DISSOLVED ORGANIC CARBON DYNAMICS IN A CUTOVER AND RESTORED PEATLAND

DISSOLVED ORGANIC CARBON DYNAMICS IN A CUTOVER AND RESTORED PEATLAND

By

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ABSTRACT

The effects of restoration on dissolved organic carbon (DOC) dynamics were examined at the Bois-des-Bel peatland. This study included both laboratory measurements of DOC production by different peatland vegetative components and field measurements of DOC dynamics within a recently restored, a cutover and a natural peatland.

Shrub and herbaceous plant material were found to be the most significant producers of DOC in the short term. Moss, peat and straw samples had a high potential to release DOC continuously under warm, moist and aerobic conditions. On a short timescale, all components have the potential to release the three dissolved organic matter (DOM) fractions examined with humic acid (HA) most prominently being produced by shrubs and herbaceous plants and hydrophilic (HPI) and hydrophobic (HPO) fractions by mosses, peat and straw.

Comparison of growing season results over three study years at the restored and cutover site indicated that DOC concentrations increased after restoration while DOC export decreased due to lowered runoff caused by the blockage of drainage ditches. Compared to the natural peatland, both the restored and the cutover site had a more humic DOM character. No difference could be found between the character of DOM released from the restored and cutover sites. The most active layer of DOM production was the top 75 cm where the water table fluctuated during the season. Water storage units such as pools and ditches also play an important role in DOM export from the site.

Spring snowmelt was found to be the most significant DOC export event of the study season in 2001, when export values were significantly larger than those measured during the growing season. Solubility of the different DOM fractions was the main controlling factor on the DOM character seen at the outflows. Storm events contributed significantly to the summer DOC output. DOC dynamics were affected by antecedent moisture conditions and differences emerged between the restored and cutover site during this period.

The results of this study emphasize the importance of managing water table fluctuations and the restoration (reestablishment) of *Sphagnum* species in order to improve the retention of DOM within cutover peatlands. .

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CHAPTER 1: INTRODUCTION

1.0 Introduction

Peat bogs are a common landscape feature in temperate, boreal and sub arctic regions of the world, covering 346 million hectares globally (Gorham, 1991). Above ground net primary production in peatlands is lower than that of other northern ecosystems due to low nutrient concentrations and saturated conditions (Damman and French, 1987; Grigal et al., 1985), however, due to anoxia and acidic conditions, decomposition rates are also low (Clymo, 1984), resulting in an ecosystem favouring organic mater accumulation. The estimates of carbon storage are wide ranging, from about 243-252 (Lappalainen, 1996) to 450 (Gorham, 1991) Gt of carbon as peat, which represents about one third of the world's soil carbon. Thus, peatlands are an important component of the global carbon budget.

One distinguishing characteristic of peatlands is the brown colour of their waters. This colour arises from dissolved organic matter (DOM) leached from the organic material accumulated in peatlands. DOM is made up of several components such as dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). DOC is often used as a measure of DOM since it is easily measured and makes up approximately 50% of DOM (Hem, 1985). DOM can have profound impact on the acidity (Gorham et al., 1986; Kerekes et al., 1986; Urban et al., 1989) and nutrient and pollutant transport (Thurman, 1985; Tipping, 1981; Kalbitz et al., 1997), of natural waters. Several works have dealt with DOM patterns and export from peatland ecosystems (e.g. Moore, 1987; Urban et al., 1989; Waddington and Roulet, 1996; Fraser et al., 2001).

The demand for peat in horticultural and industrial uses as well as demands for increased arable land have severely impacted peatlands across Canada. Drainage and harvesting activities, especially vacuum harvesting, have altered these ecosystems to a point where the natural regeneration of *Sphagnum*, a keystone genus, is no longer possible in the resulting cutover peatland (Campeau and Rochefort, 1996; Johnson et. al., 2000). Increased environmental awareness has brought increased pressure on the peat producing industry to restore these cutover peatland ecosystems, furthering the need to understand the processes that are important in restored peatlands. Restoring the hydrology of a cutover peatland can improve conditions for *Sphagnum* re-growth (Price, 1997).

Few studies have measured DOC concentrations after drainage or harvesting (Bourbonniere, 1989; Lundin and Bergquist, 1990; Gonet and Debska, 1998; Glatzel, 2002). Glatzel et al. (2002), studied the relationship of CO_2 emissions and DOC concentrations in abandoned cutover and restored peatlands, however, no detailed studies were conducted on the effect of harvesting and consequent restoration on DOM dynamics in northern peatlands. The goal of this thesis is to study the effects of changing hydrology and biogeochemistry on DOM in a restored vacuum harvested peatland.

1.1 Peatland ecosystems

Warner and Rubec (1997) define wetlands as lands that are saturated with water long enough to promote wetland or aquatic processes to occur and are characterized by poorly drained soils, hydrophytic vegetation and various kinds of biological activity that is adapted to wet environments. Wetland areas in Canada are estimated to cover 127 million hectares (Zoltai, 1988). Classification of wetlands is based on vegetation, hydrology and water quality. At the most generalized level, wetlands are divided into five categories: bogs, fens, swamps, marshes, and shallow open water wetlands (National Wetlands Working Group, 1987). Water chemistry can also be used for wetland classification. Thus minerotrophic wetlands, such as fens and swamps, are classified as wetlands receiving both atmospheric and telluric nutrient inputs, while ombrotrophic wetlands, such as bogs, receive nutrients from direct precipitation only (Warner and Ruebec, 1997).

In Canada, wetlands that have a peat accumulation of more than 40 cm are classified as peatlands (Zoltai, 1988). Peatlands are an important land feature in Canada since they represent 90% of all wetlands (Tarnocai, 1998). Peat is mainly composed of the remains of several different vegetation types such as mosses, woody litter and herbaceous material (Mitch and Gosselink, 1986).

While under acidic conditions, peat can accumulate up to 30 cm under well drained forest soils, the greatest accumulation of peat occurs in wet fens and bogs, where they commonly reach depths of up to 4.5 m, and in extreme cases 9 m in thickness.

Elaborating on work by Romanov (1968), Ingram (1978) suggested the division of the peat column into two distinct layers, which have differing biochemical and hydrometric properties: the acrotelm and the catotelm. The acrotelm, which can range between 10 to 60 cm thick depending on topography and hydrology, is the aerobic and active layer, where organic material is readily decomposed (Ingram, 1978). Also the water table oscillates, moisture is variable, and oxygen in the acrotelm originates from diffusion of air and rainwater (Hobbs, 1986). It is loosely compacted, poorly decomposed, has high hydraulic conductivity and a high specific yield (Clymo, 1984). The water storage capacity of the acrotelm is high and its ability to shrink and swell with differing moisture conditions minimizes water table fluctuations (Ingram, 1983). Due to this large storage capacity, once this layer is saturated it can yield significant runoff.

The catotelm is the inactive, highly decomposed layer that, in most cases, is permanently saturated, favouring the development of anaerobic conditions (Ingram, 1978). The thickness of this layer usually increases with bog development. Due to the presence of highly decomposed organic material, pore sizes are small increasing the ability of the peat to withhold significantly more water than in the acrotelm (Woo, 2002). Thus, both the hydraulic conductivity and specific yield in this zone are low (Clymo, 1984). Hydraulic conductivity values for this layer can range from 10^{-7} to 10^{-6} ms^{-1} (Ingram, 1983). Therefore, the catotelm has the longest water retention time and runoff is small. Composition of the peat can have a strong effect on the properties of the catotelm (Hobbs, 1986). Vegetation that has deep penetrating roots, and vegetative debris such as woody remains, or the tussocks of *Eriophorum*, may provide preferential flow paths for water, altering the overall hydraulic character of this layer (Hobbs, 1986) and providing a system that can deliver water to the subsurface quickly (Woo and diCenzo, 1988).

Groundwater movement in a peatland is assumed to follow Darcy's law, where flow is determined by both hydraulic gradients and hydraulic conductivity. Since peatlands have low topographic gradient, the direction of flow is not easily determined from this gradient. Also groundwater mounds and depressions do not necessarily correspond to surface contours (Woo, 2002) and flow reversals may occur in wet versus dry conditions (Waddington et al., 1996; Devito et al., 1997). General water movement is more easily determined in peatlands that contain flarks and strings, where the water usually flows perpendicular to these features (Swanson and Grigal, 1988). Surface water movement, however, is most prevalent during the flooding season, especially during spring snowmelt (Woo, 2002).

1.2 Carbon cycling in peatlands

Due to the nature of the acrotelm and the catotelm, peatlands tend to accumulate organic matter as they age, thus creating a sink for atmospheric carbon (Gorham, 1991). Moore et al. (1998) suggest a general conceptual model of the carbon budget in a peatland as follows. The growing active plant layer of the acrotelm takes up CO_2. Plant material decomposes in both the acrotelm and catotelm and CO_2 is released back to the atmosphere. The anaerobic zone produces CH_4 that travels up in the peat profile where it is either oxidized or released into the atmosphere. Leaching of plant material in both layers releases DOM that can be exported into adjacent water bodies. Thus the carbon storage of the peatland is the difference between CO_2 uptake through photosynthesis and the outputs of carbon through respiration, CH_4 release and DOC export.

Clymo et al. (1998) calculated the average carbon accumulation rate in these systems to be 18 g m^{-2} a^{-1}. The estimates for carbon stored in peatlands are wide ranging. Gorham (1991) estimated 455 Gt or about one third of the world's soil carbon storage, equivalent to approximately 60% of the atmospheric carbon pool. However, Lappalinen (1996) estimates the storage to range between 234 and 252 Gt globally. Laine and Vasander (1996) suggest that leaching of DOC can be equal to the accumulation of carbon as peat, which is approximately 5-10% of the annual growing biomass. Waddington and Roulet (1996) found that 80% of the dissolved carbon export is DOC and suggested that the large sources of CH_4 and CO_2 from peatland pools is transported in the dissolved phase. Estimates of DOC export from boreal ecosystems are around 66 Gt of C where most of the DOC originates from peatlands (Molot and Dillon, 1996). DOC, therefore, is an important direct and indirect component of a peatland carbon budget (Fraser et al., 2001).

Because peatlands can potentially store large amounts of carbon, several attempts have been made to estimate the effects of climate change on these ecosystems. Kirschbaum (1995) noted that with increasing temperatures northern peatlands could be severely impacted, since the temperature change can cause great increases in decomposition while production rates will not be affected to the same extent. Moore et al. (1998), however, concluded that the stimulation of plant growth by elevated levels of atmospheric CO_2 will be offset by increased respiration, and the export of CH_4 and DOC will decrease by lowering of the water tables and decrease in runoff. Recently Freeman et al. (2001) observed that DOC concentrations from upland peat systems have increased in the past 10 years. They attribute this change to the stimulation of a temperature sensitive enzyme that is key in organic matter decomposition and DOC release.

1.3 DOM in peatlands

The ecological role of DOM is wide ranging. DOM is involved in nutrient cycling, acidification (Thurman, 1985; Urban, 1986; Marin et al. 1990) and light penetration (Schindler and Curtis, 1997; Frimmel, 1998) in aquatic systems. A comprehensive review of DOC, its origin, and character was compiled by Thurman (1985). More recently Kalbitz (2000) reviewed studies dealing with DOC release from soils. The origins of aquatic and soil humic matter share some commonalities. Humic matter in soils originates from the detritus of plants, while those in aquatic systems originate from the extraction of soils by water and the production of aquatic vegetation (Thurman, 1985). Since the treatments for the characterization of humic matter of both origins is similar, a comparison to results of soil studies is appropriate (Bourbonniere, 1989).

DOC concentrations of water found in natural peatlands range between 20 to 30 mg l^{-1} (Scott 1998; Moore et al., 2000), with a distinct seasonality observed with highest concentrations measured during the summer months and lowest in the autumn and winter (Moore, 1987; Bourbonniere, 1989; Waddington and Roulet, 1996; Moore et al, 2000). DOC exported from northern peatlands varies between 5 to 20 mg C m^{-2} a^{-1} (Urban, 1986; Moore et al., 2000). This makes it an important component of the carbon balance of peatlands (Moore et al., 1998). The internal distribution of DOC within peatlands has also been studied (Moore, 1987; Waddington and Roulet, 1996; Moore et al, 2000). Moore (1987) concluded that the hydrology of a bog has the most significant effect on DOC distribution within the system. This was confirmed by Waddington and Roulet (1996) who reported on flow reversals in a Swedish bog, which was accompanied by an inversion in the DOC concentration profile from highest concentration at the surface during dry periods to lowest concentrations at the surface during wet periods.

Some attempts to understand the origin of DOC in peatlands using carbon isotope studies have demonstrated that DOC at depth was much younger than peat at the same depth (Charman et al. 1999). Chasar et al. (2000) concluded that younger DOC produced in the surface layers can move downward where it can make up to 20-50% of the DOC. Because DOC concentrations are lower at depth, small amounts of DOC moving downward could have a significant effect on DOC dynamics at depth (Chasar et al., 2000). This study further emphasizes the importance of hydrology on DOC distribution.

Studies on the controls of DOC release, mainly focus on soils. Since many of these studies involve sampling of fresh and decomposed organic materials their conclusions can be extended to peatlands (e.g., Zech et al. 1994; Christ and David, 1996; Moore and Dalva, 2001). The general consensus of these studies is that as water passed through organic layers its DOC concentration increased. Strong temporal and spatial variations were often found in such leaching studies. Kalbitz et al. (2000) reviewed the different aspects of DOC release and provided a table summarizing the effects of different controls on DOC release.

Tipping et al. (1999) found that the amount of DOC that can be leached from organic materials is directly proportional to the amount of organic material on the forest floor. Kruiters (1993) concluded that the amount of DOC leached is dependent on the litter quality, and therefore on the dominant vegetation type at the site. Hongve (1999) noted that in addition to tree and shrub litter, grasses, herbs and lichens might also be important in the DOM quantity and quality of the runoff from forested sites. The microbial community can also have a strong effect on DOM release. Based on alkaline CuO degradation, Guggenberger and Zech (1994) found that much of the solubilized plant material was strongly altered by microbial oxidation. They also found a high portion of monomeric sugars in these solutions that are characteristic of microbial cellular components, suggesting that the microbes themselves contribute to the DOC leachates.

Climatic conditions, such as the frequency of wetting, temperature and oxidative state, were also examined in several studies. The trends of temperature effects are not clear. DOM concentrations in leachates were found to increase with temperature (Kramer et al., 1990; Leichty et. al. 1995), however, decomposition can also increase (Kramer et al., 1990). Several researchers have noted that highest DOC concentrations in pore-water occur during the summer months in natural peatlands (Moore, 1987; Bourbonniere, 1989; Guggenberger and Zech; 1994, Tipping et al. 1999; Fraser et al. 2001). Laboratory studies by Cronan (1990) and Moore and Dalva (2001), on the other hand, observed an increase of DOM in plant and soil leachates at lower temperatures versus higher ones, suggesting that the mechanisms of DOM and CO_2 release can be competitive and switched on to differing degrees at different temperatures.

Soil moisture is the most significant factor that affects DOC release. Laboratory and field studies have confirmed that DOC concentrations increase following rewetting after dry periods (e.g., Kalbitz and Knapper, 1997; Tipping et al. 1999; Zsolnay et al., 1999). This change is attributed to the increase in microbial metabolites and the disruption and lysis of cells during the dry period (Christ and David, 1994, 1996b). Anaerobic conditions caused by saturation can also cause an increase in DOM release. Mulholland et al. (1990) found that organic matter decomposition is slower under anaerobic conditions, but the release of soluble intermediate metabolites is higher. Contact time between organic material and water is also important, with longer contact times resulting in higher DOC concentrations (Cronan, 1990).

1.4 DOM character

The composition of DOM is highly variable. In the past, studies of DOM were limited by the availability of appropriate and efficient techniques to isolate and concentrate similar groups of compounds. Leenheer and Huffman (1976) developed a fractionation technique that split DOM into hydrophilic and hydrophobic components. These fractions depend on operational definitions of hydrophobicity and hydrophilicity, namely the ability of the compounds to adsorb onto amberlite XAD-8 resin. The point at which the hydrophobic-hydrophilic break occurs is arbitrary and depends on both polarity of the solute and the ratio of the resin quantity to the volume of water passed thorough it (Leenheer, 1981). Therefore, for these purposes hydrophobic solutes are defined as those solutes that are greater than 50% retained on XAD-8 resin at a given ratio of resin to water volume, and hydrophilic solutes are those that are greater than 50% eluted at the same ratio of resin to eluent (Leenheer, 1981). Leenheer and Huffman (1976) fractionated the samples further into acids, bases and neutrals, but these go beyond the scope of this study and will not be discussed further. A modification of the fractionation technique for the high DOC water characteristic of peatlands involves the isolation of humic acid (HA) prior to application of the sample on the XAD-8 resin column (Bourbonniere, 1989). Bourbonniere and van Halderen (1989) acidified water samples before fractionation and showed that HA, the most hydrophobic component, can be precipitated over a range of pH values. Thus, isolation of HA early in the analytical scheme as a separate fraction allows for three fractions to be isolated in a series of decreasing hydrophobicity: HA > hydrophobics > hydrophilics. Some of the common characteristics of these fractions isolated by resin have been established (Bourbonniere, 1989; Guggenberger et al., 1994) using a combination of analytical techniques and these are described below.

HA is similarly defined by both soil and aquatic scientists as the fraction of the DOM that is insoluble at pH 1 (Thurman, 1985), however Bourbonniere and van Halderen (1989) found that HA can be precipitated at pH up to 4.6. The formation of humic matter is thought to involve both processes of polycondensation of small molecules as well as the stepwise biological degradation of natural biopolymers (Bourbonniere, 1979). Bourbonniere (1989) found HA to be prominent in porewaters of deeper bog layers as well as samples where the processes of oxidative polycondensation can readily occur.

Bourbonniere (1989) found that the hydrophobic (HPO) fraction is a large component of DOM in water samples collected from wetlands and river systems. He found that its origins are mainly terrestrial and HPO is responsible for most of the colour of DOM. Based on observations Bourbonniere (1989) concluded that the HPO fraction is more of an intermediate in humic matter formation that can be degraded to smaller components or smaller components can form HPO through polycondensation. The description of the HPO fraction is made somewhat difficult by the different fractionation methods used by researchers. In studies such as those by Guggenberger et al. (1994), the HA fraction was not isolated, but was included into the HPO fraction, which then was subjected to several chemical and physical analyses. Their findings indicate that the HPO fraction contains biodegraded plant and microbial polysaccharides and highly altered lignin degradation products. These highly altered lignin products can be considered to represent the HA fraction described above. The HPO fraction also contains compounds that are highly apolar, and rich in moeties that closely resemble plant sources (Guggenberger et al., 1994). Bourbonniere (1989) concludes that some of these compounds are highly unreactive and therefore can accumulate in integrated systems such as limnic sediments.

Bourbonniere (1989), studying natural systems, found strong seasonal effects on the hydrophilic (HPI) component of DOM, with higher concentrations observed in the summer months compared to winter and spring. The HPI fraction was less coloured and contained soluble acidic components that were related to decomposition of biomass. Thus, he concluded that microbial activity has a strong influence on this component. Guggenberger et al. (1994) further confirmed this finding and added that this fraction contains both plant derived compounds as well as those directly produced by microbes. They found that the acidic portion if this fraction was more oxidatively altered than the HPO fraction and concluded that these are intermediates in the HPO degradation. The neutral part of the HPI fraction was found to be diagenetically close to its origins and contains labile compounds (Bourbonniere, 1989). Guggenberger et al. (1994) confirmed this and found that these contain free oligo- and polysaccharides that are dissolved during enzymatic breakdown of plant-derived carbohydrates and of microbial metabolites. These products are a good carbon source for microbes (Bourbonniere, 1989); therefore they do not persist in the environment for long periods.

Most of the studies that dealt with DOM character have focused on forest soils and few have dealt with wetland environments. Bourbonniere (1989) looked at DOM character in different aquatic systems including bog and bog drainage samples. He noted character differences in both the seasonality and the sources of the DOM, however no study has looked at the effects of harvesting and restoration on the different fractions of DOM.

1.5 Peatland harvesting and restoration

Peatland harvesting has a long tradition. Peat was widely used as fuel in England and several northern European countries. In countries such as Finland, Sweden and Ireland peat combustion makes up to 12% of the energy produced (Schilstra, 2001). In Canada, most of the peat extracted is used for horticultural purposes, totaling 750 metric tons of peat annually or two thirds of the peat production in North America (Keys, 1992). The major peat producing areas of Canada are Quebec and New Brunswick, where it is estimated that more than 70% of peatlands have been impacted by harvesting activities (Lavoie and Rochefort, 1996).

At present the most common method of peat removal for horticultural purposes is vacuum harvesting, a procedure whereby peatlands are drained and successive layers of peat are removed, thus exposing deeper peat layers formed during earlier parts of succession (Wind-Mulder et al., 1996). Vacuum harvesting affects large areas and causes the removal of the viable seed bank (Salonen, 1987; Jonsson-Ninniss et al., 1990). After harvesting activities stop, many sites remain devoid of vegetation for up to 10 years. Other sites are colonized by ericaceous shrubs and cotton grass (*Eriophorum* sp.) without any significant recolonization by *Sphagnum* mosses, the key component in natural peatlands (Campeau and Rochefort, 1996).

Harvesting, and especially vacuum harvesting, affects the hydrology and, in turn, the biogeochemistry of peatlands (Waddington and Rotenberg, 2000; Van

Seters and Price, 2000). Drainage and vegetation removal alter the mechanisms that control evaporation and runoff thus altering water table fluctuations (Heatwaite, 1995; Van Seters and Price, 2000). The catotelm that is exposed has low hydraulic conductivity and contains highly decomposed peat. Increased aeration of this layer causes peat to oxidize quickly which results in high bulk density and lower specific yield (Waddington and Price, 2000). This drop in specific yield causes evaporative losses to have significant effects on water table causing greater increase in water table fluctuation. The environment that results inhibits the re-colonization of *Sphagnum sp*. (Campeau and Rochefort, 1996).

In recent years the appreciation of natural wetland environments has increased and created a growing pressure on the peat industry to adjust their activities in a way that is more environmentally conscious. Natural regeneration of harvested peatlands has only been observed in peatlands where the block cutting method was used for peat extraction and drainage ditches were blocked after mining was abandoned (Lavoie and Rochefort, 1996; Robert et al., 1999), whereas vacuum extracted peatlands re-vegetate at a much slower pace and often stay bare for up to 10 years post harvest (Lavoie and Rochefort, 1996; Campeau and Rochefort, 1996; Bérubé and Lavoie, 2000), indicating a need for active restoration measures.

The blockage of drainage ditches can elevate the water table improving the water balance of a vacuum harvested site. However, water table fluctuations, retention and soil water tension do not resemble pre-drainage conditions (Price, 1998). *Sphagnum* may still be absent from the site since short periods of high water tension can adversely affect its growth (Whitehead, 1999). The addition of open water ditches can improve water retention and water table stability (Schlotzhauer and Price, 1999). Rewetting can also improve the chemistry of the site making it similar to a natural peatland (Lundin, 1998). The addition of a protective cover, such as straw mulch, can improve the microclimate of the surface, increasing humidity and therefore improving soil moisture and tension (Price et al., 1998). *Sphagnum* species can be introduced to the surface by spreading *Sphagnum* fragments (diasporas) (Ferland and Rochefort, 1996) and its growth can be increased by phosphate fertilization (Campeau and Rochefort, 1996).

The changes that occur to the hydrologic and vegetative character of peatlands after drainage and restoration have been studied extensively as demonstrated above, however, few studies have dealt with the effects of harvesting and restoration on the carbon balance. Most of the studies that examined harvested and restored pletland have CO_2 as their main focus. The changes that occur during harvesting cause a transition from a carbon accumulating system to one that is a net source of CO_2 (Price and Waddington, 2000). Waddington and Warner (2001) found that CO_2 emissions from cutover sites were approximately 2.5 times larger than those measured at a natural site. Peat oxidation rates were found to be significantly higher even after two decades of abandonment suggesting that cutover sites can remain persistent CO_2 sources for extended periods (Waddington and McNeil, 2002).

Studies of the effects of restoration on carbon storage are also few. The effects of restoration on carbon dynamics are not clear. Waddington and Warner (2001), studying a peatland in the Lac St. Jean region, Quebec, found that following restoration the affected peatland was still a persistent source of CO_2 but that these emissions were lower than those from an abandoned cutover site. Petrone et al. (2001) observed a different pattern in CO_2 emissions and found that the CO_2 flux increased by 25% after restoration compared to the adjacent cutover site. None of these works have looked at the effect of restoration on DOM.

1.6 Effects of harvesting and restoration on DOC

Although there are several works that deal with gaseous carbon emissions from restored peatlands (Tuittila et al., 1999; Waddington and Price, 2000; Waddington and Warner, 2001; Petrone et al., 2001; Glatzel et al., 2002), to my knowledge there have been only two works that examined DOC in restored peatlands. Fenner et al. (2001) studied DOC release following the rewetting of a drained peatland and found persistently higher DOC concentrations compared to the drained peatland. Glatzel et al. (2002) examined the concentration of DOC in pore-water and its effects on CO_2 efflux in natural cutover and restored peatlands, and found a good correlation between humification index and CO_2 release. None of these studies have examined the seasonality, dynamics or release mechanisms or the effects of hydrology on DOM.

1.7 Thesis objectives

This review of the literature has shown the following: (1) peatlands are unique ecosystems that can store large amounts of carbon, (2) DOM is an important component of the peatland carbon budget, potentially contributing to high carbon exports, (3) the mechanisms of DOC release are better understood in forest soils than from peatlands, (4) the potential for DOM to affect downstream ecosystems is high, and (5) the drainage and harvesting of peatlands has greatly altered these ecosystems, which presents a need to restore these wetlands. However there is a lack of understanding of how these practices will affect DOM character and dynamics. Thus the objectives of this thesis are to:

a. Evaluate the contribution that different vegetative components, within a cutover and restored peatland, make to its DOM content,
b. Compare changes in the quantity and quality of DOM in a natural, cutover, and recently restored peatland,
c. Evaluate the DOC released during different flow conditions at the cutover and restored peatlands,
d. Investigate internal pathways of DOC release.

This research will provide valuable insight into the restoration and management of vacuum harvested peatlands, by examining DOC dynamics within the site. The thesis is presented in seven chapters. Chapters 2 and 3 provide an introduction to the study site and research methods. Chapter 4 focuses on the laboratory study examining DOC contribution from different vegetative components of the peatland. Chapter 5 examines DOC characteristics during baseflow conditions. Chapter 6 focuses on DOC characteristics during storm flow and snow melt. Chapter 7 provides a brief summary of the main findings of this research.

CHAPTER 2: STUDY AREA

2.1 Bois-des-Bel peatland :

The Bois-des-Bel peatland is a 200 ha treed bog, located 14 km east of Rivière-du-Loup, Québec (47° 58'N, 69° 25'W) in the Bas-Saint-Laurent region (Figure 2.1). The mean annual temperature is 3°C and the mean January and July temperatures are –12 and 18 °C respectively (Environment Canada, 1993). An 11.5 ha portion of the bog was drained in 1972, separated into 11 approximately 30 m x 300 m peat fields, and harvested from 1973 to 1980, using the vacuum extraction method.

