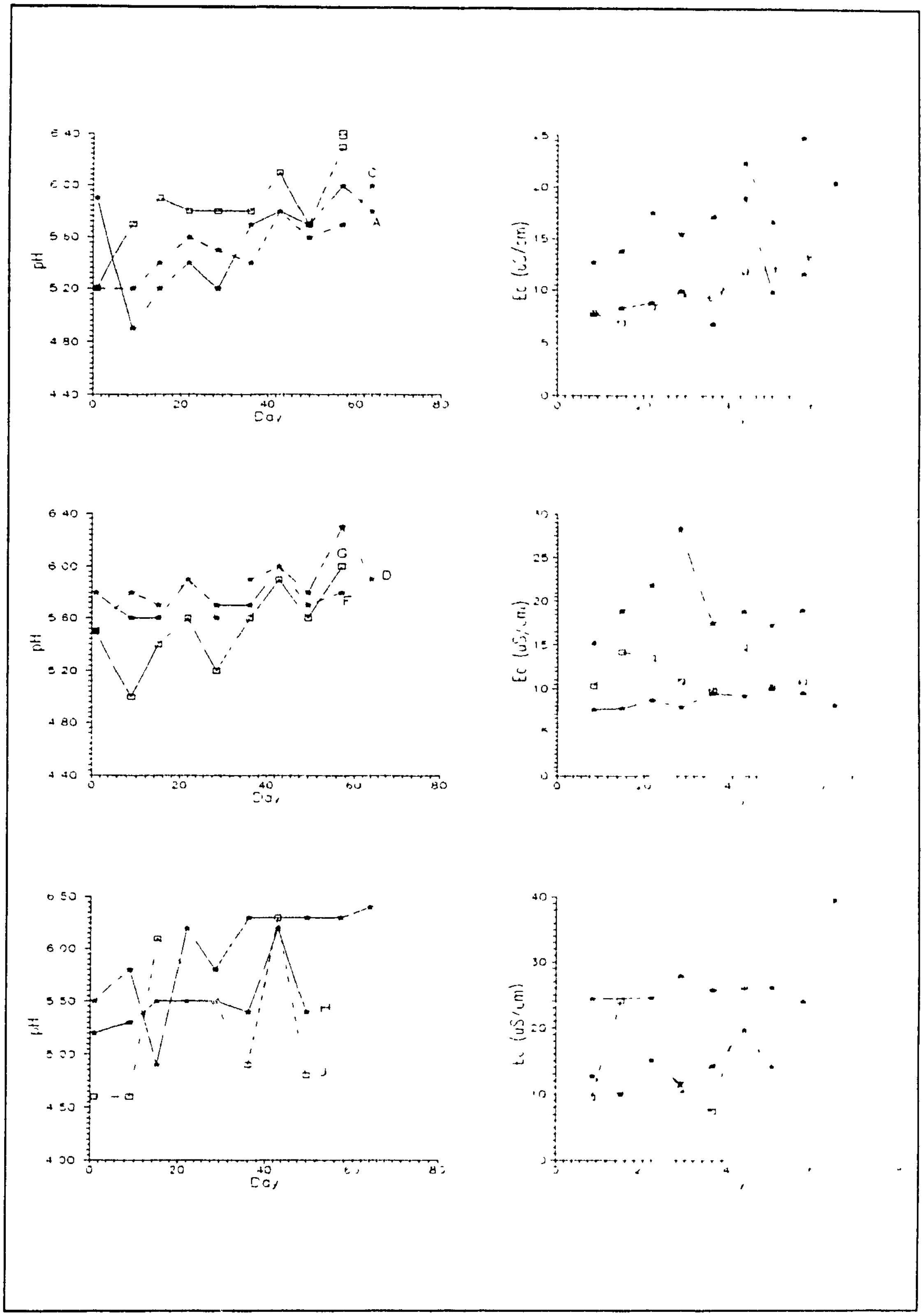

Figure 4.6: Pelletier fen surface peat water pH and conductivity (Ec) at 25°C during the sampling season, June to August 1988. Day 1 = first sampling day; day 64 = last sampling day.

Table 4.5: Conductivity (Ec) at 25°C (µS/cm) and pH versus depth in Pelletier fen peat water on three sampling days in 1988.