Restoration measures described by Campeau (2000) began in the fall of 1999, separating the area into two catchments, a 7.2 ha restored section (peat fields 1 to 8) and a 1.8 ha cutover section (peat fields 9 to 11) (Figure 2.1). Briefly, the restoration involved the blockage of drainage ditches using peat and vegetation from the site. *Sphagnum* diasporas were spread on the surface to reintroduce moss on the site. Straw mulch was added to the surface to optimize the humidity of the surface layers. Peat berms were also introduced on the restored site to increase water retention during high flow periods. These berms divided the restored area into four zones (Figure 2.1). Zones 2, 3 and 4 were restored in the fall of 1999 and zones 1 and 7, which is located between the southern most berm and the main drainage ditch, were restored in 2000.

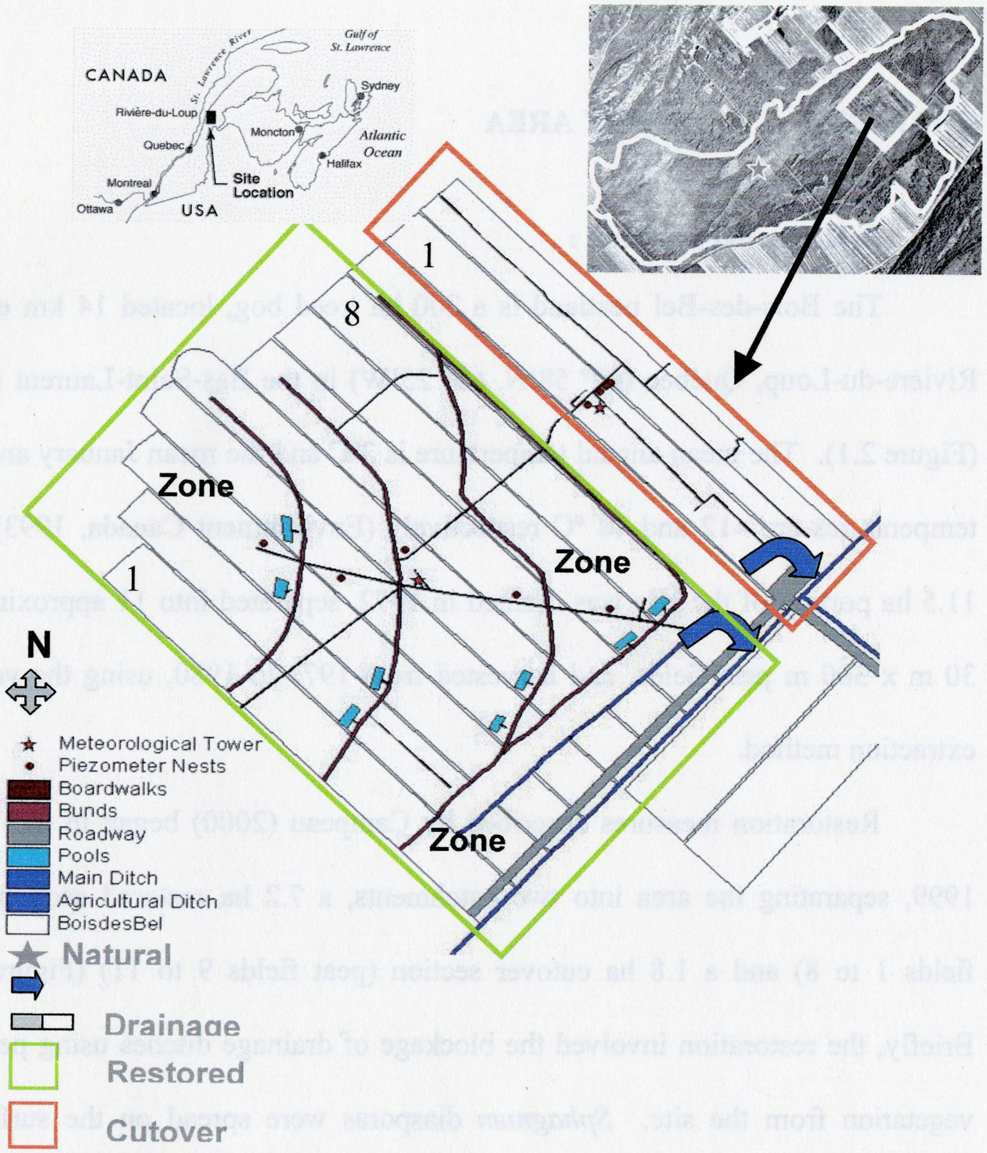


Figure 2.1 The location of the Bois-des-Bel peatland with an enlargement of the vacuum harvested site. Fields 1 to 8 were restored in 1999 and fields 10 to 11 were untouched (cutover site). The map also shows the location of the peat berms (bunds), artificial ponds, piezometers and wells where water sampling was conducted. Outflow was measured at the south end of the restored and cutover site (blue arrows). Sampling location at the natural peatland was 2 km west of the harvested site (gray star).

A collector ditch was also created at the south end of the restored and the cutover sections in 1999 to collect the runoff from the respective catchments.

Two shallow pools (max depth 1.5 m, length 13 m, width 5 m) were also created in each of zones 1 to 4, to attract aquatic and amphibian species (Figure 2.1). Vegetation from a natural peatland pond was introduced into one of the pools in each zone in the summer of 2000.

The dominant vegetation at the site before restoration was as follows: birch (*Betula populifolia*), tamarack (*Larix laricinia*), ericaceous shrubs (*Ledum groenlandicum* and *Kalmia angustifolia*), *cattail* (*Typha latifolia*), cotton grass (*Eriophorum vaginatum*), mosses (mainly *Polytricum strictum*, but some *Sphagnum* spp as well). During restoration all vegetation from the restored site was cut down and the surface was milled. The cut vegetation was used as fill for the drainage ditches.

Canadian reed grass (*Calamagrostis canadensis*), and several agricultural weeds appeared on the restored site by 2001. The area covered by mosses and other wetland vegetation at the restored site increased to 23% and 10% respectively (Campeau, unpublished data). The peat depth at the two sites ranged from 0.5 to 1.5 m.

The natural site was selected within the 200 ha bog (located 2 km west of the restored and cutover sites) (Figure 2.1). This site does not possess any pools or surface flow. Dominant species here are: *Picea marina, Larix laricinia, Sphagnum spp., Ledum groenlandicum, Chameadaphne caluculata, Kalmia* *angustifolia, and Vaccinium angustifolium* (Pellerin & Lavoie, 2000). Peat depth ranges from 2.1 to 2.4 m.

CHAPTER 3: METHODS

3.1 Lab experiments

To examine the ability of peatland vegetation and components to produce DOC a lab experiment was conducted. Different vegetation samples, peat and straw were collected from the restored, cutover and natural site and incubated under different temperature and oxidative conditions for four weeks. Both the quality and the quantity of DOC produced were assessed. A detailed description of the methodology follows.

3.1.1 Peatland components sampling

Leaves, branches or stems were collected on September 7th, 2001 from the dominant vegetation at the restored and cutover sites. The vegetation collected included the following: shrubs (birch and *Ericaceous* shrubs), herbaceous plants (cattail, cotton grass, and tall grass). Peat samples were collected from the surface, 50 cm below the surface at the cutover site and 80 cm below the surface at the restored site. Straw mulch that was used in restoration was also collected from the restored site. *Sphagnum* moss was collected from the natural site and *Polytricum sp.* was collected from the restored site. All vegetation, peat and straw samples were placed in plastic bags and stored at 4 °C until analysis.

3.1.2 DOC extraction method

In the lab, duplicate samples of vegetation, peat and straw were placed into clear 250 mL glass containers. A third sample of each was placed into 1 L containers so there would be the required volume of leachate for DOM fractionation. Vegetation and peat samples were carefully rinsed to eliminate readily soluble DOM. Distilled water was added to each extraction bottle, 175 mL and 800 mL respectively to the 250 mL and 1 L containers. An initial sample was taken immediately and the containers were loosely capped and stored in the dark. One glass jar contained distilled water only and served as a blank. Samples were incubated under aerobic conditions at 7 and 22 °C for 25 days and the peat samples from the 50 and 80 cm depth were also incubated under anaerobic conditions. For this treatment the silicone septum of the lids were pierced and fitted with Tygon® tubing and a three way valve for sampling. In the anaerobic treatments, the jars were flushed with nitrogen gas and sealed following peat and water addition..

3.1.3 Sampling

Samples of the extracts were withdrawn twice a week and analyzed for DOC. Ten mL of sample was withdrawn for this analysis, using a 20 mL plastic syringe and filtered using 0.7 μm Whatman® GF/F filters. 60 mL samples were withdrawn from the 1 L containers on a weekly basis, filtered through 0.7 μm Whatman® GF/F filters, pH measured and stored in covered plastic cups at 4°C until fractionation, however only samples taken after 21 days of incubation were fractionated completely. Due to the different DOC release rates found for shrub leachates, samples from Day 8 were also fractionated to compare the effect of incubation length on DOM character. The contribution of DOC by the storage cups on blank samples was found to be insignificant.

3.2 Field experiment

The focus of the field experiment was to examine DOC dynamics in a restored, cutover and natural peatland. For this purpose water chemistry and hydrometric data were collected during the growing season for three successive years: 1999 to 2001. In the summer of 1999, before restoration measures were applied, the study focused mainly on the quantity of DOC exported from the site. In 2000, the year after restoration, both quantity and quality of DOC was assessed. In 2001 more focus was paid to the internal distribution of DOC and high flow conditions. The natural site was also studied in 2001 to provide a basis for comparison.

3.2.1 Hydrology

Restored and cutover catchment discharge was measured continuously at the outflow of the respective collector ditches (Figure 2.1) from early May to mid October. In 1999, measurements started on June 25 when the collector ditches were constructed. Discharge was measured by developing a stage-discharge rating curve, using instantaneous measurements of the time that it took to fill a known volume. Stage was recorded continuously at the outflows in 1999 and 2000 using a potentiometric water level recorder. During the 2001 field season, stage was recorded using a Remote Data System (RDS) water table recorder that was placed either in a bucket below the outflow or behind a V-notch weir. Volumetric moisture content, precipitation and below ground thermal regime were measured continuously at the two meteorological stations located in the restored and cutover site respectively. Volumetric moisture content was measured using multiple level TDR measurements. Precipitation was measured using both a tipping bucket and a manual rain gauge. The belowground thermal regime of the peat was monitored using thermocouple arrays at 0, 2, 5, 10, 25, 50 and 74 cm below the current peatland surface at the respective sites.

A transect of piezometers in the restored site along the peatland hydraulic gradient was used to measure flow characteristic within the peat matrix (Figure 2.1). The piezometers were 5 cm in outside diameter with a wall thickness of 0.7 cm and had 15 cm slotted opening at the bottom. Piezometers were installed so that the mid section of the slotted ends sampled water at 30, 50, 70, 100 and 150 cm depths. In 2001 slotted groundwater wells (150 cm) were also installed around ponds 1P2, 2P2, 3P1 and 4P1 (Figure 2.1). Wells were located 5 m from the edge of the ponds on the north, south, east and west sides. A piezometer nest with depths 25, 50, 75, 100 and 125 cm was installed on the north side of pond 3P1. Ditches in both the restored and cutover site had groundwater wells installed to a depth of 100 cm. A transect of piezometers were installed across field 10 in the cutover site near the meteorological station (Figure 2.1). The depth of these piezometers was 50, 75, 100, 120 and 150 cm at the meteorology station and 75, 100, 125 and 150 cm at the other locations, while in the ditch between field 10 and 11, they were at depths of 50 and 100 cm. Water table depth and hydraulic head measurements were collected weekly and more often during storm events at both the restored and cutover sites.

The natural site was instrumented in 2001 with a slotted well (150 cm long), a piezometer nest with depths of 25, 50, 75, 100 and 125 cm and a RDS recorder. Groundwater wells were located 20 m north, east, west and south of the piezometer nest (Figure 2.1). Water table depth and hydraulic head were measured every two weeks at this site, while the RDS recorder measured water table continuously.

3.2.2 General water chemistry analysis

A portable Oakton pH/mV /temp (300 Series) meter (precision +/- 0.01) was used to measure the pH of water at various locations within the peatland. The probe was calibrated with standard solutions at pH 10, 7, and 4. A YSI Model 85 portable Oxygen, Conductivity, Salinity and Temperature probe (precision +/- 2% O2, +/- 0.5% cond, +/- 0.1 ppt salinity, +/-0.1 °C) was used to measure the above parameters.

3.2.3 Water sampling

Water samples from the outflow were collected from May to October, three times a week or less depending on flow conditions. In 2001, in addition to weekly sampling, the snowmelt period (March to May) and summer storm events were also included, which were sampled more frequently depending on flow conditions. Ponds and ditches were sampled once a week depending on the presence of water in these depressions. The piezometer nests were sampled twice during 2001, first on May 25th and second on September 6. Water samples from the natural site were collected two times a month during the growing period.

Water was collected in 250mL Nalgene® brand containers and stored at 4° C until analysis. Samples were filtered using 0.7 μm Whatman® GF/F filters. Sub samples for total DOC were stored in 7 mL glass vials and were shipped in coolers for analysis at the National Water Research Institute in Burlington. The remainder of the sample was stored in plastic cups at 4°C until further analysis.

3.3 DOC chemistry

3.3.1 DOC analysis

DOC analysis was accomplished using high temperature catalytic oxidation on a Dohrmann DC-190 Total Carbon Analyzer (in 1999 and 2000) or a Shimadzu TOC 5000A instrument (in 2001). Cross checking samples between instruments indicated that the results obtained were consistent with each other. Both instruments quantify the CO_2 released by combustion using a non-dispersive infrared detector calibrated daily with potassium hydrogen phthalate. Filtered water samples were acidified with 20% phosphoric acid and purged for five minutes with the instrument's carrier gas, zero air or oxygen, to remove dissolved inorganic carbon prior to injection for DOC determination (also called NPOC for non-purgeable organic carbon). All determinations were corrected for system blank, estimated daily by regressing the results of low concentration standards (0, 2, 5 mg C L^{-1}) analyzed as samples, against their "true" value. The system blank corrects for a combination of blank sources internal to the instruments and also residual carbon in the reagent water used to make the standards. All the dissolved fractions described below were analyzed in a similar manner.

3.3.2 DOC fractionation

Filtered extract-samples were acidified to pH of 2 using concentrated phosphoric acid (H_3PO_4) and stored at 4°C. These extracts were filtered no sooner than 24 hours after acidification using 0.7 µm GF/F filters. This separated humic acid (HA), which remained on the filter, from fulvic acid (FA), which stayed in solution (Bourbonniere and van Halderen, 1989). A sub-sample of FA was taken and analyzed for DOC concentration. HA-C content was calculated by subtracting the un-acidified extract DOC content from that of the FA ([HA] = [DOC] - [FA]). FA was further fractioned into hydrophobic (HPO) and hydrophilic (HPI) fractions using XAD-8 resin (Thurman and Malcolm, 1979; Leenheer 1981). A schematic of the fractionation is presented in Figure 3.1.

The methodology, however, was needed to be modified since DOC concentrations were in a high range and coloured substances broke through the resin indicating that HPO may be lost, thus, samples were diluted 10 times with distilled water. The influence of this dilution was found to be negligible. The resin volume was also reduced to 2 mL, which was used to fractionate a 132 mL sample. Thus the hydrophilic/hydrophobic break ($k'_{0.5r}$) was equal to 50 (Leenheer, 1981). This reduction was possible because the HPO fraction was not analyzed further therefore there was no need for larger quantities to be isolated. A 10 mL burette equipped with a Teflon® valve was used to contain the column and a small plug of glass wool helped to keep the resin in place. A 250 mL separatory funnel was attached to the burette using silicone tubing and was used to contain the sample. Flow-rate through the column was controlled by adjusting the valve of the burette and was set to be drop-wise.

The HPI fraction passed through the column and was analyzed for DOC concentration using the method described above. The HPO fraction adsorbed to the column and its DOC content was calculated by difference ([HPO] = [FA] - [HPI]).

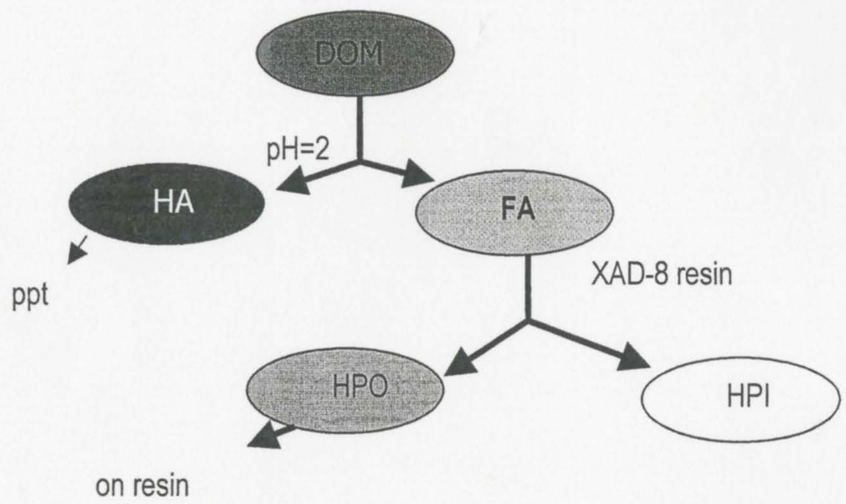


Figure 3.1 Schematic for DOM fractionation.

CHAPTER 4: DISSOLVED ORGANIC CARBON RELEASE FROM PEAT AND PEATLAND VEGETATION

4.1 Lab experiment results

In this experiment different vegetative components were evaluated in terms of their ability to release DOC. These results will help in estimating the origin of the DOM seen at the outflows of the restored and cutover sites in the Bois-des-Bel peatland. In the subsequent description production will refer to the total amount of DOC produced during leaching, while release rate refers to the overall daily DOC release rate during the experiment calculated from a linear regression of DOC quantity changes over time. Paired t-tests were used to compare the effects of different treatments and one-way ANOVA was used to statistically compare the different vegetation groupings.

4.1.1 DOC release

Samples released DOC at a consistent rate throughout the experiment (Figure 4.1 a. & b.), with the exception of shrub samples, which initially released a large quantity of DOC followed by a steadilly lessening amount (Figure 4.1 c.). DOC release rates were calculated by determining the slope of the best-fit line for a plot of DOC quantity and time. Overall, the amount of DOC produced during

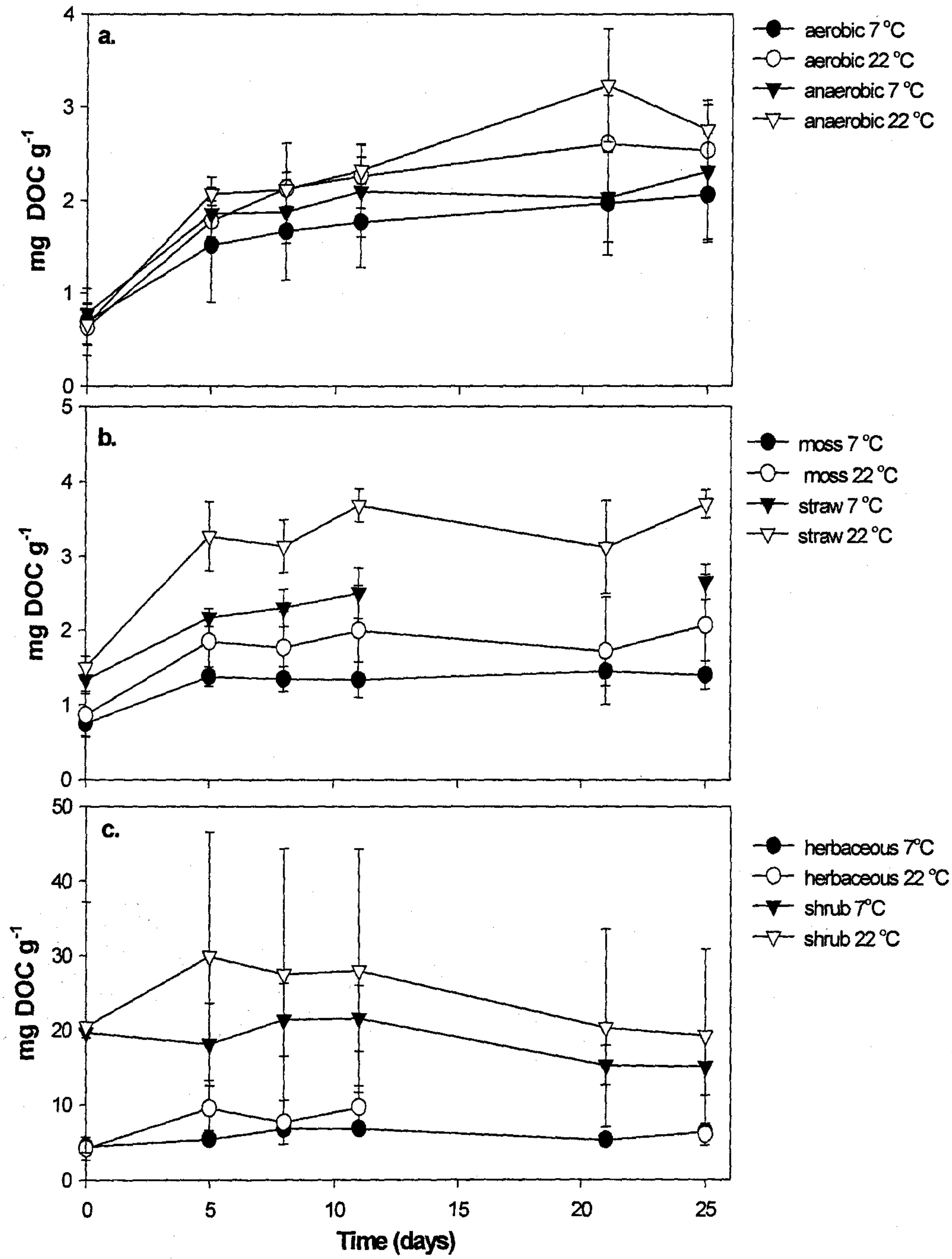


Figure 4.1 DOC release from different vegetative components at 7and 22 °C.
a. Peat, aerobic and anaerobic conditions. b. moss and straw.
c.herbaceous and shrubs (note scale difference)

the incubations ranged between 1.40 and 19.20 mg DOC g^{-1}, where moss samples produced the least and shrub samples the most DOC (Table 4.1). Minimum DOC release rate was measured at 0.018 mg DOC g^{-1} d^{-1} for mosses and maximum at 0.094 mg DOC g^{-1} d^{-1} for peat samples under anaerobic conditions (Table 4.1). DOC quantity was found to decrease in leachates from shrub samples during the incubation period and this was indicated by negative rates, suggesting that DOC produced at the beginning of the experiment was being degraded (Table 4.1 and Figure 4.1 c.).

Many values reported in Table 4.1 are associated with large standard deviations, for example shrub and herbaceous samples. Although values were adjusted for different sample weights and water volumes, the deviation within triplicate samples was still large. A possible explanation for this deviation is grouping of different plant species together. As explained in Chapter 3, the grouping categories were based on whether the samples came from shrubs, herbaceous/grass species, mosses, or peat. Thus, possible inhomogeneity among the jars may have affected relative amounts of DOC released. Differences among the vegetation groupings for DOC release rates emerged even with the high variability in some samples and these differences will be discussed further later in this chapter.

Shrub materials by far produced the darkest water of all samples, a reflection of their high lignin content. Also they released volatile organic compounds (VOC), which were strongly and pleasantly aromatic, mainly

Table 4.1 Average amount of DOC production at the end of 25 days and DOC release rate during the experiment.

Ref #	Samples	DOC produced (mg DOC g^{-1})		DOC release rate (mg DOC g^{-1} d^{-1})	
		7 °C	22 °C	7 °C	22 °C
1	Moss	1.40 ± 0.19	2.07 ± 0.68	0.018 ± 0.01	0.035 ± 0.018
2	Straw	2.65 ± 0.24	3.17 ± 0.19	0.035 ± 0.006	0.055 ± 0.010
3	Peat cutover, 50 cm , aerobic	1.93 ± 0.36	2.51 ± 0.22	0.040 ± 0.005	0.060 ± 0.030
4	Peat cutover, 50cm, anaerobic	1.77 ± 0.15	2.73 ± 0.30	0.025 ± 0.004	0.063 ± 0.005
5	Peat Cutover, surface	2.74 ± 1.72	1.98 ± 0.29	0.047 ± 0.038	0.034 ± 0.002
6	Peat Restored, 80cm aerobic	1.98 ± 0.33	3.17 ± 0.16	0.056 ± 0.01	0.090 ± 0.009
7	Peat Restored, 80cm, anaerobic	2.85 ± 1.73	2.78 ± 0.78	0.061 ± 0.028	0.094 ± 0.039
8	Peat Restored, surface	1.60 ± 0.30	2.45±0.38	0.035 ± 0.005	0.059 ± 0.010
9	Shrub*	na	na	0.084 ± 1.37	1.90 ± 0.07
10	Shrub	15.12 ± 3.83	19.20 ± 11.60	-0.193 ± 0.090	-0.243 ± 0.238
11	Herbaceous	6.42 ± 0.16	6.05 ± 1.46	0.039 ± 0.069	0.032 ± 0.094

* shrub samples after 8 days of incubation. The DOC release rate is the rate measured during the first 5 days of incubation.

characteristic of Labrador tea (*Ledum groenlandicum*). These samples produced the highest initial DOC release upon water addition (Figure 4.1 c.) and the highest amount of DOC at the end of the experiment (15.12 to 19.20 mg DOC g^{-1}) (Table 4.1). Initial release rates were high for the first five days of the incubation (0.084 to 1.90 mg DOC g^{-1} d^{-1}, Figure 4.1 c. and Table 4.1), however during the later part of the experiment negative rates ranging between -0.193 to -0.243 mg DOC g^{-1} d^{-1} were observed (Table 4.1). Incubation temperature did not have a significant effect on the overall release of DOC from these samples.

Vegetation samples from herbaceous and grass plants behaved much the same as the shrub samples (Figure 4.1 c.). The water in these samples was also highly colored, however the odour of the VOC released was not as pleasant as from the shrubs. DOC production was significantly lower than from shrubs and it ranged between 6.05 and 6.42 mg DOC g^{-1}. The initial release rate was not as high as with shrub samples and DOC rates could be calculated by integrating over the entire 25 days of sampling (Figure 4.1 c.). Overall these samples released DOC at a slow rate and in some of the triplicate samples a slight decrease in DOC was observed over time. Release rates ranged between 0.032 and 0.039 mg DOC $g^{-1}d^{-1}$ (Table 4.1). Incubation temperature did not have a significant effect on these samples.

Straw, moss and peat behaved similarly to each other and no significant ($p<0.05$) differences existed between among their respective production values and release rates. The potential for straw to produce DOC was found to be 2.65

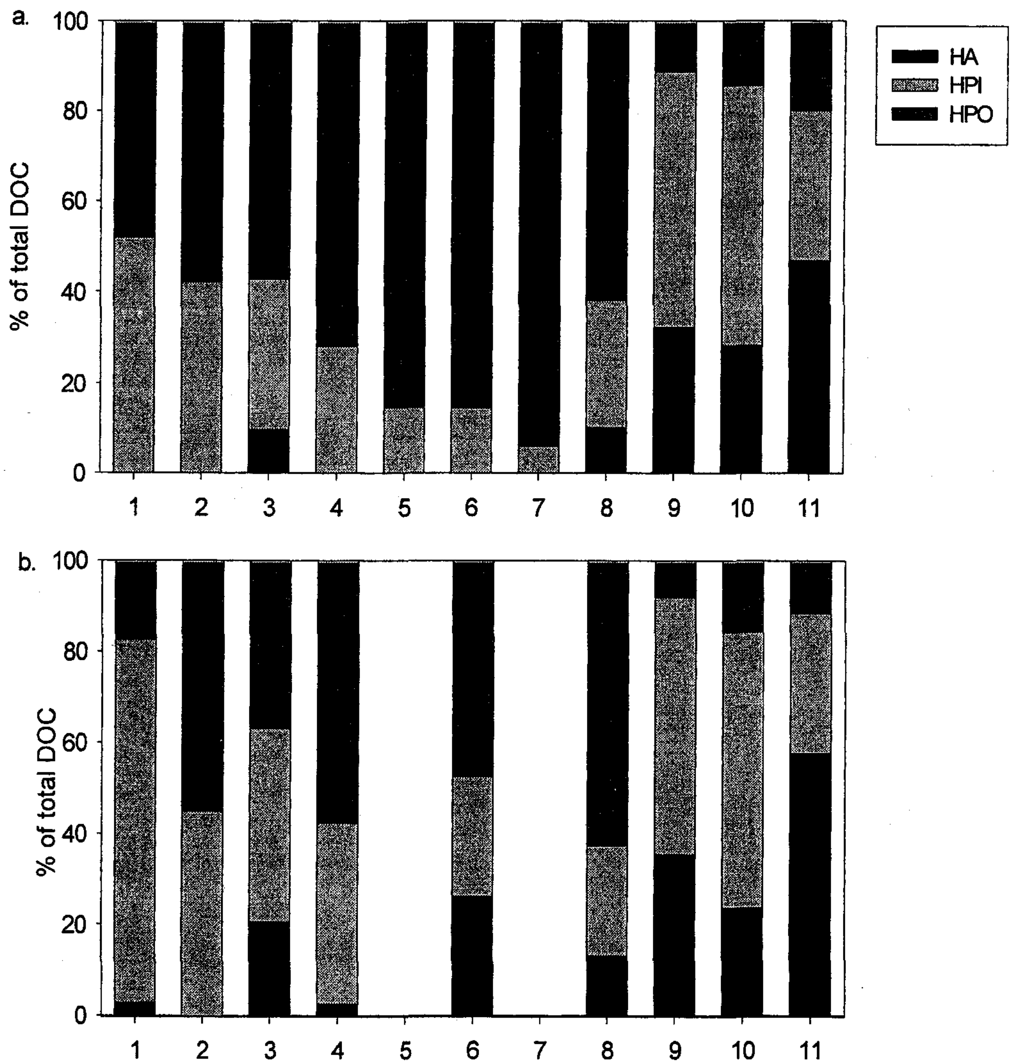


Figure 4.2 Fractions of DOM leached from peatland samples after 21 days of incubation at (a) 7 and (b) 22 °C. The fractions have been normalized to DOC concentration. The numbering in the x-axis corresponds to the reference number in Table 4.1. Shrub samples from day eight of incubation were also included as a comparison to the effect of incubation time on DOM character.

Shrub and herbaceous leachate contained appreciable proportions of all three fractions of DOC. It was notable that the greatest component of the leachate from herbaceous material was HA representing 47 to 58% of DOC while HPI ranged between 30 to 33 % and HPO between 9 and 11 %. For shrub vegetation the largest component was the HPI fraction ranging between 56 and 60%, while HPO made up a very small fraction of 11 to 15%. The HA fraction was important here as well ranging between 27 to 32% of DOC (Figure 4.2).

Peat leachates were quite variable in the relative proportions of the three fractions and showed temperature dependence. At 22°C the HA fraction was a more important component of DOC (3 to 23 %) but it was absent in some samples from peat leachates at 7°C (10% for peat at 50 and 80 cm depth) (Figure 4.2). The HPO fraction was a large component of DOC ranging between 36 to 96% of the DOC released and also showed temperature effects. At 7°C HPO was a more significant component than at 22°C (Figure 4.2) for peat leachate. The HPI fraction was also important, ranging between 14 to 60% of DOC. Samples incubated at 7°C had a lower percentage of this component than samples incubated at 22°C (Figure 4.2).

The effect of oxic conditions on peat samples can be evaluated by looking at peat from 50 and 80 cm depth, which were incubated under aerobic and anaerobic conditions. In both cases there was a shift towards higher percentage of HPO released and lower HPI under anaerobic conditions (Figure 4.2). The HPO fraction increased by 9 to 15% at 7°C, and by 21% in both cases at 22°C, however comparison could not be made at 22°C at the restored site. The HPI fraction dropped from 33 to 28% at 7°C and from 43 to 39% at 22°C. HA was more readily produced by samples incubated under aerobic than anaerobic conditions. At higher temperature, HA made up 21% of the DOC under aerobic conditions while it was only 3% under anaerobic conditions (Figure 4.2).

Leachate from shrub samples at 8 and 21 days of incubation were compared to see the effect of incubation time on DOM character. These two days were chosen since day 8 is during a period when large amounts of DOM were released and day 21 is towards the end of the incubation when a loss of DOM was observed. The changes in DOM character are presented in Figure 4.2 (# 9 and 10). A slight decrease in HA (32% to 28 %) accompanied by a slight increase in HPO fraction (11% to 14%) and HPI fraction (56 to 57%) (Figure 4.2 a.) between 8 and 21 days of incubation at 7°C. Changes at 22 °C are slightly more pronounced with HA, that decreased from 36 to 24%, while both the HPI and HPO fractions increased from 56 to 60% and 8 to 16% respectively (Figure 4.2 b.). Thus, overall a shift towards lower HA and higher HPI and HPO were observed with increasing time of incubation

4.2 Discussion

A general schematic of how DOM can form was suggested by Tipping et al. (1998) and elaborated by Kalbitz et al. (2000). Organic material from plant litter, root exudates, or microbial biomass can be decomposed, leached, or humified, creating a potential DOM source. This pool of DOM can become mobilized by desorption, dissolution, diffusion, decomplexation, deprotonation or a combination of these reactions. DOM can also become immobilized by the opposite of the above-mentioned reactions. Therefore anything that can affect these reactions can have a controlling effect on DOM release.

4.2.1 DOC release

As noted in Chapter 1 the effects of temperature on DOM dynamics is not clear. Many studies of natural systems have noted seasonality in DOM concentrations with increasing DOC during the summer (e.g., Bourbonniere, 1989, Fraser et al, 2001), implying that temperature, among other variables, can also have a controlling effect on DOC production. However, this relationship was not so clear in laboratory tests. Gödde et al. (1996) and Moore and Dalva (2001) reported Q_{10} values of 1.5 to 2.0, however, McDonald et al. (1999) reported little change with incubation temperature, and Christ and David (1996) showed constant Q_{10} values over a broad range of temperatures. Kirschbaum (1995) concluded that the effect of increased temperature would be more significant on the decomposition of organic matter and not on the production. Qualls and Haine (1992) studying the degradation of DOM through different soil layers found that adsorption rather than biodegradability of DOM is the most important DOC loss process and therefore temperature effects are not as important. Marschner and Bredow (2002) studying DOM degradation in natural and sterilized soils samples, however, found a strong effect of temperature on soil samples containing microbes but no temperature effects in sterilized soils.

Therefore, it is not surprising to find that in this incubation experiment some of the samples were insensitive to temperature changes. Samples such as shrubs and herbaceous plants showed an initial high release of DOC followed by a decrease in production. Christ and David (1996) studied DOM release from spodosols and found that most of the DOM released initially is part of an adsorbed DOC reservoir that can be easily mobilized upon water addition. This pool is quickly replenished in the initial extractions but decreases significantly after two days of incubation. Most of the DOC in leachates of shrubs and herbaceous plants in the present study was produced upon the initial wetting of the samples (Day 0, Figure 4.1). This implies a pool of readily soluble DOM as observed by Christ and David (1996). DOC produced by shrubs decreased with time of incubation indicating that the initial pool of DOC has been released and it is not being replenished as quickly to offset degradation. This further indicates that the material released from these plants is highly labile and will stay in the environment for only short periods. Moore and Dalva (2001) had a similar finding. The highest amounts of DOC were produced in the first leaching of fresh maple leaves and rewetting a second and third time did not release DOC to the same extent as before. The steady release rates observed in leachates of herbaceous plants can be attributed to their lower lignin content. These plants may be more easily degraded therefore capable of producing DOM at a steadier rate than shrub samples. Meredith et al. (1996) examining leachates of *Thyphus angustifolia* found that 25 to 80% of the carbon originally present, was converted to microbial biomass or released as CO_2, indicating that the leached DOM is highly labile. Therefore, it is likely that in this short-term experiment, the DOM produced by shrub and herbaceous plants is mainly affected by the initial pool of readily soluble DOM and not the effects of temperature on DOM degradation and production. Moreover, because many of these vegetation types are found in depressions in the peatland where water can collect, they have a high potential to release DOM on short time scales, and rain events can be particularly important.

Straw was utilized to improve the physical conditions for *Sphagnum* re-growth at the restored site. Since it is used in agriculture as mulch, studies have dealt with its decomposition and nutrient release (e.g., Wessen et al., 1986), but there are no studies that examined DOC production. CO_2 release from straw in a peatland was studied by Waddington et al. (submitted) who found that age, temperature and moisture had strong effects. They determined that straw produces CO_2 at a rate of 145.0 to 151.5 µmol CO_2 d^{-1} or about 0.00174 to 0.00182 g of C d^{-1}, about 20 times smaller than the potential DOC release measured in this experiment. Since there was about 300 g m^{-2} of mulch spread over the peatland (Petrone et al, 2001), the potential for DOC production under ideal conditions over one growing season (May to October) would be approximately 10 g DOC m^{-2}. This indicates a large potential to release DOM at the Bois-des-Bel peatland, however, this estimate is about the same as the total

DOC export calculated for the peatland (Chapter 5), indicating that climatic conditions as well as DOM degradation and immobilization within the peatland will have a strong effect on DOM release from this component.

Peat samples collected in this experiment are catotelmic peat samples that have been exposed to aeration and drainage causing shrinkage and an increase in bulk density. Few studies have incorporated degraded peat in their examination of DOM release. Hongve (1999) used peat from 25 cm depth and Moore and Dalva (2001) used hemic peat. DOM release rates calculated in this experiment (0.034 to 0.094 mg DOC $g^{-1}d^{-1}$) correspond well with those reported by Moore and Dalva (2001) (0.025 to 0.041 mg DOC $g^{-1}d^{-1}$).

Based on hydrometric measurements performed by Von Waldow (2002), it is possible to estimate the potential of the peat at the Bois-des-Bel site to release DOC. He reported an average bulk density to be about 0.119 g cm^{-3}. Knowing that the average peat depth at this site is about 1.5 m and applying the DOC production rates calculated in this experiment results in a DOC production of approximately 2 kg DOC m^{-2}. This value is excessive compared to the DOC export measured at the cutover and restored sites over the study periods (Table 5.2) indicating that the changing hydrologic and climatic conditions also have a strong effect on DOC released from peat.

The effect of temperature on the release of DOC from peat is consistent with the observations of Moore and Dalva (2001). However no direct conclusion can be made on whether the controlling factor in this release is physical leaching or microbial degradation. There are differences that emerge between the two sites where the peat samples were collected. The restored site, considered to be wetter than the cutover site, has peat that is clearly differentiated. Surface samples are constantly exposed to aerobic conditions and large water fluctuations produced less DOC than that collected at 80 cm, a layer that is saturated most of the year. This pattern was not observed at the cutover site where samples were collected from 50 cm depth, however there are occasions when the water table falls below this level. Surface layers at the restored site produced higher amounts of DOC than those at the cutover site. As indicated in Chapter 1, the oxic environment and the frequency of rain events can have a positive effect on DOC release. Since these layers have been exposed to such conditions for long periods the labile carbon pool may have already been depleted. The restoration measures, including the mechanical tilling of the peat layer to level the surface at the restored site, exposed "fresher" peat layers compared to the cutover site, thus providing a better source for DOM.

This part of the leaching experiment did not reproduce the highly colored water that is found at the Bois-des-Bel site. Hongve (1999) found similar results. He concluded that the high DOC seen in such sites is more a result of long residence time rather than the abundance of organic material. It is generally accepted that water moves slower at depth within the peatland. Therefore following Hongve's (1999) conclusion, the highest DOC concentrations from peat should be observed at depth compared to the surface. This, however, is not the case at the Bois-des-Bel peatland. As will be seen in Chapter 5 DOC concentration decreases markedly with depth. This suggests that the conditions at the surface, such as increased aeration, higher microbial activity and fluctuation in moisture content, can significantly alter the upper layers of peat to produce water with high DOC concentration

Moss samples produced the least amount of DOM in this study. Production rates measured in this experiment (0.018 to 0.35 mg DOC g^{-1} d^{-1}) were lower than those reported by Moore and Dalva (2001) (0.1 mg DOC g^{-1} d^{-1}). However extrapolating the incubation curves for moss (Figure 4.1 b) to 60 days yields probable production values of 2.1 to 3.3 mg DOC g^{-1} which compare well to the range of 1.93 – 5.59 that Moore and Dalva (2001) observed. Hongve (1999) reported DOC concentration during an incubation experiment of moss and peat from the surface to 25 cm depth. He found the highest concentration increase in the surface layer and no change in concentration at depth. He concluded that the surface layer has a much higher potential to release DOC than the peat further down. He, however, squeezed the porewater out of these samples and could have mechanically damaged the fresh moss, increasing the DOC released. A possible reason for low DOC release that was found in the present experiment could be that these species that are naturally accustomed to growing in wet environments may have simply just "weathered" the 25 days of incubation not releasing much material for degradation.

Christ and David (1996b) concluded that cool and wet conditions favouring anoxia would produce the highest amount of DOC. No significant difference was found in the present study between samples incubated under aerobic and anaerobic conditions, similar to the results of Moore and Dalva (2001), who conclude that the increased production of CO_2 under oxic conditions could be responsible for the degradation of the released DOM, thus blurring any effect of oxic conditions.

4.2.2 DOM character of the leachates

Since the fractionation in this experiment did not extend beyond that of the XAD-8 resin, some of the literature values had to be summed for comparison. For example, the HPO fraction reported here is equivalent to the HPOA+HPON, and HPI to HPIA+HPIN of Bourbonniere's (1989). In some cases, however, the hydrophobic components (HA and HPO) were not separated initially (e.g. Guggenberger 1994; Hongve, 1998). Their results can be compared to the HPO+HA fraction in this study by adding the HPO acid, neutral and basic fractions. These studies found HPO+HA to be an important component ranging from 30 to 70% of the DOM of litter percolates and its origin to be closely related to plant material and the degradation of lignin compounds. HPO+HA fraction is also found to be dominant in spodosol, leachates ranging between 79 to 84%, while HPI fractions made up 18 to 20 % of DOM. Bourbonniere (1989) working with water samples collected from peat bogs and river systems found similar results, where the HPO fraction was the most important component of DOM, making up 24 to 40 %, HPI the second most important, ranging between 27 to 35%, and HA being the smallest component, ranged between 13 to 29%. The results of the present study fall within the range of these observations. HPO is the most dominant followed by HPI and then HA. Some deviations, however, occur from this pattern, for example shrubs and herbaceous plants, and these will be discussed later.

The shift observed in DOM fractions at different temperatures (Figure 4.2) is consistent with findings by Christ and David (1996b). In their study of spodosol leachates at different temperature and moisture conditions, HPO was found to be more abundant in samples incubated at lower temperature while HPI was seen in higher concentration at higher temperature. Microbial activity can certainly be the cause of this shift. The HPI fraction is thought to have a strong microbial signature (Bourbonniere, 1989; Guggenberger et al., 1994). At higher temperatures microbes are more active and can degrade large molecules like HPO to smaller ones such as HPI. The presence of the more hydrophobic, higher molecular weight HA (Bourbonniere, 1989) indicates that either the dissolution of this component is enhanced by increased temperature, or that it is formed from metabolites released in the degradation of the organic samples through oxidative polycondensation. Possible evidence for oxidative polycondensation can be seen by comparing samples incubated under aerobic and anaerobic conditions (Figure 4.2 #3 and #4). Samples incubated at 7°C under anaerobic condition do not produce any HA, but the aerobic ones do. The effect of increased dissolution of HA can be seen in samples incubated at 22°C where a small proportion of HA appeared in samples that were incubated under anaerobic conditions (Figure 4.2 b #3 & #4).

DOM produced by both shrubs and herbaceous plants contain all three DOM fractions. HA are present in high proportion, which is a reflection of the high lignin content of these samples. Gonet and Debska (1998) in their studies of base extracted HA from fresh materials found that these do not resemble, in their chemical composition and visible light absorbance, the traditionally accepted character of HA, and proposed that these HA's be termed precursors of HA, compounds that would degrade with more ease in natural systems. This hypothesis is further substantiated by comparing shrub leachate at 8 and 21 days of incubation (Figure 4.2). Since only a degradation of DOC is observed in the later part of the experiment, the shift toward lower HA and an increase in both HPI and HPO fractions indicate degradation of precursor HA component. Christ and David (1996 a and b) observed a similar shift toward lower HPO+HA with increasing incubation time in spodosol leachates. Thus even though these compounds released from fresh shrub and herbaceous plants precipitate at pH 2, they would not behave the same as those from older material, such as peat, and would degrade more readily.

Mosses behave in a similar way as described for shrubs and herbaceous materials. Due to their low lignin content they do not release any significant amount of precipitable HA. The small amount seen at 22°C is probably due to microbial action and the formation of HA from polycondensation.

Straw produced higher amounts of DOC when it was incubated at 22°C compared to 7°C. This same effect on the degradation of straw was noted by Waddington et al. (submitted), who found that the greatest control on CO_2 release was temperature. Straw contains large amounts of lignin products that are closer in relation to traditional characteristics of humic materials (Gonet and Debska, 1998). In the present study there was no measurable amount of HA released, but instead, the other two components HPO and HPI dominated. The proportionality was similar at both temperatures, leaving no indication of increased microbial action at higher temperatures.

4.2.3 Summary

Fresh organic material, such as shrubs and herbaceous plants have a high potential to produce large amounts of DOM on a short time scale. Much of this material is readily degraded. Straw mulch can provide significant amounts of DOC during its lifetime. Mosses, even though they are fresh organic material, produce very little DOM and this can be attributed to their ability to grow in wet environments under harsh conditions. A much larger potential source of DOM is peat, since it can be found in large quantities that can produce DOM persistently.

Fractionations of DOM produced by the different vegetation samples indicate that all components have the potential to release the three fractions of

DOM studied in this experiment. At cooler temperatures the HA is more likely to be produced by shrub and herbaceous plant material than by peat, moss and straw samples (Figure 4.2 a.). At this cooler temperature, peat samples are more likely to produce HPO while straw and mosses produce about the same of both HPO and HPI. At warmer temperatures, microbial activity is increasingly important, and the HPI fraction increases in importance, while the HPO fraction decreases. Aerobic conditions are more likely to produce the HA fraction than are anaerobic conditions.

CHAPTER 5: DISSOLVED ORGANIC CARBON DYNAMICS IN A RESTORED, CUTOVER AND NATURAL PEATLAND

In the period between 1999 and 2001 hydrologic measurements were conducted and water samples collected at the outflows of the cutover and restored sites to assess changes in DOC dynamics that occurred due to restoration. Data is presented here in two parts: 1) the base flow conditions are first described for the three seasons, including the results of the 2001 study season at the natural area of Bois-des-Bel, and 2) the results of a detailed study of DOC dynamics at the three sites in 2001 are presented.

5.1 Annual variation of DOC

5.1.1 Precipitation

Precipitation data was collected at different time intervals during the three study seasons. In 1999 data were collected between May 18 and Oct.4, whereas in the other two years the season was extended from May 8 to October 13. Cumulative precipitation for the common period (May 18 to October 4), for the three study seasons ranged between 279 mm in 2000 to a high of 370 mm in 1999. An intermediate value of 336 mm was measured for 2001. Precipitation events were relatively evenly distributed throughout the seasons. Continuous dry periods

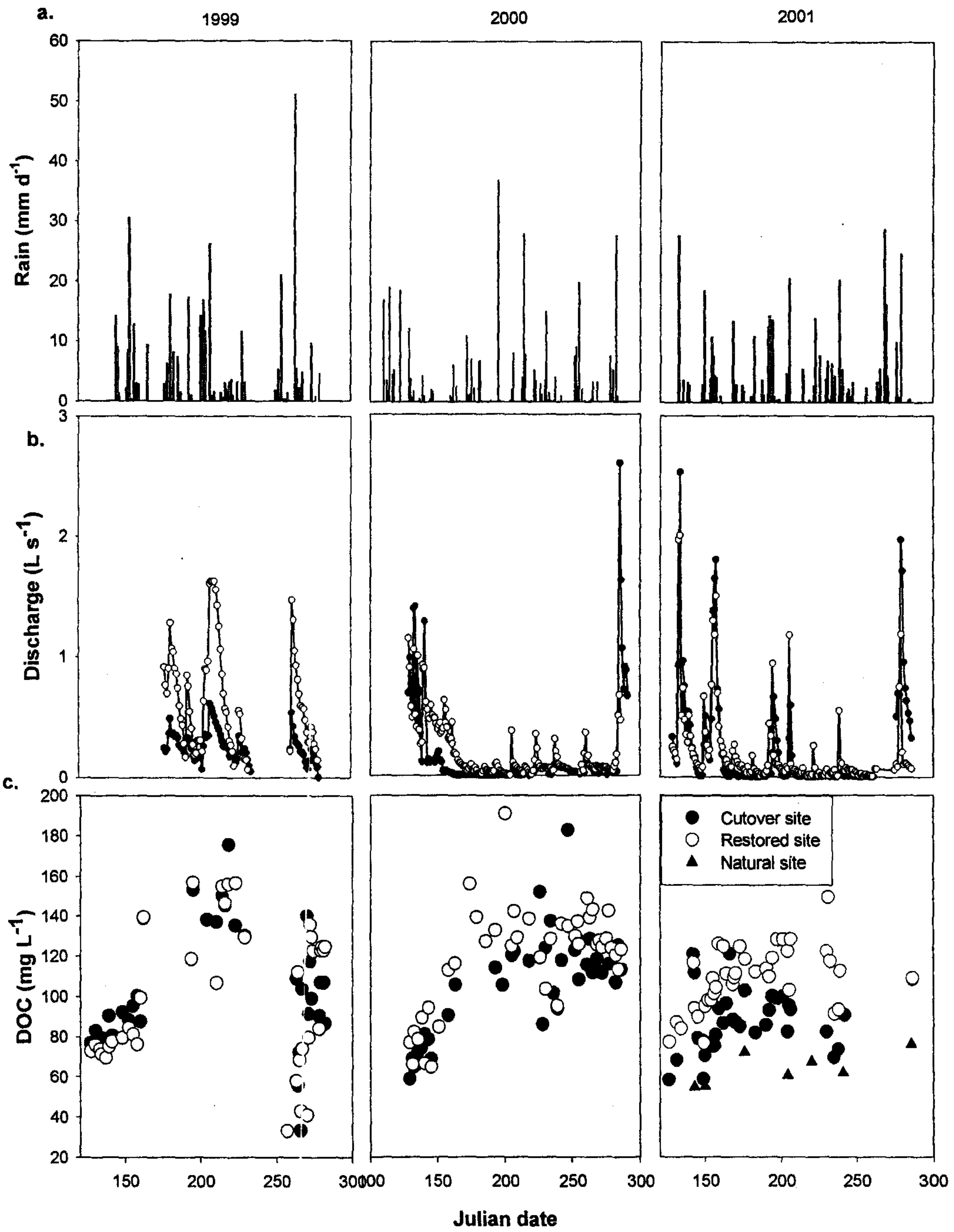


Figure 5.1 (a) Precipitation, (b) discharge, and (c) DOC concentration at the study sites during the three study periods.

lasted to a maximum of 20 days (in 1999) and were more characteristic of the later part of the season, late August to mid September (Figure 5.1 a). Given the 30-year average in the Rivière-du-Loup region of 423 mm for the May 18 to October 4 (JD=138 to 277) period (Environment Canada, 1993), the three study years were drier than normal.

5.1.2 Water table variations

In general, water table position was highly variable throughout the three study seasons (Table 5.1), with a high water table position in the early part of the season (May to end of June), which dropped steadily during the summer months (July to early September), followed by a rise at the end of the season (mid September on). Negative values are used to indicate water table positions below the peatland surface.

In 1999 water table position at the restored and cutover sites followed each other closely and there was no significant difference ($p<0.05$) found between water table position (average -49.8 and -46.3 cm at the cutover and restored site, respectively) at the two sites. The highest water table positions were -41.5 cm and -38.5 cm at the cutover and restored site respectively and were reached on June 5th (JD= 156) coinciding with a 32.5 mm rain event (Table 5.1). Lowest water table positions (-75.5 and -77.4 cm at restored and cutover sites respectively) were reached on September 6th (JD=249), following a 19-day period without precipitation (Table 5.1).

Table 5.1 Hydrologic variables at the Bois-des-Bel peatland between May 8 and Oct. 13 of each year.

Study period	Rain† (mm)	Site	Water table (cm below surface)			Runoff (mm)		Discharge maximum ($L\ s^{-1}$)
30 year normal	422		Average	Max.	Min.	May 8 to Oct 13 (JD= 138 to 286)	Jun.25 to Oct5 (JD= 176 to 278)	
1999*	370	Cutover	-49.8	-41.5	-77.4	n/a	96.7	0.54
		Restored	-46.3	-38.5	-75.5	n/a	56.8	1.60
2000	270	Cutover	-46.3	-33.2	-67.2	103.5	15.5	2.59
		Restored	-32.1	-13.1	-49.4	33.4	8.5	1.13
2001**	336	Cutover	-41.2	-24.7	-54.4	95.1	25.4	1.68
		Restored	-30.6	+3.5	-65.4	23.1	7.9	1.33
		Natural	-22.7	-14.2	-34.2	n/a	n/a	n/a

* discharge values in 1999 are between Jun. 25 and Oct. 5 (JD= 176 to 278)

** water table values were not adjusted for peat shrinkage.

† for ease of comparison of the years rain data presented between May 18 October 5 (JD= 138 to 278) (Rain data is not available before May 18, 1999)

In 2000, one year after restoration, mean water table position at the restored site was higher (- 32.1 ± 8.5 cm) than at the cutover site (-46.3 ± 7.7 cm) (von Waldow, 2002). The highest water table position was measured in the spring (May 11, JD=130) at the restored (-13.1 cm) and cutover sites (-33.2 cm), while the lowest water table position was measured during the summer dry period on July 19 (JD=200) at the cutover site (-67.2 cm) and on July 22 (JD=203) at the restored site (-49.4 cm).