		July 4		July 25		August 8	
Site	Depth (cm)	Ec	pH	Ec	pH	Ec	pH
A	0	9	5.4	19	5.8	12	6.0
	10	16	5.9	22	6.0	21	6.3
	20	18	6.1	-	-	-	-
	25	-	-	29	6.2	22	6.0
	30	19	6.1	-	-	-	-
	40	26	6.4	-	-	-	-
	50	36	6.4	39	6.6	22	6.1
	75	53	6.3	49	6.4	38	6.6
	100	40	6.3	56	6.5	54	6.4
	125	-	-	76	6.5	76	6.4
	150	-	-	66	6.5	62	6.3
B	0	18	5.8	22	6.1	25	6.3
	10	18	6.1	25	5.8	23	5.9
	20	24	6.4	-	-	-	-
	25	-	-	41	6.2	33	6.5
	30	21	6.4	-	-	-	-
	50	-	-	40	6.3	41	6.1
	75	-	-	-	-	51	6.1
F	0	22	5.9	19	6.0	19	5.8
	50	11	5.7	16	6.0	16	5.9
	75	9	5.6	16	6.0	17	5.8
	100	17	5.8	19	5.8	16	5.8
	125	45	6.0	35	5.8	31	6.0
I	0	25	6.2	-	-	24	6.3
	10	29	5.2	17	5.2	29	6.1
	20	55	5.6	-	-	-	-
	25	-	-	39	6.0	68	6.2

CHAPTER 5

DOC IN STREAMS DRAINING SUBARCTIC FEN CATCHMENTS

The streams draining ten fen catchments (including Iron Arm and Pelletier) were sampled weekly from mid-June to late August 1989. Four streams (4, 5, 6, 7) were resampled from mid-May to late August 1990. The 1989 samples were analyzed for pH, conductivity, absorbance at 400 nm, and DOC by the potassium persulfate/CO_2 method. The 1990 samples were analyzed only for absorbance at 400 nm which were transformed into DOC values using the regression equation developed for the 1989 samples where

$$\text{DOC} = 19.1(\text{absorbance at } 400 \text{ nm}) + 1.5$$

$R^2 = 0.90$, $n = 99$, standard error of the estimate = 1.5 mg/L, $p = 0.000$.

1 DOC CONCENTRATION AND % FEN AREA

For the ten catchments, stream DOC concentrations ranged from 1.7 to 15.8 mg/L (Table 5.1) which is within the range reported in the literature for streams draining wetland catchments (Table 5.2) Mean conductivity and pH values ranged from 19 - 49 μS/cm and 5.8 -6.8, respectively.

Table 5.1: Mean seasonal DOC concentrations, conductivity at 25°C, pH, and % fen area for the 10 catchments.

Catchment	DOC (range) (mg/L)	Ec (μS/cm)	pH	% Fen
1	4.7 (2.8-6.9)	38	6.6	23
2	5.3 (2.5-7.8)	45	6.8	47
3	1.7 (1.0-3.2)	49	6.8	13
4	2.4 (0-4.3)	31	6.6	11
5	3.6 (1.3-6.0)	26	6.7	26
6	5.7 (3.4-8.2)	19	6.3	48
7	4.6 (3.4-5.2)	29	6.7	20
8	12.0 (4.2-17.0)	25	5.8	59
9	10.3 (8.3-13.2)	28	6.3	36
10	15.8 (8.7-23.1)	23	6.5	36

Table 5.2: Selected literature values of DOC (mg/L) in streams draining catchments with wetlands.

Study	Site	DOC (mean)
Brinson (1976)	Guatemala	3-18
Brinson et al. (1980)	North Carolina	17-26 (15)
Clair and Freedman (1986)	Nova Scotia	(5-14)
Day et al. (1977)	Louisiana	(12)
Eckhardt and Moore (1990)	S. Québec	9-73 (14-40)
Grieve (1984b)	Scotland	0-15 (7)
Kerekes et al. (1986)	Nova Scotia	16-25
Moore (1987b)	Schefferville, Qué.	2-15
Moore and Jackson (1989)	Larry R., New Zealand	(30-37)
Mulholland (1981a,b)	North Carolina	5-30 (15)
Mulholland and Kuenzler (1979)	North Carolina	(10-20)
Perdue et al. (1981)	Oregon	(14)

DOC concentrations are positively correlated with % fen area (Table 5.1 and Figure 5.1; $R^2=0.38$, SEE=3.8 mg/L, $p=0.059$) agreeing with work done by Eckhardt and Moore (1990) in southern Québec.

The relationship of stream DOC concentration and % fen area may be better if more catchments had been sampled. The variability seen in the relationship is due to a number of factors including differences in bedrock, amount of iron present, and location of the fen areas relative to the

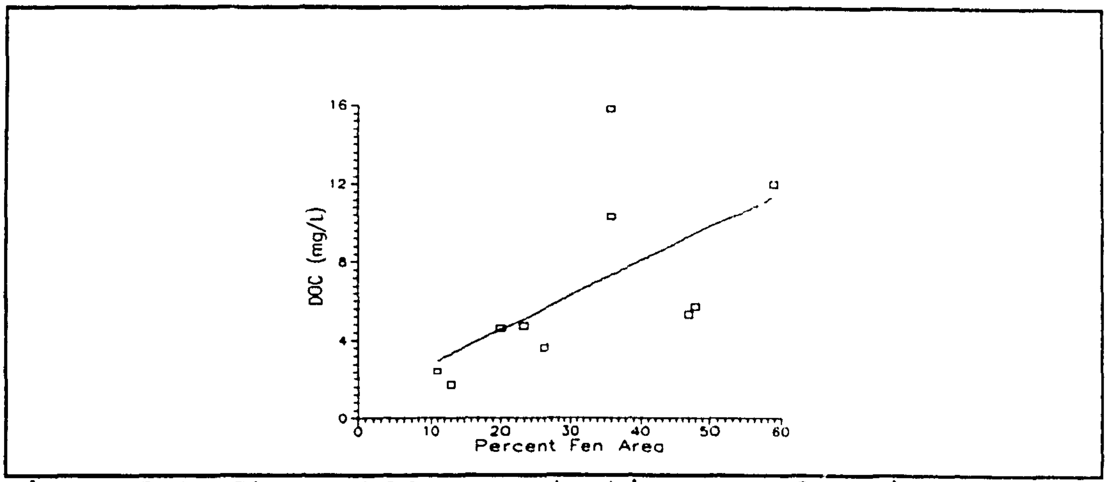

Figure 5.1: Stream DOC concentration as a function of % fen area for the ten catchments. The three streams with the largest DOC concentrations drain catchments 8, 9, and 10 where the streams are fed directly by a fen at the catchment outflow.

streams draining the catchment. Stream 3 had the lowest mean DOC concentration (1.7 mg/L) due to the relatively small % fen area in the catchment and because of dolomite bedrock and/or ground water input. The stream water had the largest mean conductivity value (49 μS/cm) indicating cation input from ground water or dolomitic bedrock resulting in dilution and precipitation of DOC compounds.

Catchment 2, with the third largest fen area (47%), had a relatively low mean stream DOC concentration (5.3 mg/L). It was noticed that the stream had reddish/orange material precipitated along the channel floor and sides indicating a high iron content. Iron is believed to adsorb and precipitate DOC, thereby reducing the DOC concentration in stream water (Heikkinen 1990).

Catchment 6 had the second largest fen area (48%) but its stream had a relatively low mean DOC concentration (5.7 mg/L) partly due to the fact that the fens are located in the upper sections of the catchment so that stream DOC concentrations will decrease after having drained that area due to adsorption and precipitation onto a mineral channel bed (McDowell 1985; Meyer et al. 1988). In contrast, streams draining catchments 8, 9, and 10 all pass directly through a fen at the outflow and thus have the three largest mean DOC values, 12.0, 10.3 and 15.8 mg/L, respectively.

2 TEMPORAL VARIATIONS OF DOC

During the 1989 sampling season, only streams 5, 6 and 10 showed a seasonal pattern in DOC, peaking in late July or early August and decreasing thereafter (Figure 5.2). A longer sampling season may have revealed a seasonal pattern of DOC for some of the other streams, however, as discussed above, there are numerous factors which affect stream DOC concentrations.

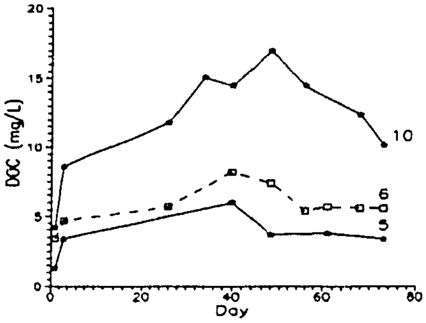

Figure 5.2: DOC concentrations during the 1989 sampling season in streams draining catchments 5, 6, and 10. Day 1 = June 16; day 73 = August 28.

During the longer 1990 sampling season all four streams sampled (4, 5, 6, and 7) showed a pronounced seasonal pattern in absorbance at 400 nm (a surrogate for DOC) indicating high DOC concentrations during spring runoff and decreasing thereafter (Figure 5.3) which implies a positive correlation between DOC concentration and discharge, assuming that discharge was highest during spring runoff and subsequently decreased.

Precipitation during the 1990 sampling season was slightly below normal during the month of May, normal through June and July, and 54% below normal during August. The small amount of rain in August is probably responsible for the continual drop in stream DOC concentrations seen. A normal amount of rain may have resulted in stream DOC concentrations rising during August, as the DOC accumulated during the warm summer months was flushed away.

During 1989, streams 1 and 2 showed significant positive correlations between DOC concentration and stage height (a surrogate for discharge) while the other streams did not show significant correlations (Figure 5.4; Table 5.3). During 1990, all four streams sampled had significant positive correlations between DOC and stage height, however, the range of DOC values for streams 4 and 7 falls within the accuracy limits of DOC determination (Figure 5.5) and thus, the correlation between DOC and stage height is actually insignificant for streams 4 and 7.