This relationship changed in 2001. The mean water table at the restored site was significantly ($p<0.05$) higher (-30.6 ± 15.8 cm) than at the cutover site (-41.2 ± 7.7 cm). During the summer dry period, (August 10 to September 27, JD = 222 to 270) the water table position at the restored site fell below that of the cutover site. On May 12 (JD=132), the day of a 27.9 mm storm, water table reached to +3.5 cm at the restored and –13.1 cm at the cutover site (Table 5.1 and Figure 5.1 a.). Lowest water table depths of –65.4 cm and –54.4 cm at the restored and cutover sites respectively, were measured on September 20 (JD = 263) following a prolonged dry period.

Water table position at the natural site in 2001 followed a similar trend with high water table position in the spring, decreasing through the summer months and increasing again in the fall. Values ranged from -14.2 cm (June 7, JD = 158) to -34.2 cm (September 20, JD = 263), and the mean value of -22.7 ± 4.9 cm was significantly higher ($p<0.05$) than at the restored and at the cutover sites in the same year (Table 5.1). Different responses to precipitation events among the natural, restored and cutover site were exemplified by a 20 mm rain event on August 26, 2001 (JD=238). This rain event followed a dry period and caused the water table to rise by 6.3 cm at the natural site, 9.9 cm at the cutover site and 19.1 cm at the restored site.

5.1.3 Discharge

Discharge values in 1999 were unavailable until June 25, when the main outflow ditches were constructed. Therefore, for the purposes of comparison runoff values are presented for two time periods: June 25 to October 5 (JD= 176 to 278) (the length of the 1999 study season) and from May 8 to Oct 13 (JD= 128 to 133) (the length of the 2000 and 2001 study seasons) (see Table 5.1).

During the 1999 study period the restored site showed less total seasonal cumulative runoff (56.8 mm) than the cutover site (96.7 mm) (Table 5.1). In general, discharge increased with precipitation, and higher discharge was observed at the restored site (Figure 5.1 b.). Maximum discharge values for the two sites were 0.54 (on July 26, JD = 207) and 1.6 L s^{-1} (on July 29, JD = 210) at the cutover and restored site respectively. The number of days when discharge was lower than 0.01 L s^{-1} (a point indicating very low to insignificant discharge) was the same at both sites lasting 25 days between August 22 (JD= 234) and September 16 (JD= 259). Discharge at the two sites during the summer period was significantly higher ($p<0.05$) than for the subsequent two years even though summer precipitation was similar in quantity (276, 215 and 280 mm in 1999, 2000, and 2001 respectively) and in distribution (Figure 5.1 a.).

In 2000, the year following restoration, cumulative runoff from the restored site (33.4 mm) was lower than at the cutover site (103.5 mm) and lower than the preceding year (56 mm). Discharge from the two sites decreased steadily after the spring wet-period, when the maximum peak discharge was measured at the restored site (1.13 $L\ s^{-1}$) on May 9 (JD = 129). Discharge increased again in the fall when the maximum discharge at the cutover site was measured (2.7 $L\ s^{-1}$) on October 12 (JD = 285). During these high flow periods discharge from the restored site was lower than the smaller cutover site. During the summer dry period of mid June to late August, discharge values decreased at both sites, with rain events producing less response than in the spring and fall. At this time the restored site was discharging at a higher rate than the cutover site, and both sites experienced periods when average daily discharge was lower than 0.01 $L\ s^{-1}$. The cutover site experienced 35 consecutive days between June 15 and July 20 while the restored site experienced 3 consecutive days (July 21 and 23) of no flow from the catchment outflows (Figure 5.1 b.).

A similar trend to those in 2000 was observed for 2001. Maximum daily discharge was measured at 1.7 and 1.3 $L\ s^{-1}$ on May 13 at the cutover and restored site respectively, which coincided with a 27.9 mm rain event (Figure 5.1). Such a high response was not observed during the summer period when rain events of similar magnitude failed to produce significant increase in discharge (Figure 5.1

b.). Although the cutover site generated higher discharge during the wetter spring and fall, the restored site responded at a higher rate during the summer dry period experiencing fewer days (four non-consecutive days, and three consecutive September 17 to September 20) when average daily discharge fell below 0.01 L s^{-1}, while the cutover site experienced 24 (June 18 to July 12) and 38 (August. 3 to Sept. 20) consecutive days when discharge was lower than 0.01 Ls^{-1}. Runoff during the entire 2001 study period was higher at the cutover site (95.7 mm) than at the restored site (23.1 mm). This relationship did not change during the June 25th and October 5th period when the runoff was measured at 7.9 and 25.4 mm at the restored and cutover sites, respectively.

5.1.4 Dissolved Organic Carbon

DOC concentrations were highly variable at the outflows of the restored and cutover sites over the three study seasons (Figure 5.1 c.), with a general trend of increasing concentrations from ~60 to 70 mg L^{-1} in early May to peak concentrations of 150 to 190 mg L^{-1} in mid July to August and decreasing to about 90 to 110 mg L^{-1} once the more frequent fall precipitation events started. An exception to this was observed in 1999 when the overall lowest DOC concentrations were measured at the outflows (33.2 and 36.7 mg L^{-1}at the restored and cutover site respectively) on September 16 during the largest storm event (51.2 mm) recorded during the three study seasons (Figure 5.1). Maximum DOC concentrations through the three study seasons were reached in 2000 when

Table 5.2: DOC variation at the cutover, restored, and natural sites for the 1999, 2000, and 2001 study periods.

Study period	**Site**	**Sample size**	**DOC concentration** (mg L^{-1}) Average	Min.	Max.	**DOC export** (g C m^{-2}) May 8 to Oct 13	Jun 25 to Oct 5
1999	Cutover	38	104.2 ± 30.4	33.2	175.4	n/a	10.3
	Restored	38	99.4 ± 35.1	36.7	156.9	n/a	4.8
2000	Cutover	44	107.6 ± 25.6	58.8	182.6	8.5	1.7
	Restored	46	119.0 ± 26.9	64.9	191.0	3.4	1.4
2001	Cutover	38	87.5 ± 14.8	76.9	121.0	6.2	1.9
	Restored	39	108.7 ± 15.9	58.5	149.3	3.5	1.5
	Rain	12	3.51 ± 2.23	0.9	8.6	1.2	1.4
	Natural	7	64.1 ± 8.2	54.9	76.2	3.8*	3.0*

* units are mg C m^{-2}

concentrations at the restored site climbed to 191.0 mgL^{-1} on July 19 following an extended dry period (Figure 5.1), and at the cutover site to 182.6 mgL^{-1} on Sept. 4 (Table 5.2).

Generally low DOC concentrations were observed during high flow periods in the spring and fall, and high concentrations during the summer when discharge was low (Figure 5.1 b, c). However, no significant correlation could be found between discharge and DOC concentrations in 1999 and 2001 ($R^2 < 0.1$) even when the data was separated into low and high discharge periods. In 2000, a weak negative correlation ($R^2=0.52$) existed at the restored site but not at the cutover site. Further investigation was carried out into correlations with other environmental variables such as water table position, volumetric soil moisture content and peat temperature. There was a fairly strong negative linear correlation ($R^2=0.68$) at the restored site, between water table position measured at the meteorology station and DOC concentration at the outflows, but no significant correlations could be found at the cutover site ($R^2=0.31$). Better correlations could be found with volumetric soil moisture content. At the cutover site a more significant exponential correlation ($R^2=0.63$) was found with soil moisture at 10 cm depth. At the restored site good correlation was found at both 10 ($R^2=0.83$) and 20 ($R^2=0.79$) cm depths. Peat temperature changes exhibited stronger correlations with outflow DOC concentration at the cutover site. Correlations increased in significance with increased depth, especially at 25 ($R^2=0.65$), 50 ($R^2=0.87$), and 75 cm ($R^2=0.91$). At the restored, site correlations were weaker with highest correlations found at 25 (R^2=0.55) and 50 cm (R^2=0.54). Correlations were somewhat improved when daily DOC export was used instead of DOC concentration. This variable incorporated some of the moisture effects at the site, increasing R^2 to 0.67 and 0.62 at 25 and 50 cm respectively.

Differences in DOC concentration between the two sites were observed after restoration took place. In 1999, DOC concentrations were similar at the two sites (mean 99.4 ± 35.1 mgL^{-1} and 104.2 ± 30.4 mgL^{-1} at the restored and cutover site respectively), and no significant difference ($p<0.05$) could be found between the sites (Table 5.2). There was no significant difference ($p<0.05$) between average DOC concentration at the cutover site before and after restoration (mean 107.6 ± 25.6 mg L^{-1}) in 1999 and 2000, however in 2001 DOC concentrations decreased (mean 87.5± 14.8 mg L^{-1}) (Table 5.2). Analysis of variance indicates that there was a significant ($p<0.05$) shift to higher DOC values after restoration at the restored site, which remained consistently high in 2000 (mean 119.0± 26.9 mg L^{-1}) and 2001 (mean 108.7 ± 15.9 mg L^{-1}). DOC concentrations at the restored site were significantly ($p<0.05$) higher than at the cutover site in 2000 and 2001.

DOC concentrations at the Bois-des-Bel natural site in 2001 were 64.1 ± 8.2 mg L^{-1} that was significantly lower ($p<0.05$) than those at the restored and cutover site (Figure 5.1 c. and Table 5.2). Seasonal variation was also lower. While concentrations at the restored and cutover site changed by ~70 and ~60 mg L^{-1} respectively, DOC concentration at the natural site changed by only 21 mg L^{-1}

(Table 5.2). Trends in DOC concentrations were similar to those at the other two sites. Minimum DOC concentration (54.8 mg L^{-1}) was measured early on in the season (May 23, JD= 143) followed by a period of higher concentrations in the summer (up to 72.1 mg L^{-1}), but no significant decrease was noted in the fall when the highest DOC concentration of the season (76.2 mg L^{-1}) was measured on October 13 (JD= 286) (Figure 5.1 c.).

DOC concentration of rainwater was measured in 2001 and it was found to be on average 3.5 ± 2.2 mg L^{-1}. The variation within the samples was large, especially with samples from small storm events following long dry periods. Concentrations ranged from 0.9 to 8.6 mg L^{-1}.

5.1.5 DOC export

DOC export at the three sites was calculated for the periods when discharge values were available (Table 5.2). Overall the cutover site exported more DOC than the restored site in all three study seasons, with highest exports in 1999 (10.3 and 4.8 g m^{-2} at the cutover and restored sites, respectively). In 2000, 8.5 g C m^{-2} was released from the cutover site, while the restored site released less than half this amount (3.4 g C m^{-2}) (Table 5.2). In 2001, the restored site released about the same amount of DOC as in the previous year (3.5 g C m^{-2}) while the cutover site load dropped to 6.2 g C m^{-2} (Table 5.2).

The DOC input from rain in 2001 was found to be 1.2 g C m^{-2}. Both sites were found to be net exporters of DOC (5.0 and 2.3 g C m^{-2} at the cutover and restored sites, respectively).

Hydraulic conductivity at the natural site was only available for 75 cm depth and was found to be 0.015 cm s^{-1} that is in the range of hydraulic conductivities calculated in acrotelmic peat in natural bogs in eastern Canada (Fraser et al., 2001). DOC export was calculated based on this value, using Darcy's Law to calculate discharge, and was found to be small compared to values obtained at the restored and cutover site for the same period (3.8 mg C m^{-2}). Since hydraulic conductivity can range over several orders of magnitude through the peat profiles, another estimate of DOC export was calculated using the results of van Seters and Price (2001), who studied a natural peat bog 5 km from Bois-des-Bel peatland. They found that the overall saturated hydraulic conductivity was 4.1 x 10^{-4} cm s^{-1}. Based on this value, DOC export was even smaller at 4.3 x 10^{-4} mg C m^{-2}.

5.1.6 Baseflow DOM quality in 2000

On a seasonal average, the three DOM fractions examined in this study were represented evenly at the outflow of the two sites. The humic acid (HA) fraction of DOM presented the greatest seasonal variation (cutover mean = 26.3 ± 18.3 % and restored mean = 33.2 ± 16.4 %) with minimum values at 4.7 % (cutover site) and 1.9 % (restored site), and maximum values observed at 48.5 %

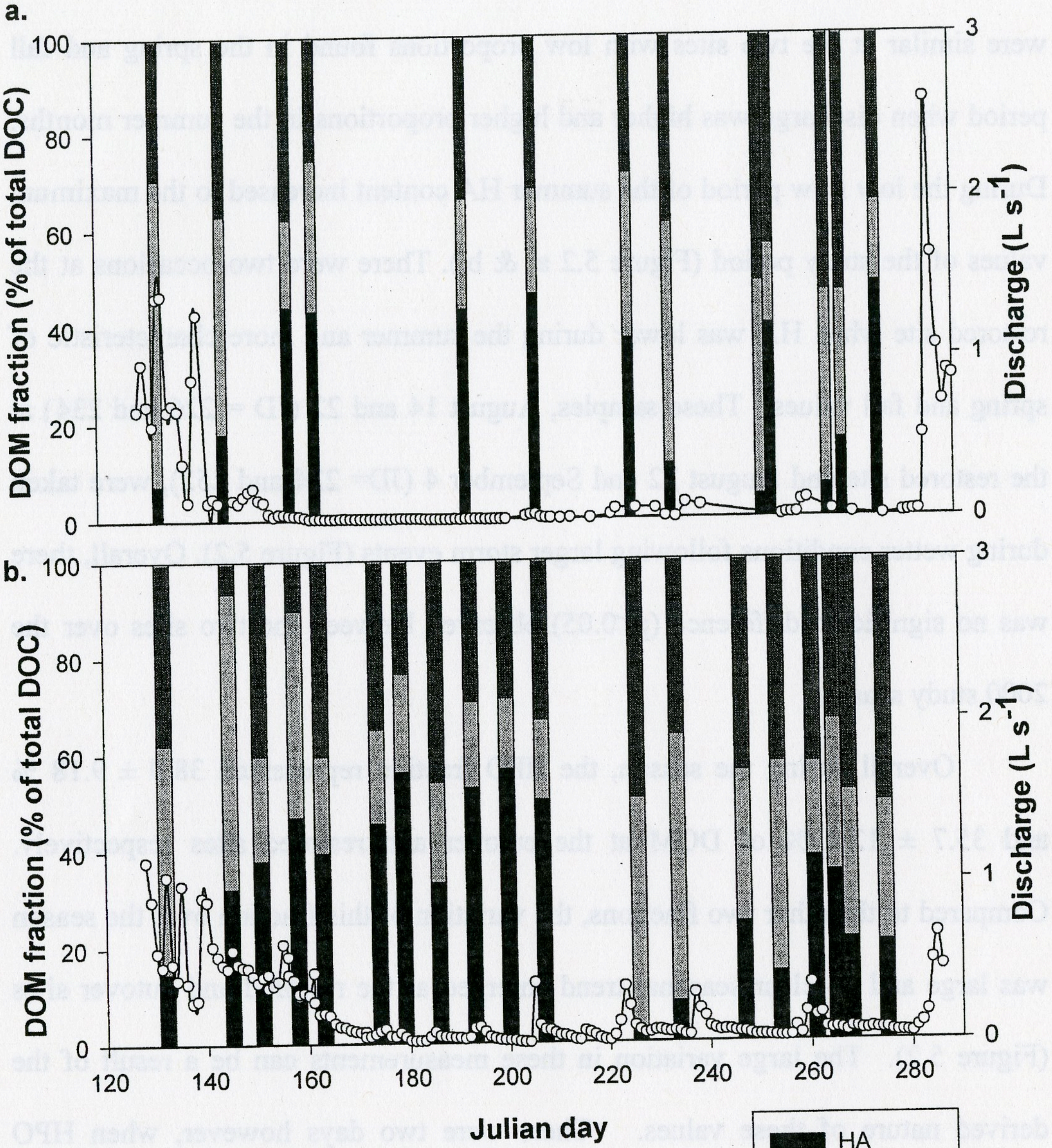


Figure 5.2 DOM fractions at the cutover (a.) and restored (b.) sites in 2000. Discharge values are inserted as reference for flow conditions.

and 56.7 % at the cutover and restored sites respectively. Seasonal trends in HA were similar at the two sites with low proportions found in the spring and fall period when discharge was higher and higher proportions in the summer months. During the low flow period of the summer HA content increased to the maximum values of the study period (Figure 5.2 a. & b.). There were two occasions at the restored site when HA was lower during the summer and more characteristic of spring and fall values. These samples, August 14 and 22 (JD = 226 and 234) at the restored site and August 22 and September 4 (JD= 234 and 252), were taken during wetter conditions following larger storm events (Figure 5.2). Overall, there was no significant difference ($p<0.05$) observed between the two sites over the 2000 study season.

Overall during the season, the HPO fraction represented 38.0 ± 9.18 % and 35.7 ± 12.1 % of DOM at the cutover and restored sites respectively. Compared to the other two fractions, the variation of this fraction over the season was large and no clear seasonal trend emerged at the restored and cutover sites (Figure 5.2). The large variation in these measurements can be a result of the derived nature of these values. There were two days however, when HPO fractions at the restored site were noticeably low (May 22 and June 7, JD= 142 and 158). Both of these periods coincided with storm events. Maximum proportions of this component were observed in the fall (53.4% and 50.6% at the cutover and restored sites, respectively). Lowest proportions were found in the spring to early summer months at 12.5% and 6.5% at the cutover and restored sites.

The HPI fraction represented 35.7 ± 16.4 % and 31.7 ± 14.4% of DOM at the cutover and restored site over the study season. Proportions were high in the spring when the maximum value was reached at the restored site (61.2%, Figure 5.2 b.) and high in the fall when the maximum was reached at the cutover site (66.0%, Figure 5.2 a.). This fraction decreases in the early summer period when the minimum values were observed at 16.3% at the cutover site and 14.5 % at the restored site, followed by an increase in mid August and early September (Figure 5.2).

5.1.7 Internal DOC variations in 2001

A distinguishing feature at the restored site is the abundance of areas that collect water during high flow periods as well as the artificial pools created during restoration. Such features were absent at the natural and the cutover site. Water in the ditches at the restored site collected during wet conditions and progressively dried up as rains diminished. Artificial pools, however, contained water through the entire study season in 2000 and 2001. Water samples were collected from the artificial ponds and flooded ditches located in the restored site. DOC concentrations measured in these features in 2001 follow closely values at the restored outflow (Figure 5.3 a, b). A similar trend was found between ditch and outflow samples at the cutover site (data not presented). For pond samples

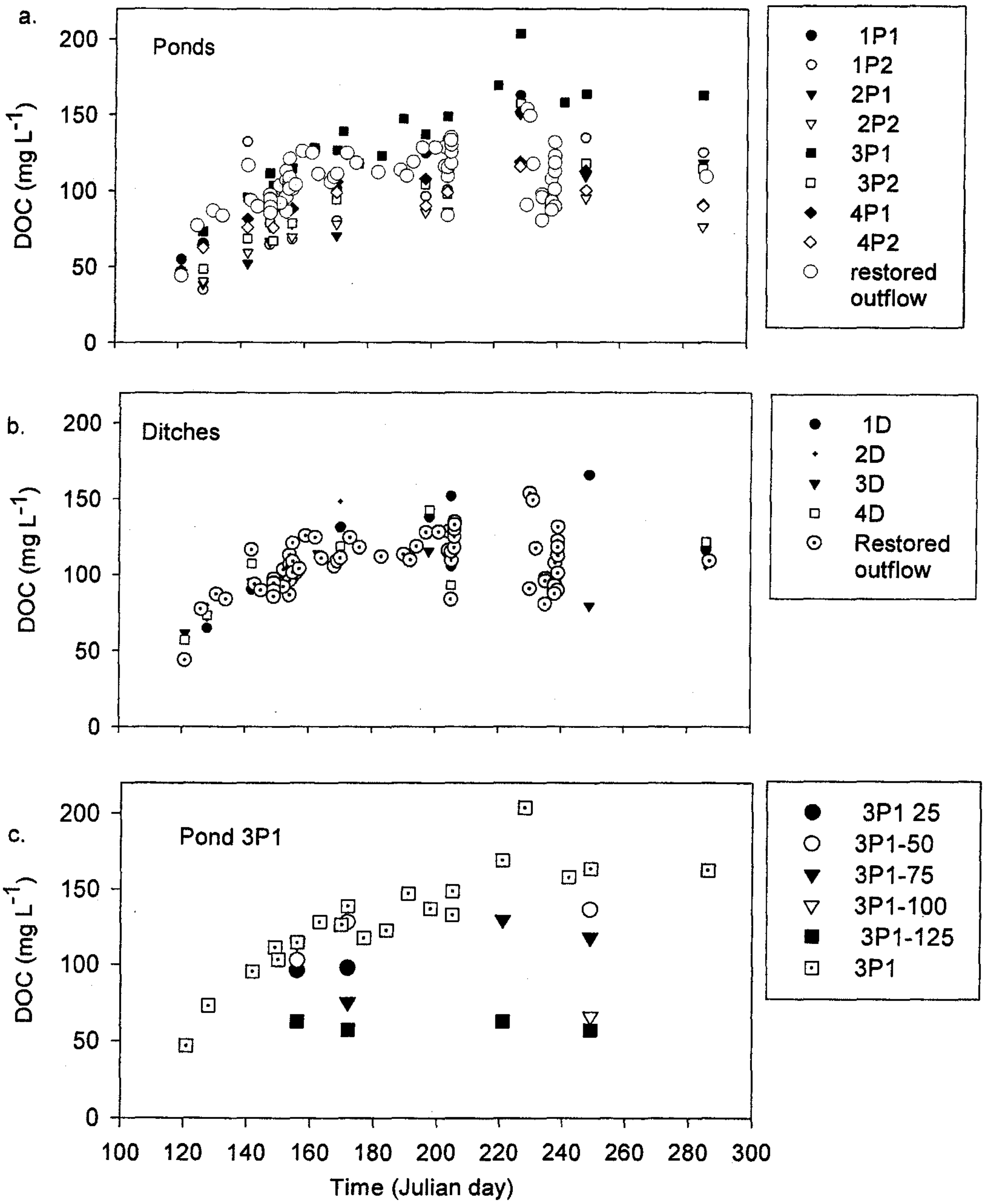


Figure 5.3 Seasonal variations in DOC concentration in open water areas at the restored site. DOC concentration of the restored outflow compared to DOC concentration of the ponds (a.) and ditches (b.). (c.) DOC concentration of pond 3P1 and the piezometers near the pond.

minimum values (47.7 mg L^{-1}) were observed in the spring following the snowmelt period and maximum values (203.6 mg L^{-1}) were reached during the summer months (Figure 5.3 a.). This maximum was also the highest DOC concentration measurement observed in the Bois-des-Bel peatland in 2001. Water samples collected from ditches had DOC concentrations ranging between 57.1 mg L^{-1} (ditch 4D) early in the season and 128.3 mg L^{-1} towards the end of the growing season (Figure 5.3 b.).

Bathymetry measurements (Drolet, unpublished data), water level variations, and DOC concentrations were used to calculate DOC storage in pond 3P1 during the 2001 study season. The seasonal average storage was calculated to be 0.9 kg C, corresponding to 14.6 g C m^{-2}. Hydraulic head measurements in groundwater wells located around this pond indicated that during most of the season water drains from the peat matrix into the ponds. Only during prolonged dry periods like the one in early August did we see some reversal of water flow from the pond into the surrounding peat matrix. A strong gradient in electrical conductivity was observed in the peat matrix ranging between 196 µS cm^{-1} at 50 cm depth to 823 µS cm^{-1} at 125 cm depth. This gradient was also observed in other parts of the peatland at both the restored and cutover site (Day, unpublished data). Electrical conductivity in the ponds was most similar to that measured at 50 cm in the peat matrix and never reached the high values measured deeper in the profile. There was no strong gradient in the pond where electrical conductivity over the summer increased from spring to fall as water levels decreased in the pond (mean 159 ± 54 $\mu S\ cm^{-1}$). Water samples were collected throughout the season from piezometers located near pond 3P1. Highest DOC concentrations were measured closer to the surface and lowest at depth (Figure 5.3 c.) A seasonal trend was observed in piezometers to a depth of 75 cm where DOC concentrations were lowest during the spring and increased during the summer (Figure 5.3 c.). No seasonal trend was noted at 125 cm depth where the lowest concentrations were measured. DOC concentration of pond-water samples was slightly higher than those measured in piezometers to a depth of 75 cm, while those from deeper were significantly lower. A weak negative correlation (R^2 = 0.48) between water level and DOC concentration indicated that evaporation from the pond may have caused DOC to concentrate here.

While DOC concentrations of the outflow followed those in the ponds and ditches, DOM fractions were different (Figure 5.4), indicating that there were changes occurring in DOM quality as water flowed through the peatland. Ditch 4D, which had the closest sampling location to the outflows, bore the closest resemblance to the outflow of all samples analyzed.