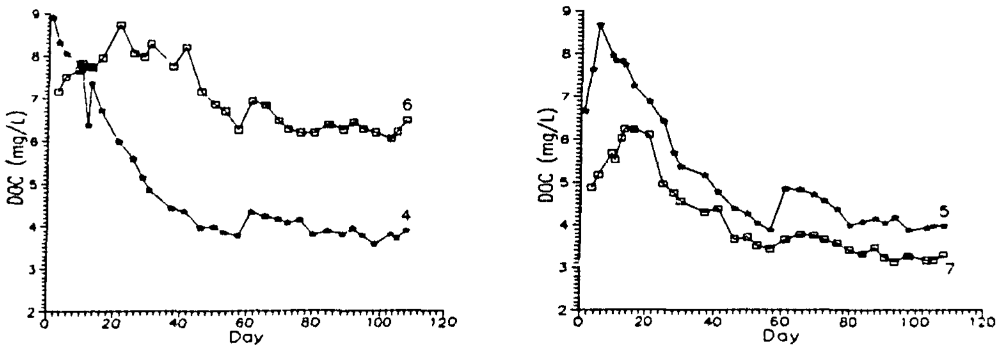

Figure 5.3: Stream DOC concentrations (determined from the DOC:absorbance regression) during the 1990 sampling season for catchments 4, 5, 6, and 7. Day 1 = May 13; day 108 = August 28.

Table 5.3: Correlations between DOC concentrations and stage height for selected streams during the 1989 and 1990 sampling seasons. SEE = standard error of the estimate (mg/L). Mean DOC is in mg/L.

Stream	R^2	SEE	Mean DOC	n	p	Regression
(1989)						
1	0.78	0.85	4.7	7	0.008	DOC = 0.49(SH) + 3.6
2	0.63	1.11	5.3	9	0.011	DOC = 0.43(SH) + 3.8
3	0.45	0.62	1.7	7	0.085	DOC = 0.23(SH) + 1.1
6	0.01	1.50	5.7	9	0.762	DOC = -0.04(SH) + 5.9
7	0.23	0.57	4.6	7	0.276	DOC = -0.03(SH) + 4.9
9	0.12	1.51	10.1	12	0.268	DOC = 0.07(SH) + 9.4
(1990)						
4	0.51	0.17	4.0	20	0.000	DOC = 0.06(SH) + 3.7
5	0.72	0.21	4.3	20	0.000	DOC = 0.05(SH) + 3.9
6	0.46	0.42	6.6	20	0.001	DOC = 0.06(SH) + 6.0
7	0.42	0.27	3.5	20	0.002	DOC = 0.05(SH) + 3.4

In catchment 9 (Iron Arm) discharge was monitored continuously during two seasons and it was found to generally increase within 24 hours of a precipitation event larger than about 2 - 3 mm and decrease over a period of time determined by the intensity and duration of the event (Figures 5.6 and 5.7). DOC concentrations did not respond

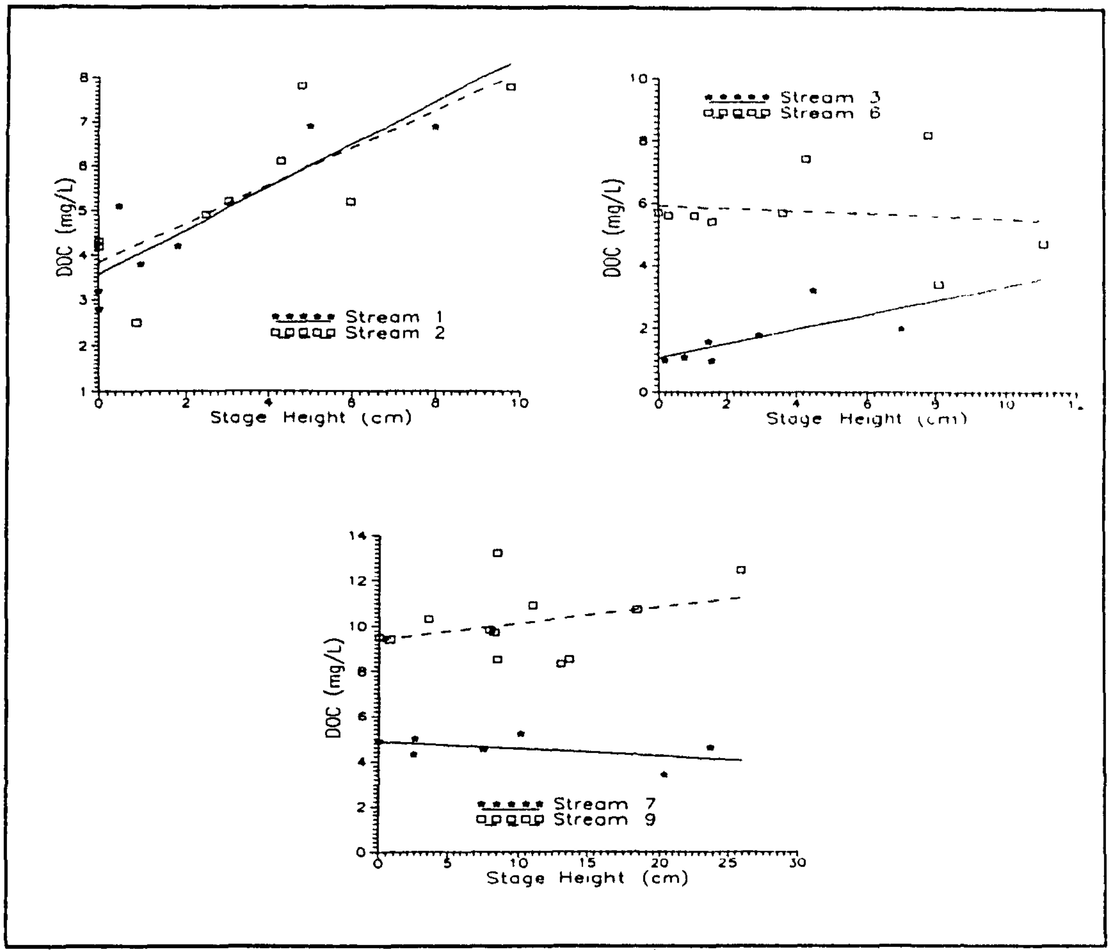

Figure 5.4: Stream DOC concentrations versus stage height for selected streams during the 1989 sampling season.

to changes in discharge in a predictable way in the stream draining Iron Arm fen (stream 9 in Table 5.3) as was the case for streams 1 and 2 which had a significant positive correlation between DOC concentration and stage height.

It may be that there are significant correlations between stream DOC concentrations and discharge but they are not apparent in this data set due to the sampling scheme used whereby DOC and stage height were measured weekly which may not be frequent enough to catch the changes in DOC, if they occur.

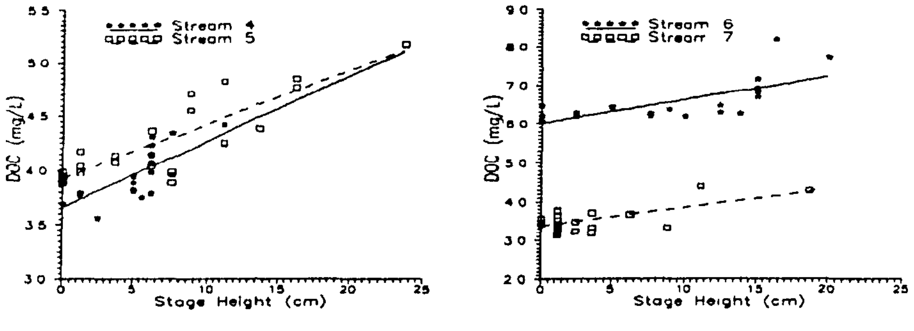

Figure 5.5: Stream DOC concentrations versus stage height for streams 4, 5, 6, and 7 during the 1990 sampling season. DOC values were calculated from the DOC:absorbance regression equation.

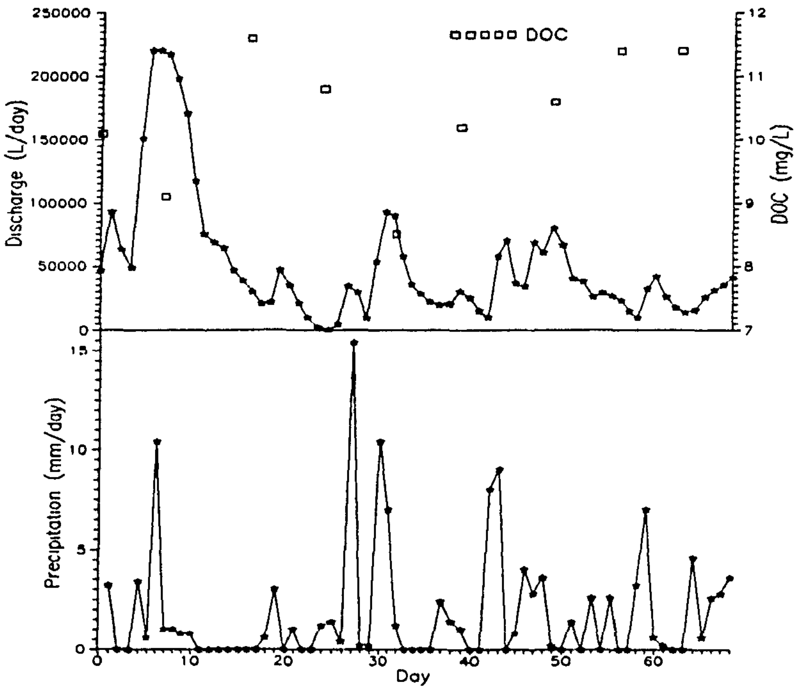

Figure 5.6: The daily response of discharge to precipitation at Iron Arm fen during the 1988 sampling season. DOC values are also given. Day 1 = June 15, day 68 = August 21.