DOM fraction changes were more apparent in samples collected from the artificial ponds. There were some general patterns in the DOM character, during the summer period as the HPI fraction became more dominant in samples compared to other fractions and ranged between 48 to 83 % while the HA fraction was more notable in the spring and fall samples ranging between 14 and 64 %. The pattern for the HPO fraction was not clear as it disappeared in some samples

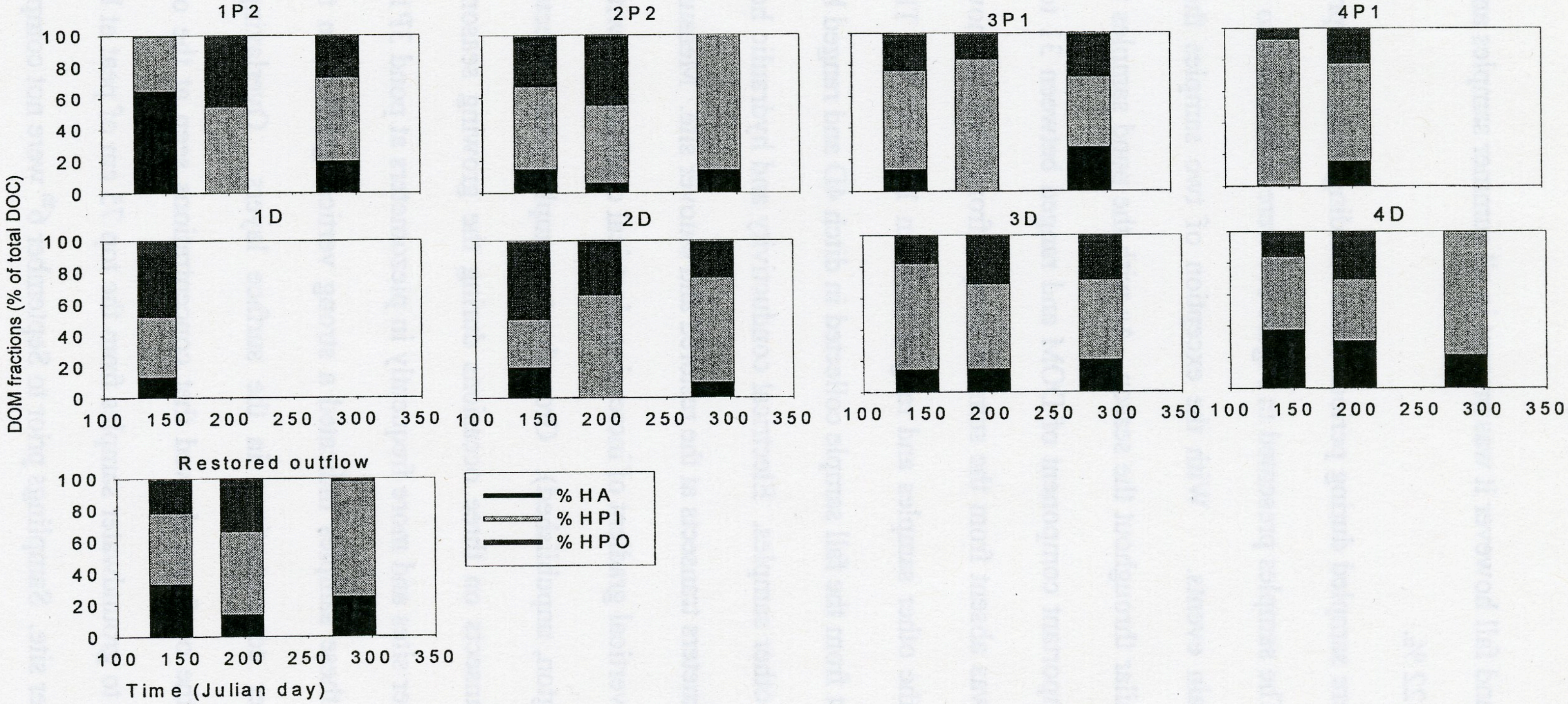
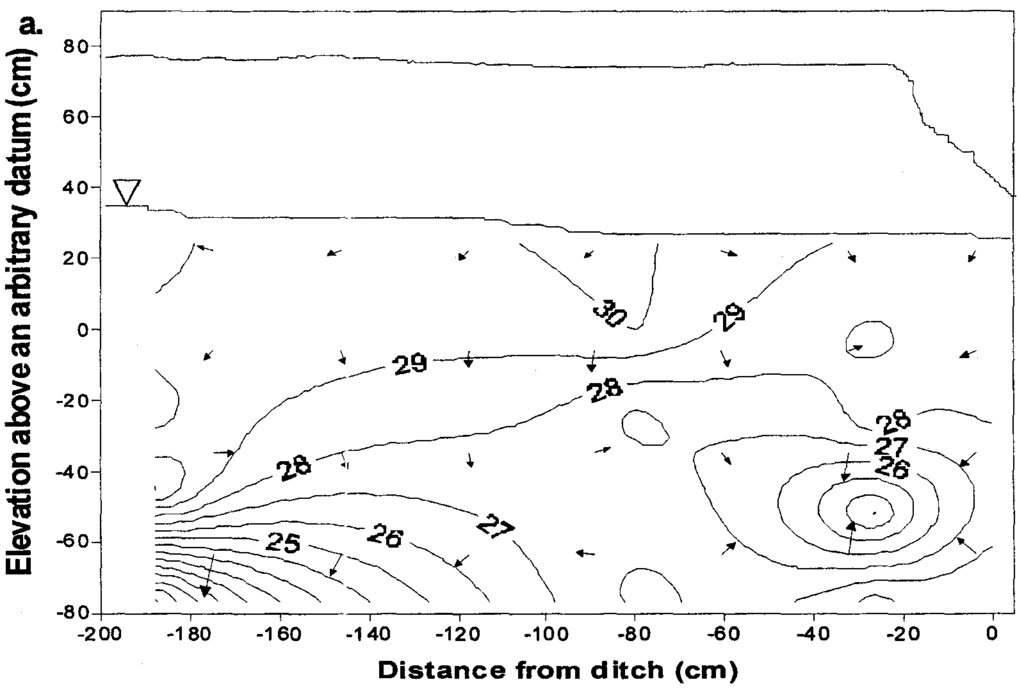


Figure 5.4 DOM character changes in ponds 1P2, 2P2, 3P1, and 4P1; ditches 1D, 2D, 3D and 4D and restored outflow during the 2001 study season

during the spring and fall however it was present in all summer samples and it ranged from 16 to 22 %.

Ditches were sampled during periods when standing water was present in the depressions. The samples presented in Figure 5.4 were collected 4 to 10 days after significant rain events. With the exception of two samples the DOM fractions were similar throughout the season. As with the pond samples the HPI fraction was an important component of DOM and ranged between 31 to 78 %. The HA fraction was absent from the summer sample from ditch 2D however it was important in the other samples and ranged between 10 to 37 %. The HPO fraction was absent from the fall sample collected in ditch 4D and ranged between 16 to 50 % in the other samples. Electrical conductivity and hydraulic head was measured in piezometers transects at the restored and cutover site. Measurements indicated a strong vertical gradient of increasing electrical conductivity with depth (Day and Waddington, unpublished). Groundwater samples were collected from the piezometer transects on three occasions during the growing season at the restored and cutover sites and more frequently in piezometers at pond 3P1. DOC concentrations of these samples indicated a strong vertical gradient in the peat matrix with higher concentrations in the surface layers. Overlaying DOC concentrations at the outflows showed that concentrations seen at the outflows were more similar to groundwater samples from the top 75 cm of peat at both the restored and cutover site. Samplings prior to September 6th were not complete for



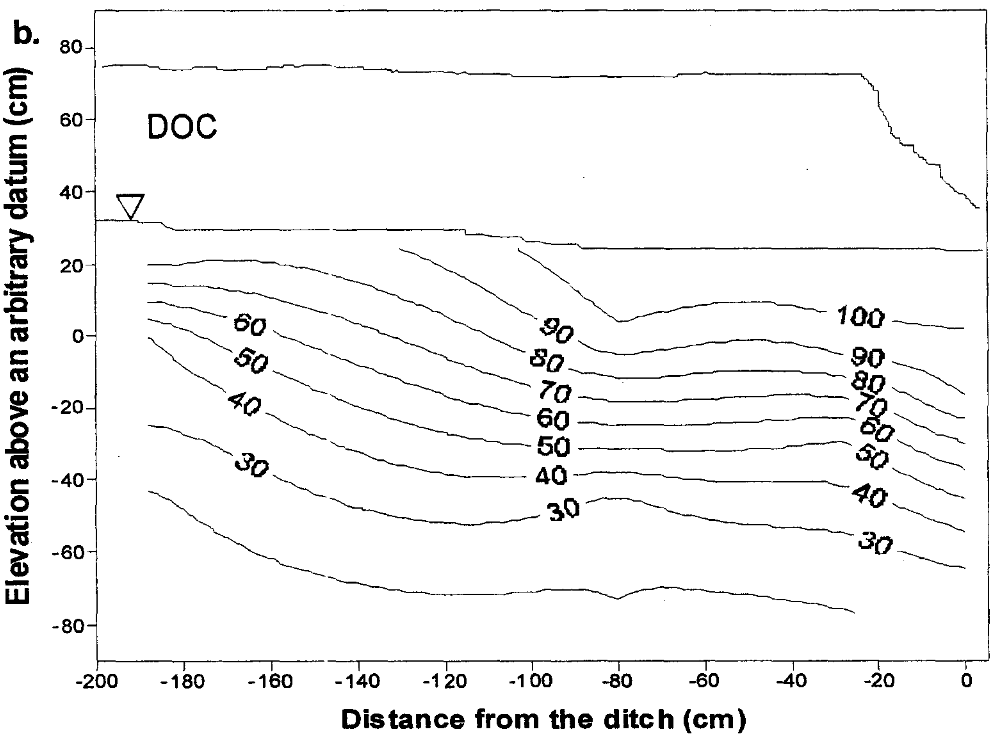


Figure 5.5 Flownets (a.) and DOC concentration (mg L^{-1}) gradient at the cutover site across the minor transect in across field 10.

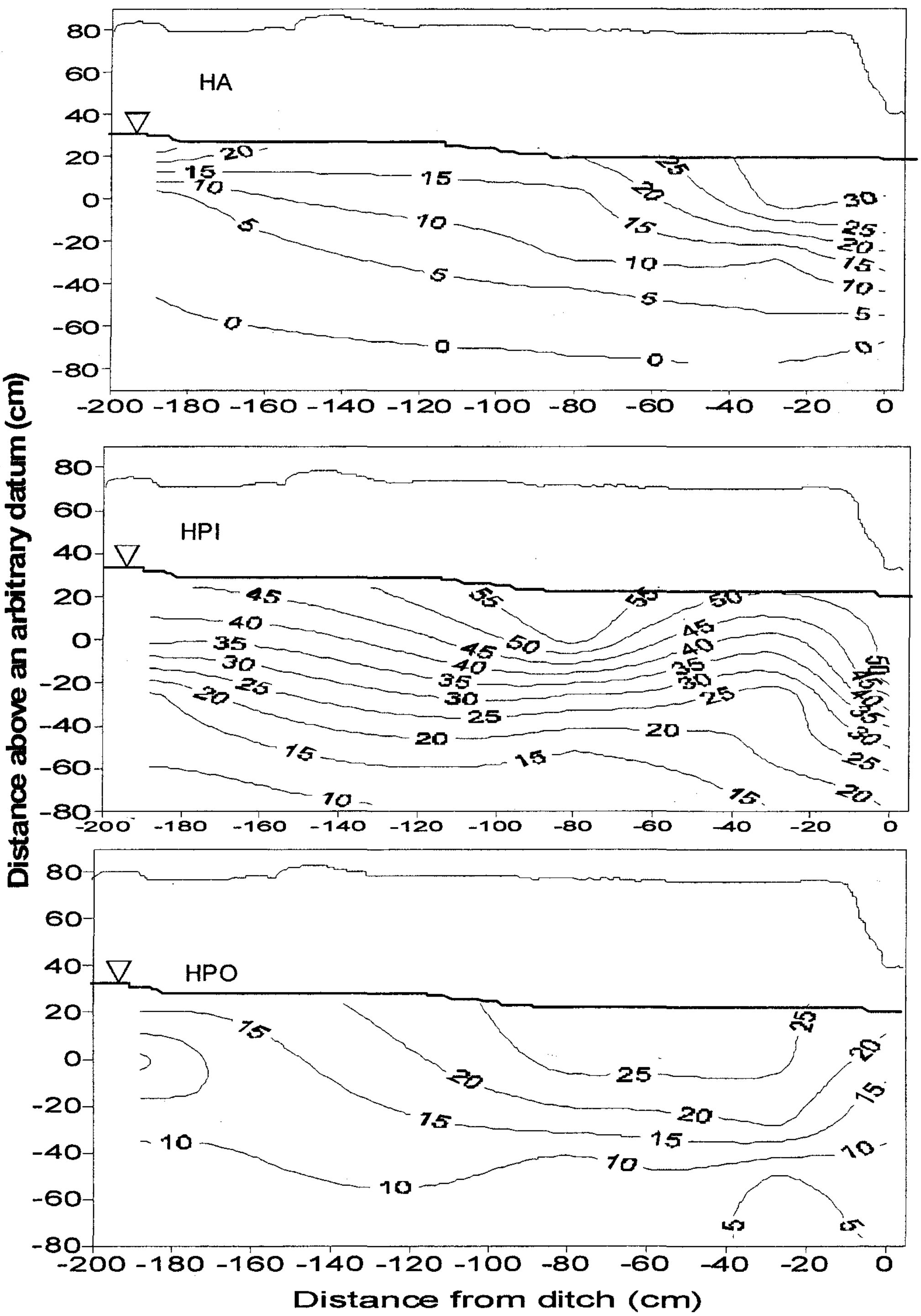


Figure 5.6 Distribution of DOM fractions (concentration mg L^{-1}) along the minor transect across field 10 at the cutover site (September 6, JD=249).

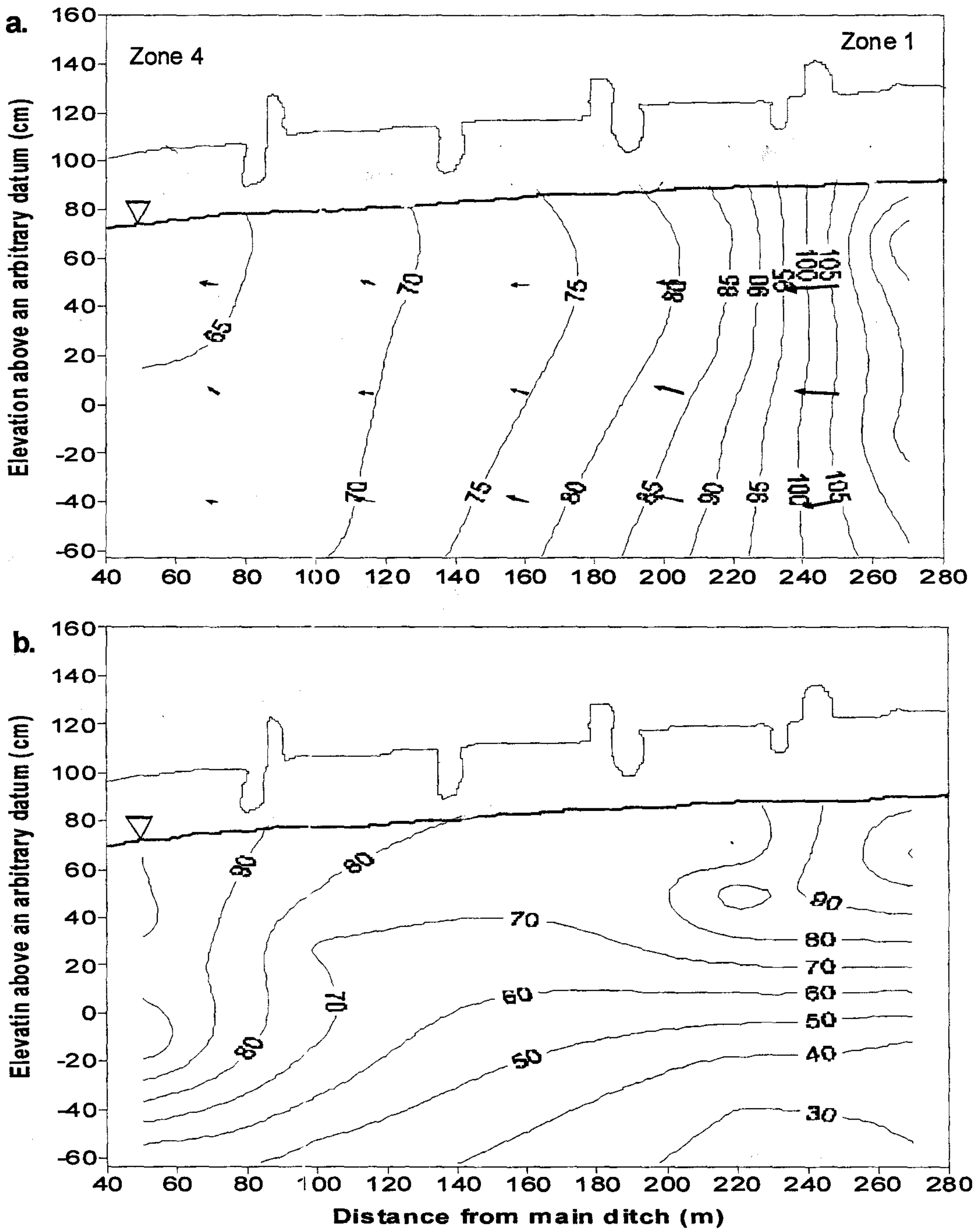


Figure 5.7 Cross section along the main transect of the restored site illustrating flownets (a.) and DOC concentration (mg L^{-1}) distribution within the peat matrix

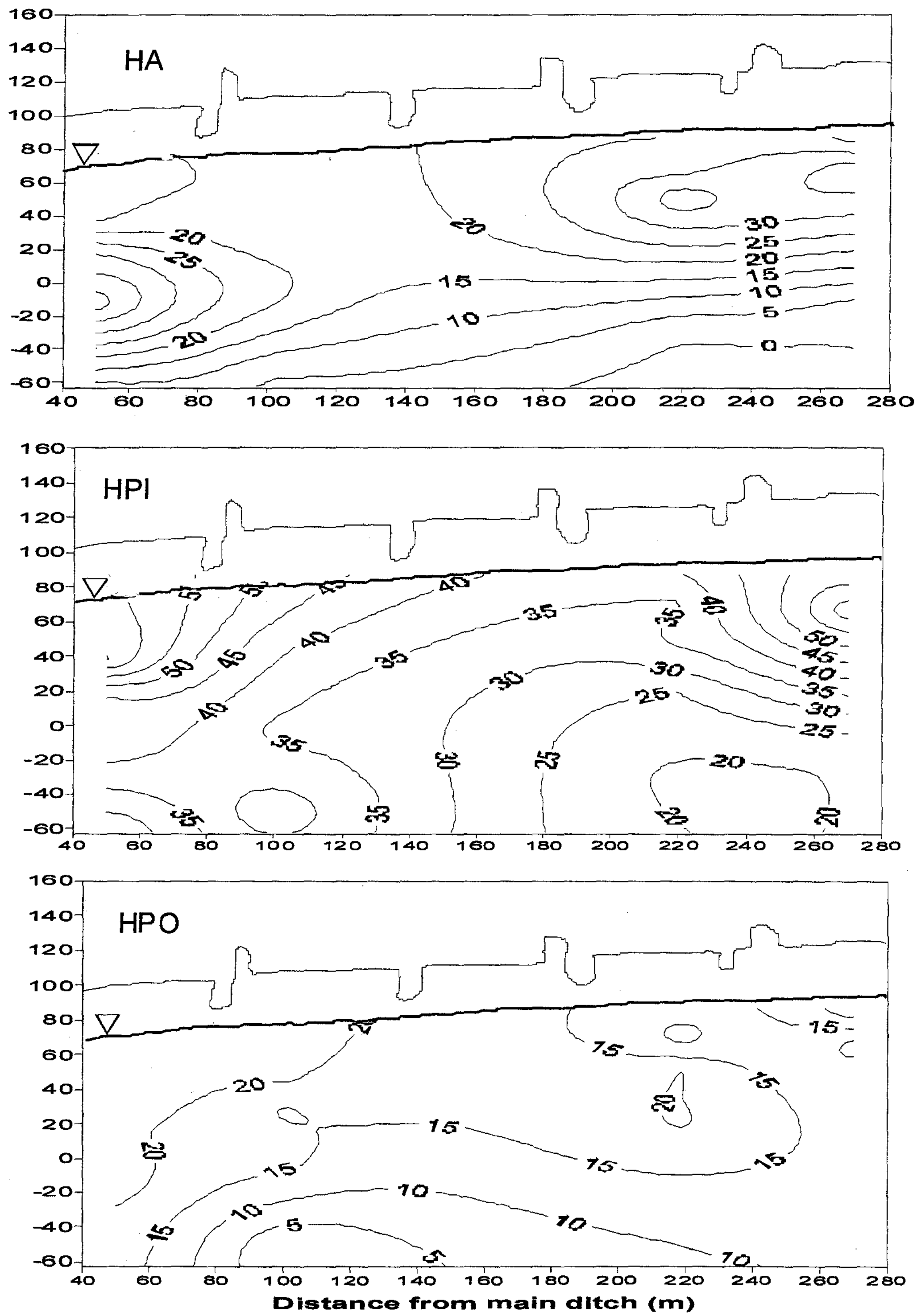


Figure 5.8 Distribution of DOM fractions (concentration mg L^{-1}) along the main transect of the restored site on September 6 (JD= 249).

the entire transect therefore we are only presenting data for this date (Figure 5.5 through 5.8).

Hydraulic head measurements at the cutover site indicated a downward movement of ground water into the peat profile however, near the drainage ditch located at the eastern end of zone 10, water was moving out of the ditch and into the peat matrix (Figure 5.5 a.). DOC concentration isolines were fairly flat as DOC concentrations decreased with depth (Figure 5.5 b.). Concentrations ranged between 15.3 mg L^{-1} in the deepest piezometers near the center of the zone, to 95.1 mg L^{-1} near the drainage ditch. Groundwater directly below the drainage ditch contained the highest amount of DOC and concentrations decreased with distance from the ditch. DOC fractions were distributed similarly with concentrations decreasing with depth (Figure 5.6). Interestingly HA fraction was the lowest in water samples collected from depth (Figure 5.6.) while HPI and HPO fractions were found to be present in increased concentrations.

At the restored site a larger area was investigated. Here ground water was found to move on two levels (Figure 5.7 a.). In the near surface peat, water was moving horizontally from Zone 1 to Zone 4, while at depth, some upwelling was noted from Zone 1 into higher peat layers of Zone 4. In general, a similar trend of decreasing DOC concentration was seen as in the cutover site (Figure 5.7 b.). Measured DOC concentrations ranged between 31.8 mg L^{-1} at 150 cm below the surface in Zone 2, and 111.2 mg L^{-1} at 70 cm depth in Zone 1. Areas with increased DOC concentrations were noted in Zone 1, which is located near a

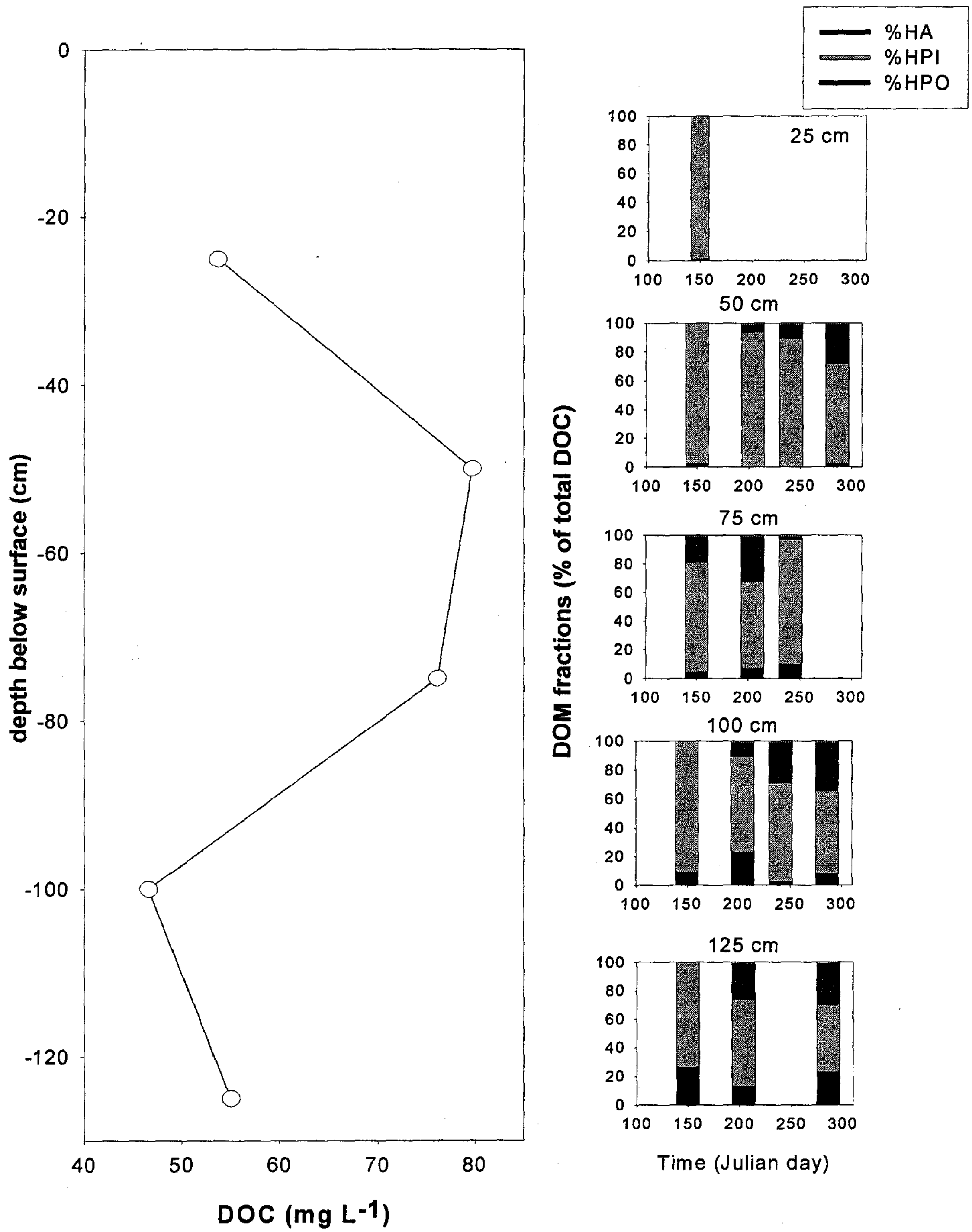


Figure 5.9 Average DOC concentrations and DOM fractions at various depths at the natural site.

natural forested site, and in Zone 4. As with the comparison site, the HA fraction was observed to be in decreasing proportions with increasing depth (Figure 5.8). The areas of high DOC concentration noted previously also coincided with areas where the HA fractions were found to be in highest proportions. These areas also contained the highest concentration of HPI which fraction was found to be the dominant fraction in ground water samples. There was less variation observed in the HPO, which was a more important fraction in the mid layers of the peat matrix.

As mentioned in a previous section DOC concentration at the natural site did not change significantly through the study period. The average DOC concentration profile observed at the natural site is presented in Figure 5.9. DOC concentration was low in the surface layer and increased with depth up to 75 cm and decreased once more in deeper layers. The HPI fraction was the most important fraction of DOM at this site. Its proportion ranged between 47 to 98%, however, its importance decreased with increasing depth. The second most important fraction was the HPO fraction that was found to be in similar proportions through the peat profile and reached up to 35% of DOM. Opposite to what was observed in the restored and cutover site, the HA fraction became more important in the deeper peat layers, increasing to a maximum of 27% in deeper porewater samples. A seasonal trend was also noted in DOM fractions. Spring samples contained more HPI fraction and very little HA or HPO. As the season progresses the HPI fraction decreases while both HA and HPO fractions increase. Slightly less variation was found in water samples collected from depths of 100 – 125 cm and strongest changes were observed in the upper 75 cm of the peat layer.

5.2 Discussion

The measurements of DOC export from a peatland are often made difficult by the lack of natural channelized outflows. Bogs often form in depressions that are hydrologically isolated from the surroundings and the ground water systems. The Bois-des-Bel peatland was such a peatland and in order to assess the changes that occurred during restoration two artificial channels were dug which collected runoff from the restored and cutover site respectively. In this section the quantity and the quality of DOM seen at these outflows is discussed, then a discussion of the internal DOM dynamics followed with relevance to what is measured at the outflows.

5.2.1 Hydrology

In this study, the changes that occurred in a cutover peatland were monitored from a stage of abandonment to restoration. One of the main changes was in the hydrology of the site. Evaporative loss was the most important water loss process at the restored and cutover site and dominated the water balance. Runoff was an order of magnitude smaller than evaporation (von Waldow, 2002). This relationship did not change over the three study seasons. However, the significance of runoff decreased after restoration, making up only about 2 to 3% of the precipitation input compared to 15% prior to restoration during the same time period. Blocked drainage ditches reduced flow from the restored site, surface bunds retained more water in the system following spring melt, and heavy rain events, which resulted in higher average water table. Discharge from this site was more continuous and the site experienced fewer dry days after restoration compared to the cutover site. Fluctuations in water table were more significant in 2001 at the restored site, when there were more days when water table dropped below that observed at the cutover site. Another interesting observation in 2000 was that after several rain events in the summer, soil moisture did not change but the water table increased (von Waldow, 2002). This finding suggests that macro-pore flow may be an important flow path at Bois-des-Bel. Observations of the peat composition at both sites indicated that there was a large amount of woody debris throughout the entire peat profile.