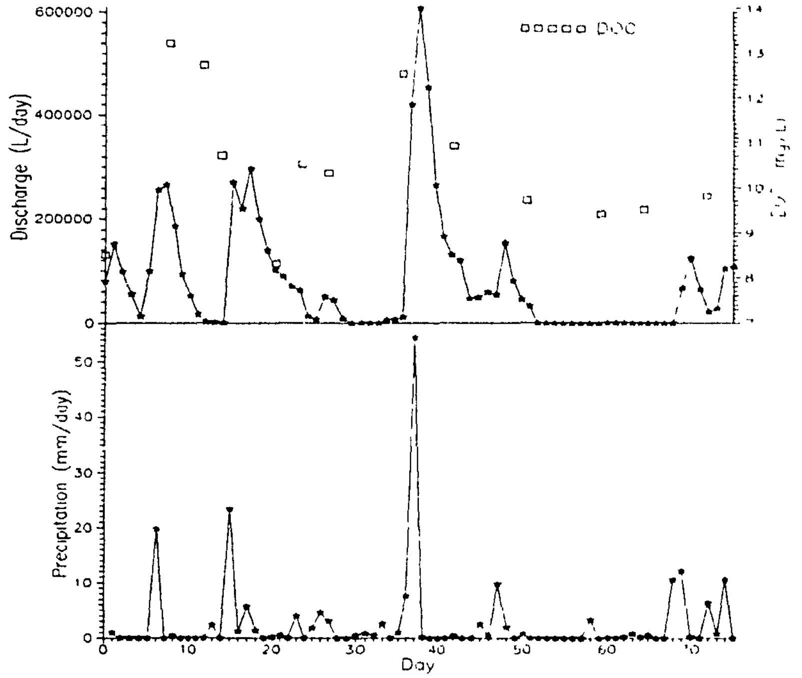

Figure 5.7: The daily response of discharge to precipitation at Iron Arm fen during the 1989 sampling season. DOC values are also given. Day 1 = June 13, day 75 = August 26.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

1 CONCLUSIONS

The purpose of this research project was to investigate the sources, sinks, fluxes, spatial distributions, and temporal variations of DOC in subarctic fen catchments as well as the temporal patterns of DOC concentrations in streams draining fen catchments. In the Iron Arm catchment, it was found that precipitation and canopy and understory throughfall were all important DOC sources with seasonal DOC fluxes to the forest floor of 0.1 - 0.4, 0.5 - 1.3, and 0.8 - 1.7 g DOC/m^2 of forest, respectively. Stemflow water had the largest DOC values, however, the small volumes of stemflow made it an unimportant DOC source. The lichen and moss mats and soil A horizon were also found to be DOC sources whereas the soil B horizon was found to be a DOC sink. As a whole, the soil column was estimated to export 0.4 - 0.5 g DOC/m^2 of forest.

The latter findings were confirmed in the laboratory with soil, lichen, and moss samples from the field sites. The lichen and moss mats were both found to be either sources or sinks of DOC depending on the DOC concentration of incident water. The soil A horizon was found to be a DOC source except when water with a high DOC concentration (112 mg/L) was incident on it. The B horizon was a DOC source when the incident water had <8 mg DOC/L. Thus, under normal field conditions the soil B horizon is a DOC sink since water percolating through the soil A horizon has a mean DOC concentration of 35 - 42 mg/L. The adsorption of DOC by the B horizon is due to its iron-rich nature.

The amount of precipitation was found to be an important determinant of the flux of DOC leached from tree canopies. An increase in the amount of precipitation from 1988 to 1989 did not result in a statistically significant increase in the mean DOC concentration in canopy and understory throughfall, due to the variability of DOC concentrations from one sampling day to the next. The magnitudes of DOC fluxes however, which depend on precipitation depth, showed a significant increase from 1988 to 1989 due to the increased precipitation. A weak correlation was found between DOC concentration and rainfall amount suggesting that factors such as rainfall intensity and duration, time elapsed between rain events, and temperature may all be important factors in determining DOC leaching from vegetation.

Iron Arm catchment exported more DOC during the 1989 sampling season since there was more rain and runoff that summer than during the 1988 summer. Despite the increase in DOC exported as a result of increased discharge, there was no significant correlation between stream DOC concentration and discharge, probably due to dilution of the DOC.

No correlation was found between mean seasonal DOC concentrations in peat water and inferred vegetational biomass and plant diversity at Iron Arm and Pelletier fens. The high spatial and temporal variability in peat water DOC concentrations is probably related to three factors, namely production, consumption, and hydrology. Production depends on plant type, microbial population, and temperature. Consumption depends on microbial uptake and adsorption mechanisms by, for example, iron compounds and calcium and magnesium carbonate. Finally, hydrology (water table height and water movement) determines the amount of DOC being moved from one place to another in the catchment.

Weekly sampling of streams draining fen catchments showed that there was a significant positive correlation between stream water DOC concentrations and the percent of the catchment occupied by fens. The variability seen in the relationship was due to differences in bedrock type between catchments, the amount of iron compounds present in the soils, and the location of the fens in the catchment relative to the streams sampled.

Of the 10 streams sampled, only 3 showed a seasonal pattern in DOC concentrations. Four streams which were sampled again in 1990 all showed a pattern of decreasing absorbance at 400 nm (a surrogate for DOC) from mid-May to late August. This pattern may be due to the fact that during August there was 54% less precipitation than normal and thus DOC accumulated during the summer was not being washed into the streams.

Since absorbance values and thus DOC concentrations were largest during the spring runoff this indicates a positive correlation between DOC and discharge. The large DOC concentrations during the spring are the result of accumulated litter from the fall and DOC in the snow. During snowmelt the DOC moves over the frozen land into the water system, thus never coming into contact with mineral soils where it could be adsorbed and precipitated.

The data indicate that for some streams there is a significant positive correlation between stage height (a surrogate for discharge) and stream water DOC concentrations. Other factors are important however, since only two of the ten streams sampled during 1989 showed significant positive correlations between DOC concentration and stage height. A weekly sampling scheme may not be frequent enough to catch DOC changes which may last only a number of hours.

2 SUGGESTIONS FOR FUTURE RESEARCH

There are some general issues which should be investigated in the future. The release of DOC by vegetation was found to be an important source of DOC. It was thought to be dependent on rainfall intensity and duration, time elapsed between rain events, and temperature. Lab experiments simulating these conditions should be done to better understand the effects of these processes on various types of vegetation and thus lead to predictions of how changes in vegetation and climate affect DOC fluxes, chemistry, and composition. A field component whereby stemflow, throughfall, and soil water are sampled after each rain event would also be useful.

The spatial trends of DOC concentrations in streams draining fen catchments would lead to a better understanding of the sources and sinks of DOC into and within the stream channel. Combined with knowledge of the composition and chemistry of the DOC, it would also provide a guide of where to look for the numerous physical, chemical, and biological processes affecting DOC.

Characterization of DOC should be done for different types of water (stream, stemflow, throughfall, and soil water) and compared to other studies (e.g. Cronan and Aiken 1985; McDowell and Likens 1988). This would give cross-biome comparisons of the chemistry and composition of DOM and may lead to a better understanding of how changes in environmental conditions (e.g. vegetation, soil type, climate, drainage) affect them (Cronan and Aiken 1985). In addition, characterization of stream water DOC during baseflow and storm events may tell us where the DOC is coming from within the catchment i.e., it may give us an idea of the drainage patterns (McDowell and Likens 1988).

Since peat has been shown to concentrate numerous metals (Bonnett and Cousins 1987) more research needs to be done to understand these interactions as well as the interaction of humic acids with metals in natural waters as suggested by Weber (1988).

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APPENDIX I

TWO METHODS FOR MEASURING DOC

A) Dichromate wet oxidation method (modified Walkley-Black)

A known volume of filtered sample is evaporated in a 250 ml Erlenmeyer flask in an oven set at 95°C. Once evaporated, add 10 ml of $K_2Cr_2O_7$ (made by dissolving 2.542 g of $K_2Cr_2O_7$ in 1 L of distilled water) and 25 ml of acid mix (made with 700 ml concentrated H_2SO_4, 350 ml H_3PO_4, and 5 g Ag_2SO_4 to eliminate chloride interference). Swirl the flask and digest for 3 hours at 105°C. $Cr_2O_7^{2-}$ will oxidize the organic matter to CO_2 which is lost as gas. Dilute with 100 ml of distilled water and add 1 ml of indicator (dissolve 0.16 g of barium diphenylamine sulphonate in 100 ml water). Titrate the remaining $Cr_2O_7^{2-}$ until a green end point with a solution (titrant) made by dissolving 9.6 g of ferrous ammonium sulphate in 1 L of water containing 5 ml of concentrated sulphuric acid.

DOC is calculated as:

$$\text{DOC (mg/L)} = \frac{(B - S)}{B} \times 1.28 \times C$$

where: 1.28 is a correction factor for unoxidized organic carbon; B = volume of titrant used when titrating a blank; S = volume of titrant used when titrating a sample; C = a correction factor based on the original volume of sample evaporated: (aliquot, C), (250, 6), (100, 15), (50, 30), (10, 150).