5.2.2 Dissolved organic carbon export

The importance of DOC exported from natural peatlands has long been established. Many studies indicate that a major source of DOC in natural waters are upland peat systems (Urban, 1989) and this source becomes increasingly important during periods of high runoff, when runoff generating pathways shift and include wetland systems (Scott et al., 1998; Schiff et al., 1998). Estimates of DOC export from northern peatlands range from 1 to 48 g C m^{-2} yr^{-1} (Urban, 1989). However, exports are smaller in wetlands such as bogs where relief is negligible and here DOC export values are more likely to be less than 10 g C m^{-2} yr^{-1} (Fraser et al., 2001). Summer exports from the restored site were within this range. Export at the natural site was much lower as the natural peatland has no natural surface water outflow.

Fraser et al. (2001) stated that DOC could be an important component of the carbon budget of sites where gaseous carbon fluxes are low. At the Bois-des-Bel peatland the major carbon loss to the atmosphere is due to respiration. Estimates for 1999 for CO_2 flux based on the results of Waddington and McNeil (2002) are between 520 and 703 g C m^{-2} for the study period. The DOC flux during this study period was only 1 to 1.5% of this flux. The year after restoration Petrone et al. (2002) measured CO_2 fluxes at the restored site and found them to be 358 and 478 g C m^{-2} at the cutover and restored sites respectively. While CO_2 fluxes increased at the restored site DOC export decreased overall and it was 0.7 % of the CO_2 flux. Although there was a 27 % decrease in precipitation from 1999 to 2000, runoff at the restored site decreased more significantly and was about 84 % of that measured in the previous year. Since hydrology has a controlling influence on DOC export (Urban et al., 1989; Waddington et al., 1997; Fraser, 2001), it is not surprising that a change in the hydrologic conditions brought about by restoration decreases DOC export as well. The export of DOM may be small compared to gas fluxes, however, low concentrations of DOC have the potential to acidify natural waters of low alkalinity (eg. Gorham et al., 1988;

Urban et al., 1989), as well as affect nutrient and metal cycling. Therefore, the downstream implications of high concentration of DOC release are great.

5.2.3 DOC concentration at the outflows

DOC concentrations measured at the three study sites are within the range of other reported values. The average concentration at the natural site (64.1 mg L^{-1}) was within reported values, however it is in the upper range (eg. 2 to 40 mg L^{-1} Moore, 1987; 29 to 47 mg L^{-1} Bourbonniere, 1989; 40 to 70 mg L^{-1} Fraser et al., 2001). There are few reports of DOC concentrations from harvested and abandoned sites. Glatzel et al. (2002) reported a wide range of DOC for abandoned peatlands ranging from 35 to 625 mg L^{-1} and measurements at the cutover site certainly fall in this range. They also measured DOC concentration at several restored peatlands in the Bas St. Laurence region and found DOC to range between about 30 to 70 mg L^{-1}. Concentrations at the restored site of the Bois-des-Bel peatland are higher and stay consistently high for two consecutive years after restoration.

In a model for examining shifts in DOC concentration after harvesting and restoration, Glatzel et al. (2002) proposed a shift to higher DOC in actively harvested sites, which when abandoned, would produce lower DOC concentration, as the readily degradable carbon decreases. They further proposed that DOC concentrations remain low following restoration since degradable carbon is still absent. Concentrations would than increase once peatland vegetation becomes more established. Findings of this thesis do not follow this model. While DOC export from the restored site was lower than that from the cutover site, DOC concentration was found to increase each year for two consecutive years after restoration, and was higher than the cutover site. These results are consistent with the findings of Hughes et al. (1998) and Fenner et al. (2001). They found an increase in DOC concentration of rewetted peatlands, reporting a 20 times increase in concentration, which stayed consistently high for a four year study period. Hughes et al. (1998) suggested that it was not simply a matter of increased leaching due to higher moisture conditions, which should have decreased as time passed, but a change in the way carbon is processed within the system. This idea is further substantiated by findings of Petrone et al. (2002) who found a 25% increase in CO_2 flux from respiration at the restored site of the Bois-des-Bel peatland after restoration.

To investigate controls on the release of DOC, correlations between discharge, soil moisture, water table position and DOC concentrations were examined. Poor correlations found between DOC concentration and discharge ($R^2 < 0.52$) in all three study seasons are consistent with reports by Hinton et al. (1997) who found no correlation at two small catchments dominated by wetlands. Correlations between temperature and DOC were found to be more important than those between soil moisture, water table position and DOC at the cutover site. The opposite was found at the restored site where soil moisture and water table had a stronger correlation than temperature. von Waldow (2002) found a difference between the unsaturated zone of the restored and cutover sites. At the cutover site, during summer storm events, soil moisture was not sustained, while it was sustained at the restored site, further indicating that moisture conditions were improved by restoration. These results suggested that the change in DOC release mechanism that occurred from a cutover to a restored site was due to the hydrologic control on DOC release. While the cutover site was more aerated, it was also much dryer, which negatively affected microbial communities and the transport of DOC within the system. Since the restored site stayed wetter after storm events, there was an increased potential for leaching and distribution of DOC within the peat matrix. Also a moister environment could have positively affected microbial activity thus increasing the release of DOM.

5.2.4 Seasonal trends in DOC

Seasonal variations in DOC concentrations are consistent with findings by other researchers (Moore, 1987; Bourbonniere, 1989; Scott et al., 1998). DOC concentrations increased during the summer months when conditions were dryer and both plant and microbial activity were highest. Low concentrations in the fall of 1999 were not repeated in the following two years. Concentrations during this time decreased to a minimum of 33.2 and 36.7 mgL^{-1} on September 14 and 23 at the restored and cutover site respectively. This period was also the time when the most significant rain event of the three-study periods (51.2mm) happened at the site. This drop in DOC concentration was most likely due to dilution by rainwater, however, there was no significant correlation found between DOC concentration and discharge during that year. The correlations for the other years were also not very significant indicating that, in addition to hydrologic control, there are other factors affecting DOC concentrations, implying a close relationship between the activity of the microbial community and DOC release.

Seasonal variations were much greater at the two impacted sites where DOC concentrations increased almost two-fold in spring compared to the natural site where DOC concentrations were much more stable all year. The increased production of DOC, at the restored and cutover site, could be attributed to the changes that occurred to the impacted sites. Wind-Mulder et al. (1996) studying several cutover peatlands found that these sites become more minerotrophic compared to the adjacent natural peatlands. Nutrient and elemental composition of both peat and water samples at these sites were higher, and resemble a fen to rich fen environment, which are considered to be more productive ecosystems compared to bogs sites, where nutrient and elemental concentrations are much lower (Wind-Mulder et al., 1996). Minerotrophic conditions can increase microbial and plant activity at the site, which in turn can increase DOC production. Also water tables at the restored and cutover sites fall further below the surface than at the natural site. Thus the aerobic region of the peat layers are much larger where oxidative degradation of organic material can occur.

The above discussion leads to the question of when we should expect to see DOC concentrations at the restored site similar to those at the natural site?

The leaching experiment, reported in Chapter 4, demonstrated that peat found at the restored and cutover sites has the potential to release DOC steadily for an extended period of time, especially in aerobic and warm conditions. At both the restored and cutover site there is an approximately 40 cm thick layer of peat within which water table fluctuates and aerobic conditions are common. Following the observations of Wind-Mulder et al. (1996), it follows that these exposed layers are potentially more nutrient rich than the surface layers of a natural bog, therefore, this large amount of peat has the potential to produce more DOC. Changes in DOC production should be expected only when conditions change and production is hindered. Such a condition would be an increase in the depth of the anaerobic layer and the reduction in the availability of nutrients at the site. Abandoned harvested peatlands do not redevelop peatland ecosystem where this situation can arise. These areas are re-vegetated with invasive species, such as birches, which can produce an increase in water table draw-down due to increased evapotranspiration (van Seters and Price, 2001). However even these species have a hard time establishing in the extreme dry conditions found at these sites. The key to re-establishing bog conditions is the development of an active *Sphagnum* community, which has the potential to form an acidic, nutrient poor, heat insulating and less permeable environment. The addition of *Sphagnum* diaspores to the restored site has improved the distribution of this species over the two years of the study (Campeau, personal communication), however, the growth rate of *Sphagnum* is slow. Waddington and McNeil (2002) measured the growth of *Sphagnum* cushions at a block-cut abandoned site to be between 6 to 30 mm over the growing season. If one assumes that the thickness of *Sphagnum* that is necessary for the establishment of the above mentioned conditions is the same as that of water table fluctuations at the natural site (~ 20 cm), it would take between 7 to 33 years for conditions to change. In the mean time DOC released from the site would be similar to that from a rich fen. This time estimate however does not include *Sphagnum* decomposition rates.

5.2.5 DOM character at the outflows

The quality of DOM exported from the site is also important since the molecules and macromolecules that make up DOM have different chemical character and can affect natural water systems to varying extents. There are few reports on DOM fractionation character in peatlands. Comparison between these studies was also made difficult by the different characterization techniques used. Bourbonniere (1989) used similar technique as in this experiment and his definitions of the different fractions match those used in this study. In other studies HA was not separated initially from the HPO acids, therefore, for comparison with those studies the present results are combined (HPO+HA) for comparison to HPO. Bourbonniere (1989) reported that the HPO fraction was an important component of DOM representing between 43 and 47 %, while HA content ranged from 10 to 23 % and HPI from 32 to 34 % of DOM. Fractions at the natural site of the Bois-des-Bel peatland were slightly different (Figure 5.9).

Here the HPI fraction was a more important component, followed by HPO in deeper water samples and the HA fraction, which was found to be in a similar range as that reported by Bourbonniere (1989) in the deeper water samples (Figure 5.9). DOM fractions at the restored and cutover sites were more evenly distributed and each represent approximately one third of the DOM. These values are closer to those reported by Guggenberger et al. (1994) in acidic forest soils. The shift towards more humified DOM (higher HA fraction) at the restored and cutover peatland, compared to the natural site, is representative of the land use changes that occurred at this site. The leaching experiment reported in Chapter 4 confirms this idea. It was shown that a moss dominated environment, such as the natural site, would more likely produce HPI and HPO fraction, while old humified peat exposed through harvesting would be more likely to produce all three fractions, with HA making up a significant proportion, especially at higher temperatures. While Glatzel et al. (2002) could not show significant shifts in the absorption character of DOM from harvested sites, compared to natural peatlands, Dai et al. (2001) and Kalbitz and Geyer (2002) showed increased humification of DOM in clear-cut forests and heavily impacted peatlands.

Substrate quality, moisture and temperature were three of the main controls on the release of DOM (Kalbitz et al., 2000). It was shown previously that the quantity of DOM at the restored and cutover site was affected by both soil moisture and temperature. Christ and David (1996b) found that the character of DOM was also affected by moisture and temperature, where the HPO acid fraction was more prevalent in wet conditions, while HPI acid fraction prevailed in warmer conditions. The leaching experiment in Chapter 4 showed that the quality of DOM was affected by the substrate that produces DOM. Therefore it would be expected that the different substrate and conditions at the restored and natural site would also affect the composition of DOM released from the sites. There were, however, no significant differences in the DOM composition of the restored and cutover site one year after restoration. This indicated that the overall differences in soil moisture and temperature did not affect the quality of DOM. Therefore, it was likely that substrate quality was the most important controlling factor in the overall DOM character. When the restored site was leveled, the vegetation was not completely removed from the site but was bulldozed into the drainage ditches. Since similar vegetation grew at both the restored and cutover sites the organic material producing DOM in 2000 was still very similar. This finding was consistent with results reported by Glatzel et al. (2002) who could not correlate humification index and absorbance at 280 nm to harvesting and restoration of peatlands. Based on observations of DOM character at the natural site, it is expected that as the vegetation debris degrades in the restored site and *Sphagnum* species establish, the character of DOM will also change toward that seen at the natural site. The cutover site, on the other hand, will probably not change but will remain an active source of DOC since the vegetation growing on it promotes water table draw-down further increasing the aeration of the peat (van Seters and Price, 2001).

Even though overall there was no difference between DOM characters at the sites, there were seasonal trends seen in the different fractions. Strong seasonality was observed in HPI and HA fractions while HPO fraction did not change significantly over the season. At the natural site similar trends were observed, with HPI fraction the most important early in the season and its importance decreased during the summer when both HPO and HA fractions appeared. The reports on seasonal trends in DOM fractions from previous studies are not consistent, particularly concerning the importance of the HPI fraction during the summer season. This fraction is considered to have low molecular weight, that is strongly modified by microbial activity and to contain small easily degradable molecules that are directly leached from organic materials (Bourbonniere, 1989; Guggenberger et al., 1994). HPI was found to be in larger proportions during summer months in some peatlands (Bourbonniere, 1989; Scott et al, 1998). However, others reported a different trend. Urban (1989), based on studies of elemental composition of DOM, suggested that HPI was stored in the winter when microbial activity was low, and that HPO was high in the summer when polymerization could occur. Kaiser et al. (2001), using Leeheer's fractionation technique, observed similar trends in forest soils. Sachse et al. (2001), using size exclusion chromatography, studied a natural fen and found more humic substances in the summer. These substances were found to contain humic and fulvic polyelectrolytic acids that were UV active due to aromatic groups. Fenner et al. (2001) reported an enrichment of low to mid molecular weight DOM (5000-90000 Daltons) in the spring and fall and a sharp decrease in summer. DOM fractions at the restored and cutover site are more consistent with this later group of reports (Figure 5.2).

The seasonal variation in DOM character suggests some possible controls on DOM release mechanisms at the restored and cutover sites. These are (1) physico-chemical aspects that affect the dissolution of DOM to varying extents, (2) the transformation of one component to another that affects observed concentrations, and (3) hydrological controls that influences the release and transport of fractions.

The HPO fraction presented the least amount of variation. With the exception of two measurements, its proportionality did not change significantly over the summer period. Similar findings were reported by Bourbonniere (1989). Christ and David (1996 b), based on laboratory leaching experiments, suggested that this fraction would be more prevalent in wetter conditions implying moisture controls on this fraction. However, the lack of seasonality, during periods of varying moisture conditions, indicates that this is not such an important factor in the release of this fraction at these sites. Since there were no changes in this fraction, transformation and degradation of this fraction over the season cannot be established. Guggenberger et al. (1994) further concluded that the HPO fraction has the closest relationship to plant remains and has fewer signs of microbial degradation which is consistent with the view that its production is mainly affected by direct leaching form organic materials. In laboratory leaching experiments of forest soils, Christ and David (1996a) found that existing HPOA+HA in soil solution can inhibit further release of this component by 40%, and concluded that the dissolution of this fraction was more affected by such inhibition than by microbial activity. These results seem consistent with each other and explain the invariability seen in HPO during the summer season at the restored and cutover site.

The HA and HPI fractions follow hydrologic conditions, with periods of high flow correspond with low HA and high HPI, while low flow with high HA and low HPI. The characters of these fractions can explain this relationship. HA is the most hydrophobic portion of DOM and contains large molecules that are highly oxidized with a strong aromatic character (Bourbonniere, 1979). Due to these properties, this fraction is difficult to dissolve into the aqueous phase, particularly at pHs normally found in peatlands. Therefore in systems where water passes through the matrix very quickly, very little of this component will be able to enter the solution, while during stagnant periods, increased amounts of HA can be mobilized. HPI on the other had has low molecular weight, readily dissolves in water and thus can be easily mobilized within the peat, even when water moves quickly through the peat matrix. Christ and David (1996 a.) found that this fraction was increasingly mobilized during frequent rewetting. Therefore, the shift in these fractions during the transition from spring to fall can be explained by the increased flushing of the HPI fraction during the high flow period and the retention of HA. As more input of HPI occurs in the summer, due to increased microbial activity, a further shift occurs, and HPI is flushed again during the fall.

However, another explanation may be equally valid which supports the two general theories on the formation of the HA fraction. This involves the release from plants through successive microbial degradation and the building up from smaller components. The changes that are mirrored between HA and HPI suggests a transformation of HPI fraction to HA. This is further supported by the conditions that exist during the summer period. Water table, during that time, is low. Therefore, the aerobic layer is larger, and increased temperatures stimulate microbial activity, producing an environment where oxidative polycondensation, a process that can also produce HA, is favoured. The HPI fraction contains compounds that are highly desirable for microbial utilization, therefore, they are short lived within the soil matrix (Guggenberger et al., 1994). Increase in HPI content toward the end of the summer can be explained by both an increase in hydrologic activity at the site with increasing frequency of rain events, as well as the beginning of senescence of the vegetation.

Water table fluctuations at the natural site were less significant compared to the cutover and restored sites, therefore, the hydrologic control on the release of different fractions is less significant. Instead a stronger biological imprint is evident in these samples. The early part of the season was dominated by the HPI, which then successively decreased as the other fractions appeared. Urban (1989) explained this pattern with the storage of the HPI fraction during the winter when microbial activity is low and the subsequent decrease when microbial activity increases. The appearance of both HA and HPO during this later part of the growing season is reflective of the increased input of fresh vegetation, the degradation of organic material accumulated in the peatland, and the production of larger more hydrophobic compounds through microbial activity.

While DOC concentrations were poorly reproduced in the leaching experiment, the character of DOM at the different sites was similar to the major vegetation types analyzed. Water from the *Sphagnum*-dominated environment of the natural site was similar to that observed in DOM leached from mosses. DOM from the restored and cutover sites was slightly different. While both sites are dominated by highly degraded peat, their leaching character and the effect of environmental conditions were not well reproduced in water samples taken from the site. This indicates that other vegetation types can play an equally important role in the DOM character at these sites. Further this also demonstrates that other aspects of DOM production and distribution can have a strong effect on the DOM character seen.

5.2.6 DOC cycling within the peatland

Decreasing vertical DOC concentration gradient such as those found in the natural, restored and cutover peatland have been reported by other researchers (e.g., Moore, 1987; Bourbonniere, 1989; Waddington and Roulet, 1996). However, there are also reports of increasing DOC concentration with depth as well as no concentration gradient within natural peatlands (Moore, 1987; Waddington and Roulet, 1996) A common conclusion of these reports is that hydrology has a significant effect on the distribution of DOC (Marin, 1990; Waddington and Roulet, 1996). As well, elemental concentration can also affect the solubility of DOC (Moore, 1987). Waddington and Roulet (1996) reported a strong effect of evaporation and dilution of DOC in a Swedish peatland, where concentration gradients reversed during dry conditions compared to wet ones. During the three sampling periods at the restored and cutover site, concentration gradients did not change nor did the vertical gradient in the natural peatland. However, the possibility that DOM might be concentrated in the surface layers cannot be ruled out, since evaporative losses were very important at the site. Moore (1987) suggested that a well-developed DOC gradient, combined with low hydraulic conductivity and strong vertical gradients in electrical conductivity, can indicate slow vertical mixing of the peat water column. Thus concentration differences arise from slow water movement and slow production. This may certainly apply to the cutover site, where the DOC gradient is well defined even with weak vertical downward flux of water. The low DOC concentrations found at depth were similar to those reported by Schiff et al. (1998), who found very low DOC concentrations in degraded peat at depths of up to 8 m in a natural peatland. A similar trend to the DOC concentration was seen in DOM character, where all fractions were found to decrease with depth. The loss of HA can be indicative of the increased mineral environment in deeper layers and, therefore, increased precipitation due to interactions with iron and aluminum ions. The leaching experiment discussed in Chapter 4 also indicated that HA fraction was less likely to form under anaerobic than under aerobic conditions. Since peat found at depth is most likely to experience anaerobic conditions than is surface peat, it is likely that the production of HA is hindered by anaerobism at depth.

The transect at the restored site was more extensive and a different DOM distribution was observed. While the DOM profiles of Zones 2 and 3 were similar to that at the cutover site, Zones 1 and 4 exhibited two areas of increased production. Increased production in Zone 1 can be attributed to the changes that occurred during the restoration of this site in the previous fall compared with the other zones that were restored one-year prior to that. The close proximity of this area of high production to the surface suggests that the restoration measures, applied in this zone during the previous fall, may have had an effect on DOM release. During restoration fresh straw mulch, *Sphagnum* diaspora and phosphate fertilizer were applied, therefore, providing fresh organic material as well as nutrient stimuli for microbial degradation. This is further indicated by the presence of high concentrations of both HA and HPI. High proportions of HPI are strong indicators of an active microbial community while HA indicates a prominent oxidative environment.

The area of increased production in Zone 4 extends much deeper into the peat profile compared with that seen in Zone 1. There is some input of deeper ground water into this area (Figure 5.7 a.), however, this water has low DOC concentration. Therefore the local conditions are responsible for the high DOC production. The leaching experiment showed that deeper layers of peat from the restored site were more productive than the surface layers. Since such high concentrations were not observed in Zone 2 and 3 at similar depth, other factors must also exist that control the release of DOC. Zone 4 remained the wettest during the growing season and was the site where the most extensive ponding occurred after prolonged storm events. The old drainage ditches containing fresh organic material frequently flooded this area. This zone also possessed an active plant community, therefore, it is possible that higher moisture conditions as well as inputs of fresh organic material increased the DOC production of this site. All three fractions were in high concentration here. The HPI fraction in the top 75 cm of peat can be explained similarly as in Zone 1 with increased microbial activity due to favorable conditions, while the deeper HA hot spot is more of a result of the increased production by this layer. The leaching experiment showed that, under warm conditions, these deeper peat layers could produce a higher proportion of HA than the surface layers, even under anaerobic conditions.

Microtopographic features, such as blocked ditches and ponds, can play important roles in determining the hydrologic conditions of the site. These features also present potential environments for both the production and the re-distribution of DOC within the site. It has been noted that blocked ditches can reduce water table drawdown in adjacent peat profiles during dry conditions (Price, 1997; Schlotzhauer and Price, 1999). A detailed examination of pond 3P1 and its surroundings was used to substantiate this claim. There are two possible sources of DOM in this pond: the surrounding peat matrix and production within the pond. There was sparse vegetation in the ponds mainly consisting of two small shrubs at the north end. Algal blooms, that were common in ditches, were not noticed in this pond. The photic zone of this water was very shallow, about 10 cm, due to the high colour, therefore internal production was probably not very significant. Thus it was likely that the autochthonous input of DOC in this pond was insignificant and the high DOC seen originated from the surrounding peat. Measurements of DOC concentrations of groundwater samples to the north of this pond further confirm this conclusion. Pond-water concentrations are more similar to those from the top 75 cm of the peat while deeper groundwater concentrations are significantly lower. This region also coincides with the area where water table fluctuates during the growing season and hydraulic conductivities are higher (von Waldow, 2002). It is likely that this region would be responsible for the influx of high DOC into the ponds. Concentrations in the pond were slightly higher than the DOC concentration measured in the top 75 cm of the peat, however, the weak positive correlation between water level and DOC concentration in the ponds did indicate that evaporation from the ponds affected DOC concentrations. A similar mechanism is thought to operate in the ditches. The main difference here, however, is that these depressions contain shrub and tree debris removed during restoration. The leaching experiment demonstrated that this vegetation type has a high potential of releasing DOC in a very short term. Therefore, addition of water into these depressions can produce high DOC. Thus the main sources of DOC input are from the peat matrix as well as production from within these depressions.

The results of the study into the internal distribution of DOC have shown that DOC at the outflows is most similar to water found in the ditches, ponds and the top 75 cm of the peat matrix. Schiff et al. (1997) obtained similar results when they analyzed the carbon isotopic signature of DOC from different sources. They found that most of the DOC exported from wetlands was younger than the surrounding peat matrix, being produced from vegetation debris in the surface layers. The similarities found in this study could lead to the conclusion that the ditches and the ponds are an important control on the DOC observed at the outflows. Examining the character, however, indicates that there is a large amount of internal variation within this peatland. Peat, unlike other soil media, can act to retard movement of DOM also present a source for it. Therefore the DOM character of input water will certainly change as it passes through this matrix. While DOC export from a peatland can be quantified by measurements of concentration and water flux in a pond (Fraser et al., 2001), it is important to look directly at the outflow when characterizing DOM, since internal variation in DOM is great.

There is no hydrologic evidence to connect the ditches and the ponds to the outflow. However, a notable exception is ditch 4D that mirrors the DOM character seen at the outflow throughout the study season. It is also important to note that the contribution of this ditch is more important during wet conditions since these samples presented here were collected when water was present in this depression 4 to 10 days following rain events. It is possible that the importance of this ditch as a source of DOM at the outflow diminishes in periods of extended dry conditions, when the main source of water and DOC at the outflow is most likely the peat matrix in the vicinity of the main drainage ditch.

Not all peatlands were left with as much peat on the surface after harvesting as the Bois-des-Bel peatland. Peat thickness usually ranged between 0.5 to 1 m (Wind-Mulder et al., 1996). As deeper layers of peat were exposed through harvesting highly humified material was exposed resulting in a lower quality substrate for DOM production. It was shown here that the layer of water table fluctuation was the most important layer for DOM production by microbial degradation. Therefore, environmental conditions that affect this layer will also affect the DOM production from the site.

5.2.7 Implications for restoration

The restoration of the cutover portion of the Bois-des-Bel peatland had the goal of presenting all the different aspects of peatland restoration that have been implemented at other sites in Canada. This study has identified that DOC export decreases significantly following restoration due to changes in the hydrologic conditions of the site. It will be further identified that DOC export can be further decreased by restoration during the snowmelt period, the most significant export event of the year(Chapter 6). Therefore restoration of a cutover peatland immediately following abandonment is important in controlling DOC export from the sit.

There was no significant difference found between the character of the DOM from the restored and cutover sites one year following restoration. This was probably the result of the effort to mimic conditions commonly found at freshly abandoned cutover peatland, which involved the removal of all vegetative material from the peat surface, which was consequently discarded into the drainage ditches. The vegetation found in these ditches was found to have high potential for DOM production (Chapter 4). These areas were important in to the character of DOM seen at the outflow. Furthermore, CH_4 flux measurements at this site have indicated that these ditches were areas of high CH_4 production (Day, personal communication). Therefore, these ditches provide the conditions for the increased production of DOM as well as other gaseous carbons further increasing the loss of carbon from the site. There are two ways to remedy this problem: (1) leave existing vegetation intact and do the restoration without the removal or (2) remove the vegetation completely from the site, which in both cases eliminates the input of high quality carbon to the system on a very short time scale.

5.2.8 Summary

Restoration improved the moisture conditions at the site, making conditions more favorable for *Sphagnum* reestablishment. DOM export decreased when runoff patterns changed after drainage ditches were blocked. DOC concentration increased after restoration, due to improved moisture conditions for two consecutive years. It is expected that concentrations will remain high until water fluctuations in the matrix decrease and a active *Sphagnum* layer develops.

Substrate quality was the most important controlling aspect of DOM character at the sites, and no differences could be observed between the restored and cutover site, during baseflow conditions. Seasonal variation of DOM fractions was found to be greatest for HA and HPI. The variation of these fractions was affected by their water solubility, the changing hydrologic conditions during the year, and by their metabolism, that mainly involved the degradation of HPI and formation of HA during warm conditions. A vertical gradient in DOC concentration and DOM character existed within the peatland. While DOC concentrations were similar in the ponds, the ditches, the catchment outflow, and the top 75 cm of peat, the character observed in these areas was different, indicating the strong control that the peat matrix has on DOM release.

The restoration of cutover peatland following harvesting activities was important in reducing the annual DOC export. The removal of vegetation at the restored site during restoration created a pool of fresh organic material that was produced high quality DOM. Therefore, it is important to limit the availability of this material at the site either by removal or by choosing not to leave the existing community relatively intact during restoration.

CHAPTER 6: DISSOLVED ORGANIC CARBON DYNAMICS DURING SNOWMELT AND STORMFLOW IN A CUTOVER AND A RESTORED PEATLAND

6.0 Introduction

In 2001 discharge and water sampling was undertaken at the catchment outflows during the spring snowmelt and the summer months in order to study DOC dynamics at the two sites during high flow events. Snowmelt was sampled from late March to the end of April (JD = 87 to 120), with the largest event occurring in mid April (JD = 101 to 115). Three summer storms were studied in detail: a medium intensity storm with wet antecedent conditions in May (JD = 132 to 133), a high intensity storm with dry antecedent conditions in July (JD = 205) and a medium intensity storm with dry antecedent conditions in August (JD = 238 to 239).

6.1 Snowmelt

6.1.1 General hydrology

A snow survey, in mid March at the Bois-des-Bel peatland, indicated that 137 and 150 mm of snow water equivalent had collected at the restored and cutover sites respectively (Shantz & Price, unpublished data). There was no significant melt event during the winter months. Prior to snowmelt both the restored and the cutover site were discharging water at a slow rate (0.05 L s^{-1}) (Figure 6.1 a.). Discharge increased during the main snowmelt period in mid April (JD = 101 to 115) at both sites to a peak of 16.6 and 25.1 L s^{-1} at the cutover and restored sites, respectively (Table 6.1). The restored site returned to baseflow conditions sooner than the cutover site. Shantz and Price (personal communication) calculated runoff for the snowmelt period to be 517 mm and 176 mm at the cutover and restored sites, respectively, which represented 81 % and 86 % of the total runoff for the 2001 study period. However, the large runoff for the cutover site is likely due to either a failed or unblocked ditch in the north-east section of the cutover site. This likely caused large inflow to the site (see later). Runoff during this period from the restored site was smaller than that from the cutover site (data not presented) and it was "flashier" than that at the cutover site, which had a much wider peak in the hydrograph.

The snow pack in the peatland melted before that of the adjacent agricultural ditch and this differential melting rate caused flooding during the peak discharge period. During this time interval discharge was estimated using salt dilution experiments. These estimates corresponded well with direct discharge measurements made when the culverts were partially flooded. Tracer dye experiments during snowmelt indicated that flow was from the peatland to the agricultural ditch.

On some occasions (JD 110 and 112) the peat berms at the southern portion of Zone 4 (Figure 2.1) broke and water rushed into both outflows,

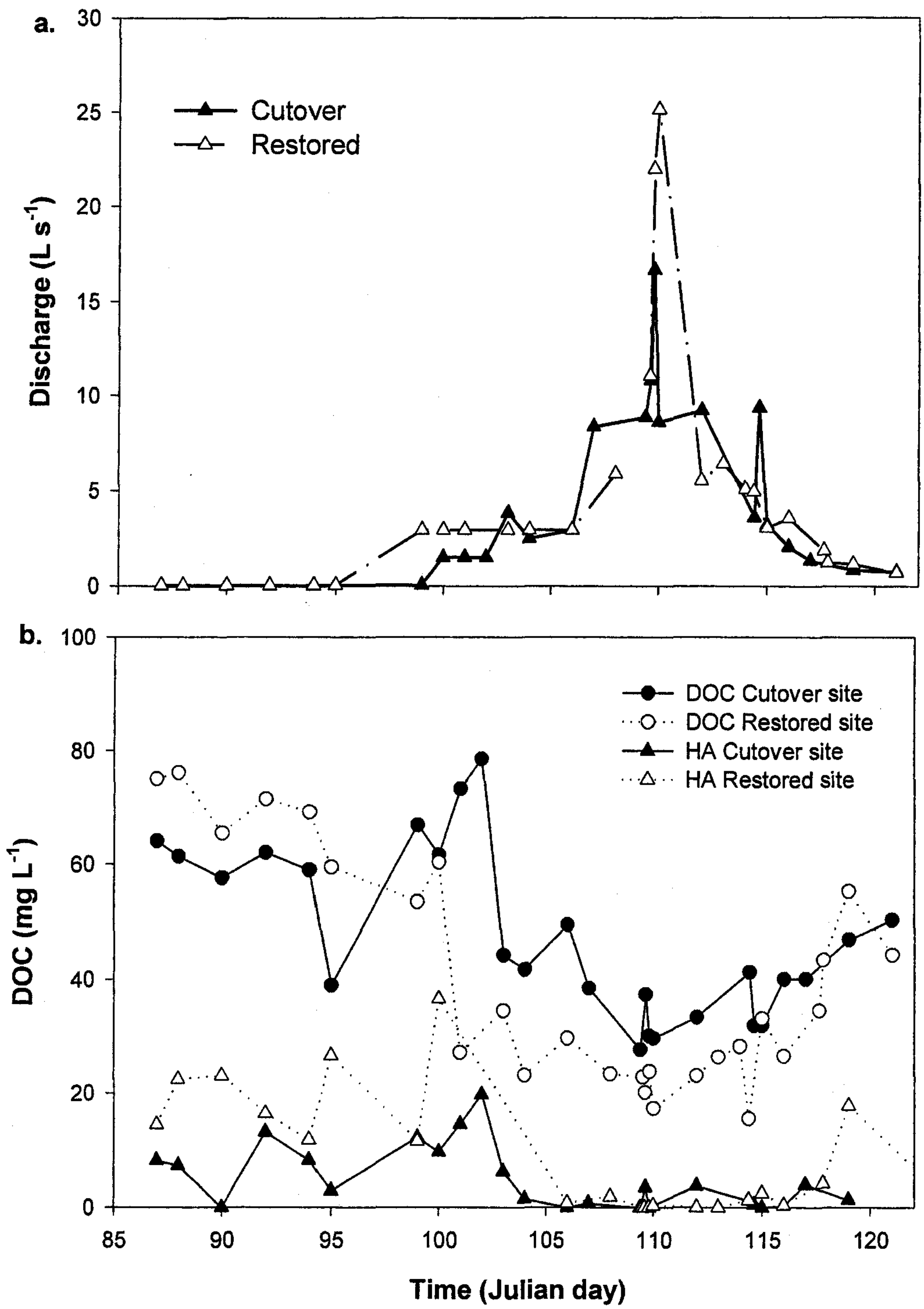


Figure 6.1 Runoff (a.) and DOC and HA concentration (b.) for the 2001 snowmelt. The main melt event took place between Julian days 105 and 115.

Table 6.1 Hydrometric variables and DOC concentration during high flow events.

Study period	**Rain** (mm)	Site	**Water table** (cm) Min.	Max.	**Discharge** ($L\ s^{-1}$) Min.	Max.	**DOC** ($mg\ L^{-1}$) Average	Min.	Max.	**DOC export** ($g\ C\ m^{-2}$)
Snowmelt	150*	Cutover	n/a	n/a	0.05	16.6	47.6 ± 14.5	27.3	78.0	43.6
	137*	Restored	n/a	n/a	0.05	25.1	42.1 ± 20.6	15.5	76.1	8.3
May	27.9	Cutover	-34.1	-21.9	0.18	2.12	58.3 ± 2.5	54.7	61.9	0.2
12-13		Restored	-15.5	+3.5	0.35	2.50	81.6 ± 5.2	75.9	97.2	0.6
July	20.4	Cutover	-38.7	-33.1	0.006	0.57	91.6 ± 6.7	76.1	97.2	0.02
24-25		Restored	-31.0	-11.0	0.05	2.5	120.7 ± 15.4	83.7	135.0	0.06
August	22.6	Cutover	-48.3	-37.6	0.002	0.06	82.1 ± 11.0	66.5	94.1	0.007
26-27		Restored	-50.4	-30.7	0.01	0.56	101.6 ± 4.4	87.4	131.4	0.02

* Pre-snowmelt snow-water equivalents.

however, this did not have a significant effect on the outflows. A drainage ditch in the northern part of the cutover site was not completely blocked and may have been contributing for a time, to the discharge measured at the outflows, however, the contribution of this ditch is not certain.

Several open water pools formed during the snowmelt period, especially in the southeast corner of Zones 3 and 4 and also in the depressions that were still present along the old drainage ditches (Figure 2.1). Surface water was actively moving between the different zones either through pipes placed in the berms to reduce water retention to a fixed level, along the boardwalks, or through breaks where the water washed out of the berms. Such water retention and movement was not present at the cutover site. Water moved from the peat fields into the drainage ditches or along the surface and then to the outflow. A solid ice layer covered the ponds in the winter, which was distinguished from the snow above by its darker colour. Ice break-up began during the major melt event (JD = 113) and became ice-free three days later. This day also coincided with the main melting of the peat profile.

6.1.2 Dissolved Organic Carbon

In general, DOC concentrations decreased with increasing discharge, and a strong negative correlation ($R^2 = 0.76$) was found between discharge and DOC concentration at the restored site, while a weaker negative correlation existed at the cutover site ($R^2 = 0.56$) during the snowmelt period. Prior to snowmelt, discharge from the two catchments was low and had DOC concentrations (60 to 70 mg L^{-1}) comparable to late summer values (Figure 6.1 b. and Figure 5. 1 c.). Overall there was no significant difference in DOC ($p<0.05$) between the two sites. The average DOC concentration during the snowmelt-sampling period was 47.6 ± 14.5 and 42.1 ± 20.6 mg L^{-1} at the restored and cutover sites respectively. Prior to the main melt event the DOC concentrations increased at the cutover site, which then decreased once water was moving faster from the site. This was not observed at the restored site where DOC concentrations decreased steadily as the melt began. During the high flow period of the snowmelt (JD = 101 – 115) the cutover site released water containing higher DOC concentration (average of 42.1 mg L^{-1}) than the restored site (average of 26.0 mg L^{-1}). The DOC concentration of the snow pack ranged from 0.9 to 1.5 mg L^{-1}.

DOC export for the snowmelt period at the restored and cutover site was 8.3 and 43 g of C m^{-2} respectively. The export from the cutover site, however, seems unreasonable suggesting that there was significant water being contributed from the upstream area where the ditch was not completely blocked or it failed.

Prior to snowmelt, all three DOM fractions were present in the runoff at both sites (Figure 6.2). At the restored site, DOM was distributed more evenly among the three components (Figure 6.2 b.), while at the cutover site, the HA fraction was in smaller proportions and the HPI and HPO fractions were more (Figure 6.2 a.). The HA fraction was in larger concentrations prior to snowmelt

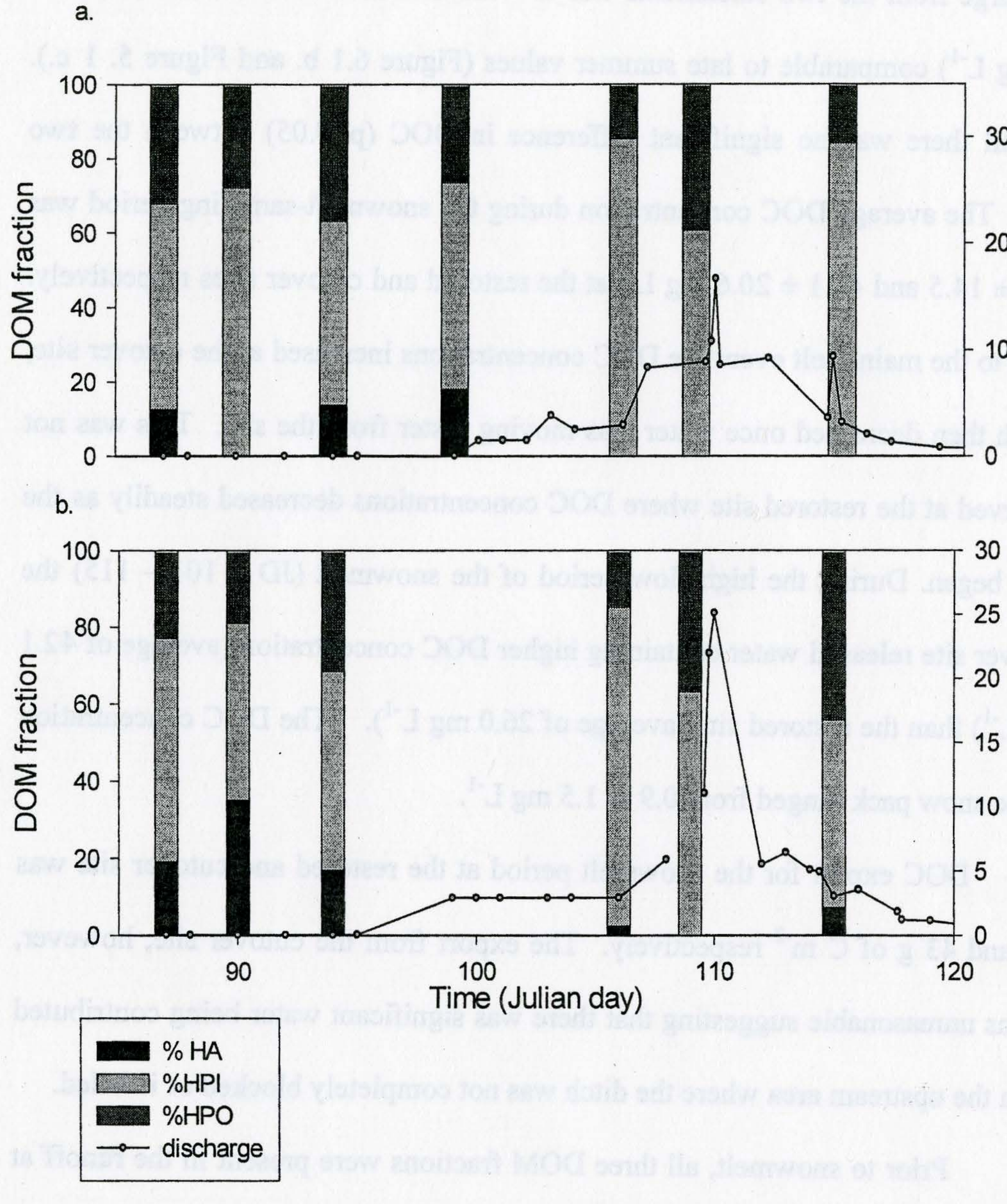


Figure 6.2 DOM fractions during the snowmelt period at the cutover (a.) and restored (b.) sites. Discharge values are inserted as a reference.

to maximum concentrations of 36.6 and 19.7 mgL^{-1} (Figure 6.1 b.), making up 60 and 18 % of the DOM at the restored and cutover site respectively (Figure 6.2). This fraction decreased to near zero values during the main melt event between (JD = 101 to 115) and increased once again after the melt subsided (Figure 6.1 b. and 6.2).

Of the other two fractions HPI was the more dominant component, representing maximum proportions of 98.8 and 71.4% of DOM at the cutover and restored sites, respectively (Figure 6.2). It remained high during the lag part of the melt at the cutover site and decreased to pre melt values at the restored site. The HPO component accounted for approximately 33% of the DOM prior to snowmelt. Once discharge increased HPO reached maximum values at 39.4 and 31 % of DOM at the cutover and restored sites respectively (Figure 6.2). Following snowmelt HPO decreased to pre-melt values (14%) that coincided with another peak in discharge. At the restored site HPO reached maximum proportions (44%) following the melt (Figure 6.2 b.).

6.2 Stormflow events

6.2.1 Hydrology

The May storm event (JD = 132 – 133) was a 27.9 mm rain event lasting 11 hours. This storm occurred early in the season, when there was still some residual ponding from snowmelt at the restored site in Zones 3 and 4 (Figure 2.1),

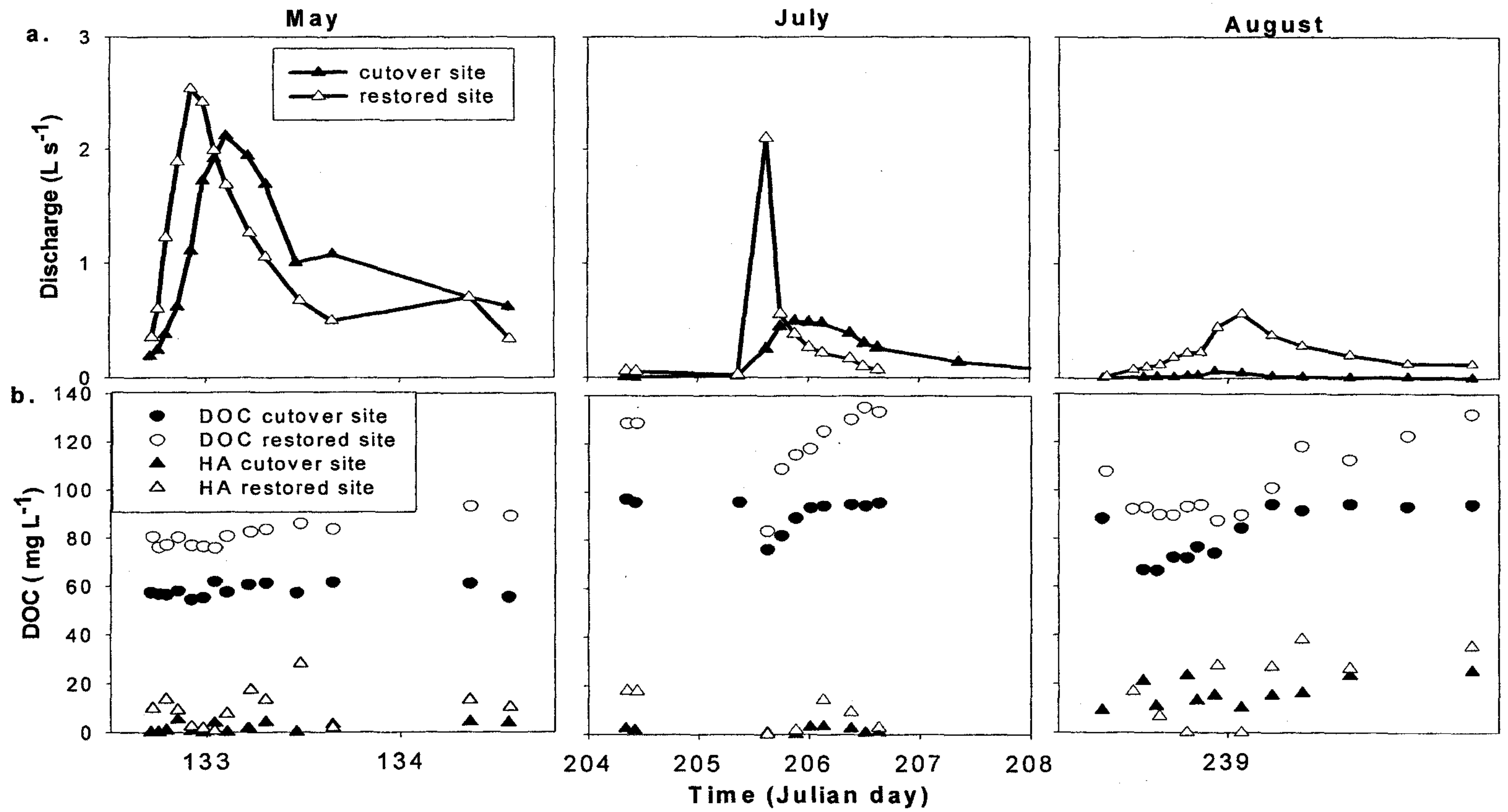


Figure 6.3 Discharge and DOC concentration during three summer storms: medium intensity storm with wet antecedent conditions in May (JD = 132 –133), high intensity storm with dry antecedent conditions in July (JD = 205), medium intensity storm with dry antecedent conditions in August (JD = 238 –239). (a.) Discharge. (b.) DOC and HA concentration.

water levels in these ponds increased during the storm and all the depressions of the drainage ditch depressions filled with water. There was active surface flow from Zone 4 into Zone 7 (Figure 2.1) and then to the main collector ditch of the restored site through a pipe placed in the berm to decrease flooding in Zone 4. At the cutover site water collected in the drainage ditches on either side of Field 10. Discharge at the cutover site during the May storm increased from 0.18 L s^{-1} to 2.12 L s^{-1} in 9.4 hours. At the restored site discharge started off higher. It increased from 0.35 L s^{-1} to 2.5 L s^{-1} in 4.8 hours. Water table at the meteorology station rose by 19 cm at the restored site and was 3.5 cm above the surface (Table 6.1). Water table at the cutover site increased by 12.2 cm and stayed below the surface (Table 6.1).

The July storm (JD = 205) was a high intensity thunderstorm lasting 30 minutes. During this time 18.1 mm of rain fell on the site. This storm followed a ten-day period when the total precipitation was 8.9 mm (Figure 5.1 a.). At this time there was no open water present at the site other than the constructed pools at the restored site (Figure 2.1). Flow at the cutover site prior to the storm was insignificant (0.006 L s^{-1}) and at the restored site it was ten times higher (0.05 L s^{-1}) but still low compared to earlier spring conditions (Figure 6.1 a.). Following the storm, discharge increased quickly at the restored site reaching the peak of 2.5 L s^{-1} in 1.2 hours. At the cutover site, peak discharge (0.57 L s^{-1}) was reached in 4.3 hours (Figure 6.1 a.). Water table position rose 5.6 cm at the cutover site and 19.4 cm at the restored site (Table 6.1). Following the storm, water level in the artificial ponds rose five cm and water also collected in the old ditch depressions at the restored site. At the cutover site water was collected in the drainage ditches.

During the 15-day period preceding the August storm (JD = 238 - 239) 31.5 mm of rain fell (Figure 5.1 a.). Water table position was low prior to the storm at both the cutover (-48.3 cm) and restored sites (-50.4 cm) (Table 6.1). The only open water was in the ponds at the restored site. The rain event lasted 12 hours during which time 22.6 mm rain fell. Discharge at the cutover site increased from 0.002 L s^{-1} to 0.06 L s^{-1} in 7.9 hours (Figure 6.1 a.). The restored site had higher discharge (0.01 L s^{-1}) prior to the storm, which increased to a peak of 0.56 L s^{-1} in 9.8 hours (Figure 6.1 a.). Water table position rose to –37.8 and –30.7 cm at the cutover site and restored site respectively (Table 6.1).

6.2.2 Dissolved organic carbon

DOC concentration was not variable during the May storm event (Figure 6.3 b.). Water from the restored site had consistently higher DOC concentration (81.6 ± 5.2 mg L^{-1}) than the cutover site (58.3 ± 2.5 mg L^{-1}) (Table 6.1). Higher concentrations were observed following a two-day lag after the main event. This was when maximum concentrations are reached at both sites (93.2 and 61.9 mg L^{-1} at the restored and cutover site, respectively) (Table 6.1).

During the intense July storm DOC concentrations varied significantly (Figure 6.3 b.). Mean concentrations at the cutover site decreased by 19.6 mg L^{-1}

while at the restored site it decreased by 44.9 mg L^{-1} (Table 6.1) compared to pre-storm values during peak discharge. Maximum DOC concentration (97.1 mg L^{-1}) at the cutover site was measured before the storm. Concentrations returned to levels similar to pre-storm conditions in approximately six hours after the main event. DOC concentrations at the restored site increased steadily following the main event to a maximum of 135 mg L^{-1} (Figure 6.3 b.).

The lower intensity August storm had a similar effect on DOC concentration as its July counterpart, except that, reduced DOC concentrations occurred for a longer period following the storm (Figure 6.3 b.). On average the restored site was discharging water with higher DOC concentration (101.6 ± 14.4 mg L^{-1}) than the cutover site (82.1 ± 11.0 mg L^{-1}). Again minimum DOC concentrations were observed during peak discharge when DOC decreased to 66.5 and 87.4 mg L^{-1} at the cutover and restored sites respectively. Following this dip, concentrations at the cutover site increased quickly to pre-storm concentrations (94.1 mg L^{-1}), and stayed at these levels. At the restored site a steady increase of DOC was observed following the event and DOC concentrations increased steadily to a maximum of 131 mg L^{-1} (Figure 6.3 b.).

6.2.3 DOM quality during storms

As with snowmelt the HA fraction was measured more frequently during the three storm events. In general this fraction was higher prior to the event,

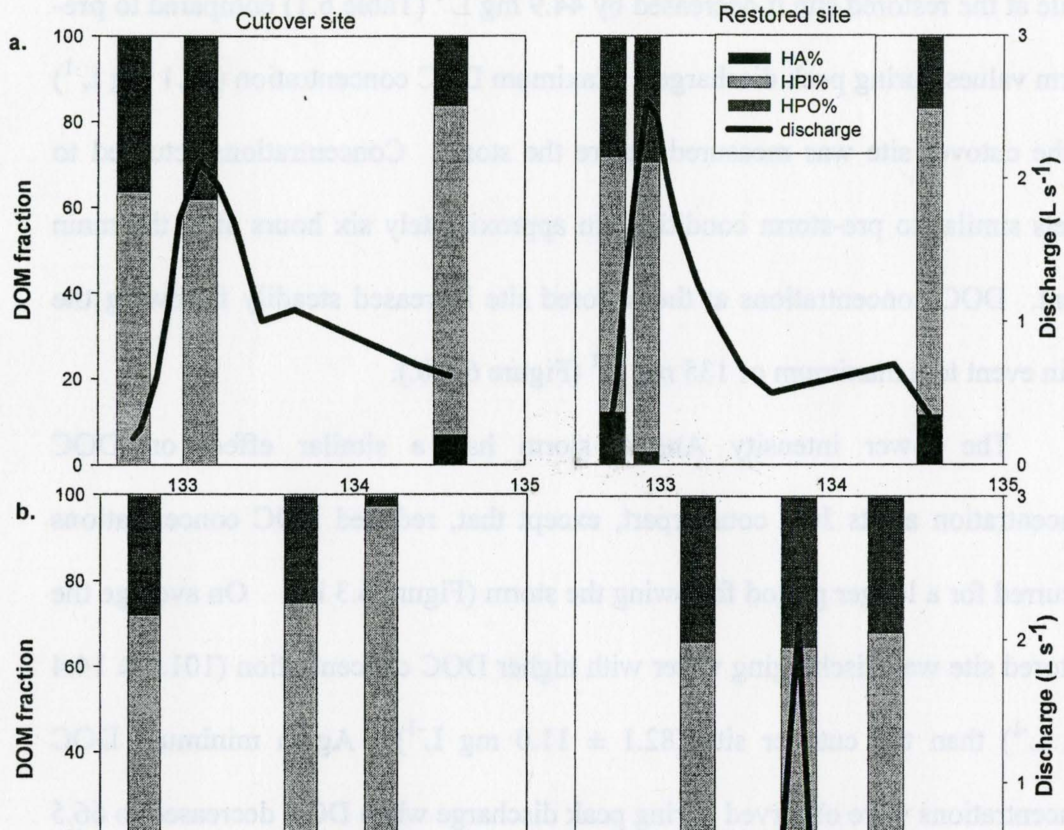


Figure 6.4 DOM quality during the (a.) May, (b.) July and (c.) August storms.

decreased to near zero during peak flow and increased during the lag part of the hydrograph (Figure 6.3 b.).

DOM quality was variable during storm events (Figure 6.4). In general all three fractions were present prior to the event with HPI and HPO being more dominant (Figure 6.4). During peak discharge they dominated an even greater extent, and HPI comprised the highest proportion.