B) Potassium persulphate/CO_2 gas chromatography method

$K_2S_2O_8$ (0.1 g) and 1 drop of concentrated phosphoric acid are added to 10 ml of a filtered (GF/C) water sample and this is mixed to dissolve the $K_2S_2O_8$. The resulting solution is pipetted into a 10 ml glass ampoule and pure nitrogen gas is bubbled through the solution for two minutes to eliminate any inorganic carbon dioxide present in the water. The ampoule is immediately sealed with a propane flame taking care not to allow flame gasses to enter the ampoule. Ampoules are then autoclaved for one hour at 121°C which oxidizes all the DOC to CO_2 (Menzel and Vaccaro 1964; Stainton 1973; McDowell et al. 1987).

The amount of CO_2 generated is determined by using a double gas-liquid phase equilibration (McAullife 1971). Once at room temperature (it is important to maintain a constant temperature) the ampoule neck is broken in a closed system to prevent any loss of gas. A 10 cc hypodermic syringe with a long needle is used to draw a 5 cc aliquot of the liquid phase. Five cc of pure N_2 gas are then added to the syringe which is then sealed and shaken vigorously for 20 seconds to get the CO_2 into the gas phase. An aliquot of the gas phase is introduced into a Perkin Elmer 3920 gas chromatogaph equipped with a thermal conductivity detector. The gas remaining in the syringe is discarded, 5 ml of pure nitrogen gas is added, and the equilibration process is repeated. A standard curve is made using known CO_2 gas concentrations. The mathematical expressions used to determine the CO_2 concentration in the original sample are presented in McAullife (1971).

APPENDIX II

DOC:ABSORBANCE RELATIONSHIPS

Numerous studies have attempted to correlate organic carbon with absorbance at wavelengths less than 400 nm in the hope of using absorbance as a surrogate for DOC (e.g. Grieve 1985; Edwards and Cresser 1987; Moore 1985, 1987a). It has been found that colored inorganic compounds (e.g. iron oxides) and those of different absorbtivities introduce variation into the relationship.

In this study it was found that stream water shows the best correlations between DOC and absorbance at 330 and 400 nm. Peat water was found to have better correlations when divided into samples taken from different depths probably because of the different chemistry at each depth (Table A1).

Table A1: Correlations between DOC and absorbance at 330 nm (2.5 cm cells) for peat and stream water at Iron Arm and Pelletier fens. Absorbance at 400 nm (10 cm cells) was used for stream water draining the 10 catchments. SEE = standard error of the estimate (mg/L); n = number of samples; p = level of significance. Mean DOC is in mg/L

Location	R^2	SEE	Mean DOC	n	p	Regression
Iron Arm:						
Peat Water 10 cm	0.21	5.3	18.3	66	0.000	DOC = 37.9(ABS) + 6.5
25 cm	0.25	5.0	16.7	64	0.000	DOC = 40.3(ABS) + 4.7
50 cm	0.18	5.8	16.2	25	0.037	DOC = 25.3(ABS) + 8.8
100 cm	0.49	6.6	15.6	19	0.001	DOC = 53.7(ABS) + 1.5
All depths	0.27	5.4	17.1	174	0.000	DOC = 39.8(ABS) + 5.2
Stream water	0.73	1.2	10.3	33	0.000	DOC = 43.8(ABS) + 2.2
Stemflow	0.85	41.3	188.4	19	0.000	DOC = 208.1(ABS) - 70.5
Throughfall	0.36	21.1	47.4	24	0.002	DOC = 77.9(ABS) + 17.5
Pelletier:						
Peat Water surface	0.77	2.7	15.9	44	0.000	DOC = 39.7(ABS) + 4.3
10 cm	0.88	2.9	24.6	12	0.000	DOC = 52.9(ABS) - 0.2
20-40 cm	0.90	5.5	31.1	14	0.000	DOC = 50.1(ABS) + 4.3
50-60 cm	0.22	6.0	20.6	17	0.055	DOC = 17.7(ABS) + 13.4
75 cm	0.60	2.0	10.1	12	0.003	DOC = 17.7(ABS) + 5.7
100-125 cm	0.41	5.0	14.3	12	0.025	DOC = 13.0(ABS) + 9.0
All depths	0.60	6.2	18.4	122	0.000	DOC = 36.0(ABS) + 5.3
Stream water	0.76	1.8	22.2	7	0.011	DOC = 41.9(ABS) + 3.4
Iron Arm and Pelletier stream water combined	0.94	1.3	12.4	40	0.000	DOC = 44.6(ABS) + 2.1
10 catchments (absorbance at 400 nm)	0.90	1.5	5.3	99	0.000	DOC = 19.1(ABS) + 1.5