Prior to the May storm even the HA fraction was lower at the cutover site than at the restored site (Figure 6.3 b.). It increased slightly at the beginning of the event to an event maximum of 5.1 mg L^{-1}. This trend was not observed at the restored site. During peak flow conditions this fraction disappeared. It increased once again during the lag part of the hydrograph when it reached maximum values (28.1 mg L^{-1}) at the restored site.

The HPI fraction was the most dominant fraction during this event representing 60 to 70% of DOM. This fraction increased slightly at the restored site but not at the cutover site during peak flow (Figure 6.4 a.). Following the main event HPI increased by 15 and 5% at the restored and cutover sites respectively.

The HPO fraction, which represented about 20 to 30% of the DOM, did not change during peak flow and decreased slightly during the lag part of the event (Figure 6.4 a.).

Prior to the intense July storm (JD = 205), the HA fraction at the cutover site was very low and was close to detection limits (Figure 6.3 b.). It was higher at the restored site and represented approximately 13-17 % of DOM (Figure 6.4 b.). During peak discharge, this fraction decreased to zero. It increased slightly following the storm at the cutover site and more significantly at the restored site.

HPI was the dominant component at both sites, representing 70-90% of DOM at the cutover site, and 50-70% at the restored site. The largest increase in this fraction occurred at the cutover site during the lag part of the hydrograph, when it reached 96.3% (Figure 6.4 b.).

The HPO fraction, representing approximately 30% of DOM, did not change significantly at the restored site during the July-storm. At the cutover site, however, it decreased to only 2.7% during the lag part of the storm (Figure 6.4 b.).

Patterns during the low intensity August storm were slightly different from the previous two events. The HA fraction at the cutover site fluctuated between 10 to 30% of DOM during the event and did not decrease during peak discharge. At the restored site, the range was similar, except that it disappeared during peak discharge and then increases at the lag part of the hydrograph to greater values than before the storm event (Figure 6.4 c.). Both HPI and HPO fractions stayed in the same range at the cutover site during the entire storm, while at the restored site the HPO fraction increases significantly during the event.

6.3 Discussion

6.3.1 DOC dynamics during snowmelt

Riparian wetlands are an important component in the DOC input from upland catchments and can often dominate DOC loading to downstream systems. Dosskey and Betsch (1994) estimated that a riparian wetland could contribute 90% of the DOC, while it only occupies 6% of the landscape. In boreal and temperate ecosystems, DOC of headwater catchments originates from the surface soil layers (Schiff et al, 1997) and the majority of this transport occurs during the snowmelt period (Hornberger, 1994; Boyer et al., 1997). There are numerous reports on DOC export during snowmelt from upland systems (e.g. Hornberger, 1994; Boyer et al., 1997; Brooks 1997; Boyer et al., 2000), however, these focus mainly on alpine systems. Several works have examined the hydrological controls that exist within wetland-dominated systems during spring melt (e.g. Roulet and Woo, 1986; Woo and Dicenzo, 1989; Shannon and Woo, 1997; Metcalfe and Buttle, 2001), however, few have looked at the dynamics of exportable materials in these systems (Fraser et al., 1991; Buttle and Fraser, 1992). Reports on DOC export during the snowmelt period are also few in number. An estimate from values reported by Schiff et al. (1997) in a forested swamp are similar to those reported by Fraser et al. (2001) in a natural peat bog ranging between 1.1 to 1.9 g C m^{-2} $(season)^{-1}$. While the values reported in the forested swamp during snowmelt comprised the major part of DOC export from the site during the year, the snowmelt portion from the natural bog was only 13% of the annual output (Fraser et al., 2001). These export values are in the range of those reported for alpine systems (Boyer et al., 1997; Brooks and McKnight, 1999). To date there are no studies that reported DOC dynamics during snowmelt in a cutover or a restored peat bog.

One of the major hydrologic inputs to peatlands is the snowmelt period. The large storage capacity for water, characteristic of these wetlands is, however, diminished by the frozen ground (Roulet and Woo, 1986), which prevents infiltration, thus causing the most significant runoff event from these systems. The restored and cutover sites in this study behaved similarly to a natural peatland, and the most significant runoff event was measured during spring snowmelt. The hydrograph of the restored site was flashier than that of the cutover site, which had a much wider base and stayed consistently high for a longer period. Metcalfe and Buttle (2001) demonstrated that conditions prior to freeze-up have a significant controlling effect on the runoff generation during the spring snowmelt. They indicated that shallower water tables reduced the amount of infiltration into the peat layer, quickly exhausting storage capacities, therefore causing a faster displacement of water to the outflows. A deeper water table was found to have the opposite effect and retarded runoff creating a wider hydrograph. Hydrographs at the restored and cutover site follow this pattern. It has been demonstrated that the restored site maintained higher water levels throughout the 2000 study season compared to the cutover site (von Waldow, 2002), and was also prone to flooding during large storm events. Therefore, it is expected that prior to freeze-up, the restored site had a higher water table position than the cutover site, which in turn caused the different patterns of runoff during the melt event.

This effect is further witnessed in the DOC concentrations during the main melt event. During the early part of the melt, DOC concentrations increased at the cutover site to higher levels than before melting began. Towards peak runoff, DOC concentrations decreased significantly. Studies of headwater catchments have noted similar trends (Boyer et al., 1997; Brooks and McKnight, 1999). They attributed this increase to increased heterotrophic activity under the snow pack, which was confirmed by increased fluxes of CO_2 and N_2O during this period (Boyer et al. 1997; Brooks et al. 1997). Large snow accumulation can protect the soil surface from temperature fluctuations experienced during the winter. Furthermore, it can promote the thawing of the surface before the thawing of the snowpack (Sommerfeld et al., 1993). Since the cutover site contained less water upon freeze-up, conditions would become more favorable for activities described above, causing a sharp increase in DOC concentration prior to snowmelt. No such event occurred at the restored site, indicating that this active layer was not exposed to the same extent as that of the cutover site. Furthermore, the cutover site produced water with higher DOC content during the melt event compared to the restored site, indicating that the thickness of peat that was actively releasing DOC, was larger during this period.

The restored site contains eight artificial pools that are not present at the cutover site. Each of these ponds were found to store ~1 kg of C during the year. Fraser et al. (2001) suggested that peatland ponds were important in DOC export during snowmelt, however, this was not evident at this site. A thick ice layer prevented the mixing of melt water with that in the ponds through the period of high runoff. Ice breakup within the ponds occurred one day after most of the snow was lost from the site (JD = 113). The entire pond became ice-free three days following that event, during the falling limb of the snowmelt hydrograph. Therefore, mixing of pond water with meltwater was only possible during the falling limb of the hydrograph, when most of the snow was gone from the site and a larger peat layer was also active. This point also marked the time when the DOC concentrations at the two sites were similar.

An imbalance exists between available snow input (137 and 150 mm snow water equivalents) and the runoff measured at the sites (176 and 517 mm), indicating that the contributing area during spring runoff was probably larger than the area of the restored and the cutover sites. Although the ditch system surrounding the two sites was effective during the summer period in isolating the restored and cutover site from the surrounding forested peatland (von Waldow, 2002), it became less effective during the snowmelt period, when the ditches flooded with water input from both areas. The contribution was even greater at the cutover site where, following the snowmelt period, it was observed that one of the ditches separating the cutover site from forested peatland, was actually not blocked, and thus was able to channel water onto the site and consequently into the main drainage ditch.

This effect can be observed in the DOC export calculated for the cutover site, which was unreasonably large for a site of this scale. Values at the restored site were more reasonable, however, at this site too, there was a 39 mm discrepancy and possibly more, since not all the meltwater ran off the site but ponded different areas of the restored site. The DOC export value calculated (8.3 g C m^{-2}) was more reasonable and was found to be the most significant DOC export from the site, representing 68% of the annual DOC export.

DOM character changed significantly during snowmelt. Prior to the melt event, DOM character was similar to that which was seen during baseflow conditions, when the DOM contribution was found to be from the active top 75 cm of peat. There was no data available on the depth of the frost zone during the winter, however, the continuous discharge of water during this period indicated that parts of this layer were still active. The character changed significantly during the main melt event, when discharge was more dominated by the HPI and HPO fractions. This character was similar to the character seen from moss and straw leached at low temperatures (Chapter 4). Following peak discharge, the character was more similar to peat leaching characters at low temperatures when larger portions of HPO were released. This resemblance indicated that organic material closer to the surface had an increased role in DOM release during this period, however, the match is not exact, indicating that other controlling factors are also important for DOM release.

The HPI fraction was a dominant component in all samples and became even more prevalent during the high flow period of the snowmelt. This result was consistent with other studies (Urban, 1989; Kaiser et al. 2001, 2002), which found this component to be high in winter and spring soil samples. Kaiser et al. (2002) suggested that this fraction contained labile carbohydrates that have escaped microbial degradation during the winter. Furthermore, Kaiser et al. (2001) suggested that winter production of this fraction was also the result of the disruption of microbial and plant cells due to freezing and thawing. Although this fraction was dominant prior to snowmelt, it was not as prevalent as during the main melt event, leading to the conclusion that this highly labile, small molecular weight fraction was easily transported through the matrix by increased fluxes of water. Therefore the presence of this fraction was strongly affected by hydrological conditions during high flow periods, such as snowmelt.

The changes in the HPO fraction indicated similar controls. This fraction was more aromatic, containing larger molecules (Bourbonniere, 1989; Guggenberger, 1994), which are more difficult to move within the soil matrix (Kaiser et al., 2001). The decrease, in both proportionality and concentration (data not shown) during the snowmelt initiation, was reflective of the short contact time between the soil matrix and meltwater, thus decreasing the HPO content of the runoff. This was also evident at the cutover site where a short pulse of high discharge caused a decrease of this fraction. Proportions increased upon slower water movement. Another explanation was, however, also possible for the increase of this component following the melt event. As the soil thawed water could penetrate deeper into the soil matrix. The HPO fraction was found to be in pool of adsorbed carbon within the soil matrix, the release of which was controlled by a concentration gradient (Christ and David, 1996a). Therefore, as more water infiltrated into the soil, more of this adsorbed carbon was released and exported from the sites.

The HA fraction, which is considered to be the most hydrophobic and degraded component of DOM (Bourbonniere, 1989), was similarly affected during the spring melt, but to a greater extent. The absence of this component during the main melt event was indicative of the greater difficulty to mobilize this fraction within the peat matrix.

6.3.2 DOC dynamics during stormflow

Hinton et al. (1998) have demonstrated that, estimates of DOC loading, based on correlations between DOC and discharge, could often underestimate actual values, since storms could present important events of DOC mobilization within these systems. The presence of wetlands made these estimates even more difficult, since often, no significant correlation could be found between DOC concentration and discharge. The effect of these features dominated the DOC input to downstream areas, even when their aerial extents were small (Dosskey and Bertsch, 1994). Peatlands could present an important DOC input to downstream environments (Urban, 1989), however, the estimate for this input, was made difficult by the diffuse nature of water flow within these systems (Price and Woo, 1988). Fluxes of dissolved carbon within a peatland were directly and indirectly controlled by hydrologic pathways within peatlands (Martin et al., 1999; Koprivnjak and Moore 1992; Waddington and Roulet, 1996) and often no correlation could be found with DOC. Since harvesting activities have an important hydrologic impact on these systems, as demonstrated in Chapter 5, they can in turn also affect DOC dynamics within the site.

Compared to the DOC export values calculated for the snowmelt period, these storms were not as significant. The most significant storm contribution to the DOC export of the sites occurred during the spring (0.6 g C m^{-2}) under wetter conditions, when the restored site released 17% while the cutover site released 3% of total DOC exported during the non-snowmelt period. Contribution of the July and August storms were much less, since dry conditions at the sites, during this period, failed to produce strong runoff responses, as observed in the spring. The only literature source for comparison of individual events was a 46 mm event reported by Hinton et al. (1998). The reported catchment contained small wetlands that were found to export ~0.2 g C m^{-2} as DOC. This indicated that the cutover and restored wetlands had a larger potential to export DOC during storm events following wet antecedent conditions compared to natural wetland systems.

The hydrological differences between the restored and cutover site were evident in the summer storm responses also, however, further discussion of these differences was not the purpose of this analysis. In general, peak discharge was reached sooner at the restored site than at the cutover site. The rain events examined were of similar size and the magnitude of the runoff responses were diminished with increasing dry conditions at the site as the season progressed. The contribution of the main drainage ditches to the runoff measured was established in order to determine the significance of on ditch rainfall to runoff, and it was found to be of significance during the August storm at the cutover site, where all the discharge originated from rain directly on the channel.

The effect of storms on the DOC release capacity of has been studied extensively. Both laboratory and field experiments have demonstrated that precipitation and water fluxes were responsible for seasonal changes in DOC concentration in runoff (Kalbitz et al., 2000). McDowell and Wood (1984) demonstrated that contact between water and the organic substrate could cause increased leaching, followed by increased dilution of DOM once the available pool was flushed. Similar conclusions were reached by Cronan (1990), who found that DOC concentrations increased in soil solution with longer contact time. Forest soil studies have indicated that the highest DOC concentrations were reached upon rewetting following a dry period (Easthouse et al. 1992). Tipping et al. (1990) suggested that an adsorbed pool of carbon, that was accumulated during the dry periods and subsequently mobilized upon re-wetting, was responsible for the increased DOC observed upon moisture input. Therefore, it is expected that the three storm events studied would present similar DOC dynamics.

Prior to the May storm, there was no dry period during which time DOC could accumulate, since this event followed the snowmelt period, when the site was still largely saturated. Even though discharge increased ~10 fold, DOC concentrations remained similar at both sites. This indicated that both the restored and the cutover site were exporting DOC at their maximum potential, and the receding meltwater was continuously leaching the peat matrix at its maximum potential. Furthermore, it indicated that the site, in terms of DOC release, was well connected, and no pools of stagnant DOC developed during this period. This was consistent with laboratory findings by Gödde et al. (1996), who found that sequential, frequent leachings of soil samples produced DOC at a constant rate.

The July and August storms examined followed dry periods, when the water table was substantially lower than those following spring melt. The pattern of DOC released during this period at the restored site was consistent with the reports described earlier with one notable exception. During these storms, DOC concentrations did not increase after the initial rewetting, as reported in other studies, but increased during the lag part of the storm. The main difference between the studies mentioned previously and this study was that, here, DOC was examined as it passed through an entire system, therefore, it was more integrated, while the other studies examined small soil-sample-leachates, and DOC was examined as a direct output of the samples, therefore in more isolation. The increase in DOC observed, at the restored sites, the end of these storm events indicated, that the rain event caused the connection of DOC pools, which had increased potential to release DOC. The intensity of the storm events, however, had some effect on DOC concentration. The lower intensity August storm caused a longer and more significant increase in DOC concentration following peak discharge, indicating that the rate of infiltration of rainwater also allowed more substantial connection of the different DOC pools.

The pattern at the cutover site was different from that described above, and the summer storms were found to have only a dilution effect and DOC concentrations. Looking at the DOC concentration there was no evidence that during these summer rain events pools of increased DOC production were connected to the outflows. This may be a result of the dryer conditions experienced at the cutover site. Both hydrographs indicate that a large portion of the rainfall is incorporated into storage rather than runoff therefore the mobilization of DOC on a larger scale was not possible.

The DOM character observed during these storm events indicated that there was a strong hydrologic control on the release of the different fractions. This control was evident in the prevalence of the HPI fraction and the disappearance of the HA fraction during peak flow. During the more integrated period following the spring melt; DOM of similar character was being exported at the cutover site prior to and at peak discharge, further indicating an integrated system. The character of DOM changed only slightly during the falling limb of the storm hydrograph. The appearance of HA and the decrease of HPO fraction in the falling limb indicated that another DOM pool had been connected to the system during this storm. The strong hydrologic effect on the DOM character was more evident at the restored site. The peak of the discharge was dominated by the smaller, more easily mobilized HPI fraction, while the HPO fraction stayed at a consistent level. Looking at the HA fraction (Figure 6.3 b.), which was analyzed more continuously, showed that as flow velocities subside, the HA fraction reappeared and became an important component of the DOM.

During the dryer periods, the DOM pools at the cutover site become disconnected. The July storm followed a period when discharge at the cutover site was insignificant. The storm occurred quickly and water moved immediately in the ditches, therefore, it's ability to pick up heavier, less soluble DOM was reduced, hence the character of the DOM was dominated by the HPI fraction and the lack of the HA component. During the following storm, DOM character did not change significantly either, and resembled more the baseflow conditions indicating, that it was probably originating form the drainage of the peat layers adjacent to the outflow.

At the restored site, the character of the rain event also had an effect on the observed DOM. The hydrologic control on the exported DOM during peak discharge was present, and HPI fraction dominated this period during both events. The HPO fraction did not change, while the HA fraction decreased to undetectable levels (Figure 6.3 b.). The subsequent increase of this fraction following peak discharge, indicated that either this fraction was more easily mobilized by slower moving-water, or that a particular DOM pool was contributing more of this component. If it were a matter of mobilization, then this fraction would be released continuously as water flow subsides, similarly to what happened during the spring storm. However, this is not the case. After an initial high input, the HA fraction steadily decreased, indicating that the supply of this component was cut off. This does not happen during the August storm, when HA increased steadily during the lag. Therefore, the intensity of the rain event had a controlling effect on DOM. While the July storm flashed through the site, the August storm lasted longer, increasing the infiltration of water into the peat matrix, and making the connection of different DOM pools possible.

The analysis of internal distribution of DOC, at the restored site, indicated that there are several areas within the peatland where water containing high DOC was found, such as the top 75 cm of the peat matrix, the old drainage ditches, and the artificial pools. DOC concentrations measured in these areas were found to correspond well with those measured at the outflows. Fractionation analysis, on the other hand, helped eliminate the ponds as a possible source, and left the peat matrix in Zone 4, an area with high HA and HPI, and ditch 4D as the possible sources of the additional DOM measured during stormflow. This contribution is certainly a possibility, since this area was often flooded near the ditches and the ponds during high flow events, however, there was no hydrologic confirmation of this process.

6.3.3 Pathways for DOM release

Based on the findings of this study, a general conceptual model of the DOC contribution areas can be postulated (Figure 6.5). During the snowmelt period (Figure 6.5 a.), the contributing area was found to be the uppermost layer of peat. Depending on the hydrologic conditions prior to freeze-up, the thickness of this layer can vary from thick during dry conditions, to thin during wet conditions. This layer can melt quickly underneath the snowpack and can have a large potential to release DOM. During periods when the peatland is wetter (Figure 6.5 b.), for example following snowmelt, the release of DOM is more integrated, and the different areas of DOM production become connected. During dry conditions when most of the water falling on the site becomes part of storage rather than runoff, the areas with high potential for DOM production become disconnected and DOM is more characteristic of the immediate surroundings of the main drainage ditches (Figure 6.5 c.). Large, low intensity storm events are required to reconnect these areas of DOM production.

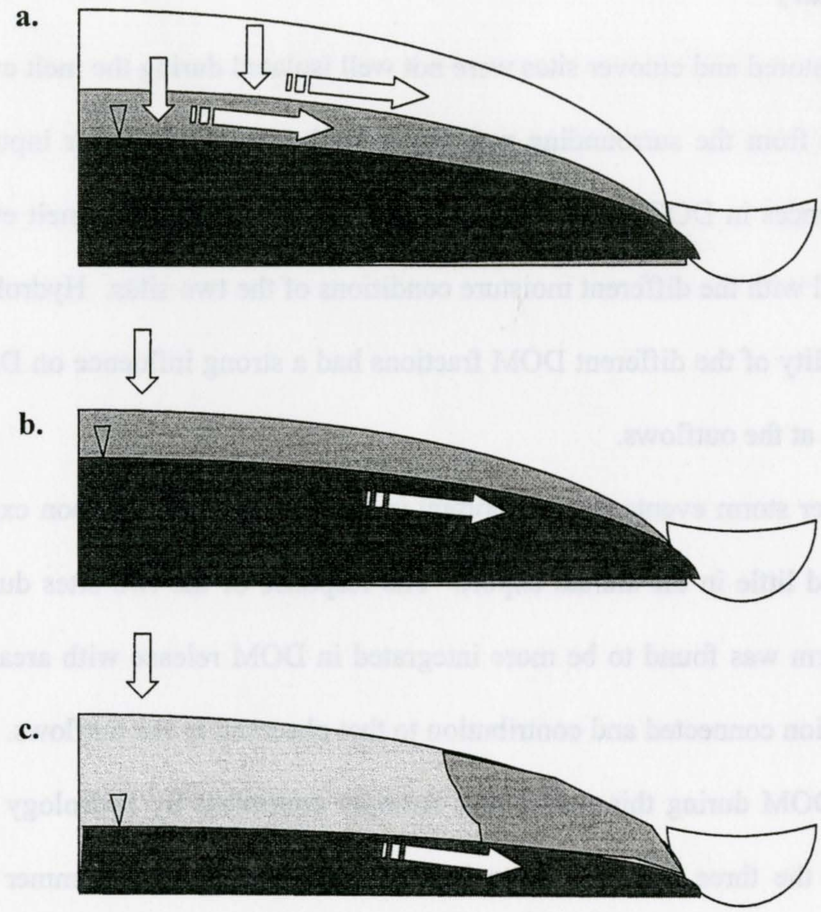


Figure 6.5 Conceptual diagram illustrating areas contributing to DOC release (light gray areas) during different flow-conditions: a) snowmelt, b) wet antecedent conditions, and c) dry antecedent condition

6.3.4 Summary

The restored and cutover sites were not well isolated during the melt event and snowmelt from the surrounding peatland provided increased water input to them. Differences in DOC concentrations measured during the main melt event correlated well with the different moisture conditions of the two sites. Hydrology and the solubility of the different DOM fractions had a strong influence on DOM character seen at the outflows.

Summer storm events were important in the non-snowmelt carbon export but contributed little in the annual export. The response of the two sites during the spring storm was found to be more integrated in DOM release with areas of DOM production connected and contribution to that observed at the outflows. The character of DOM during this period was strongly controlled by hydrology and the ability of the three components to be transported by water. Summer dry conditions caused the disconnection of the different DOM producing areas and the DOM at the outflows was more characteristic of areas immediately adjacent to the main drainage ditches. Low intensity large storms were found to reconnect these pools.

CHAPTER 7: CONCLUSIONS

The goal of this thesis was to provide some understanding regarding the changes that take place in terms of DOM dynamics in a peatland following restoration activities.

The first objective was to study the role that different peatland vegetative components play in the release of DOM. The laboratory study conducted with fresh materials indicated that shrubs and herbaceous plants had a high potential to produce large amounts of DOM. This material produced all there DOM fractions studied, however, the HA component was found to be more degradable than that released from other materials. Straw, mosses and peat all had similar potentials to produce DOM and some temperature effects were noted mainly in peat and straw samples. These materials produced mainly the HPI and HPO fractions at cooler temperatures, and HA in small proportions at higher temperatures. Aerobic conditions were more likely to produce the HA fraction than were anaerobic conditions.

This leaching experiment indicated that the highest contribution acting on a short time scale, was by herbaceous and shrub vegetation and highest acting on a longer time scale, was by peat, due to its large mass within the sites. However, caution must be exercised in scaling up from the laboratory experiment, mainly because, the conditions experienced in the field are more varied than those in this study.

The second objective of this thesis was to compare changes in the quality and quantity of DOM in a natural, cutover and recently restored peatland. The improved hydrologic conditions at the restored site also manifested in the reduction of DOC export from the restored site compared to the cutover site, however, these values were within the range of those reported for natural peatlands. This study indicated that DOC concentrations significantly increased following restoration, which was a possible result of a change in DOM release mechanisms caused by increased moisture conditions at the restored site as well as input of fresh organic materials. The seasonal variation in DOC concentration was found to be most significant at the affected sites and less evident at the natural peatland.

The character of the DOM, at the outflows from the cutover and the restored site, indicated that substrate quality had the most important effect on the DOM released and no difference could be found between the two sites. Seasonal variation of the character was most evident in the HPI and HA fractions, where HPI was found in higher proportion during the spring and fall, while HA was higher during the summer warm, dry periods. The seasonal variations in the three fractions studied were mainly a result of their water solubility, the changing moisture conditions during the study period and the metabolism and production of these fractions.

A vertical gradient of decreasing DOC concentration was observed at both the restored and cutover site. Areas of increased activity or DOC input were observed in two locations at the restored site, while areas near drainage ditches presented higher input areas at the cutover site. Depressions in the restored site, such as the blocked drainage ditches and the artificial ponds, were found to have an important control on DOM dynamics within the site. The pools were found to store a large amount of carbon, however, the flux of this water to the peatland was very low. Ditches, on the other hand, were found to be more important during high flow conditions, such as summer storms, when they were likely to contribute to the DOM. The top 75 cm, the area of intense moisture fluctuations, was found to be important in the DOM, indicating that high DOC concentrations will prevail until the moisture fluctuations decrease and mosses reestablish.

The third objective of this thesis was to examine DOM dynamics during different flow conditions. Spring snowmelt was found to be the most significant export event of the year. DOC concentration was likely affected by the thickness of the active peat layer during melting. DOM character was mainly affected by the solubility of the different fractions, with HPI being more prevalent during high flow periods, and HA fraction decreasing to below detectable values then reappearing during low flow conditions.

Summer storms contributed little to annual DOC export and were more important during wet conditions. The character of DOM exported during this period was also affected by the solubility of the fractions. However, antecedent conditions also affected character, with dry periods producing DOM with all three fractions present, and wet antecedent conditions producing DOM with the HPI and HPO more dominant.

The fourth objective of this thesis was to investigate internal pathways for DOM release. Three main types of DOM release were identified. During the snowmelt period DOM was produced in the active top layer of peat, which was subsequently diluted by rainwater. During periods when the peatland was wet a more integrated system was observed, where the DOM producing areas were connected. During dry conditions, however these pools were disconnected, as water was stored rather then released as runoff and DOM was probably originating from the near-ditch areas of the main outflows. The hydrologic confirmation of these pathways remains to be examined.

REFERENCES:

Bérubé, M.E., and Lavoie, C. (2000) The natural revegetation of a vacuum-mined peatland: eight years of monitoring. *Canadian Field-Naturalist*, **114**, 279-286.

Bourbonniere, R.A. (1979) Geochemistry of humic matter in Holocene Great Lakes sediments. Ph.D. Thesis, University of Michigan, pp.373.

Bourbonniere, R.A., (1989) Distribution patterns of dissolved organic matter fractions in natural waters from eastern Canada. *Organic Geochemistry,* **14**, 97-107.

Bourbonniere, R.A. and van Halderen (1989) Fractional precipitation of humic acid from coloured natural waters. *Water, Air and Soil Pollution,* **46**, 187-198.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., and McKnight, D.M. (1997) Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes*, **11,** 1635-1647.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., and McKnight, D.M. (2000) Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach. *Hydrological Processes*, **14**, 3291-3308.

Brooks, P.D. and McKnight, D.M. (1999) The relationship between soil heterotrophic activity, soil dissolved organic carbon leachate, and catchment-scale DOC export in headwater catchments. *Water Resources Research*, **35**, 1895-1902.

Buttle, J.M. and Fraser, K.E. (1992) Hydrochemical fluxes in the high arctic wetland basin during spring snowmelt. *Arctic and Alpine Research*, **24**, 153-164.

Campeau, S. and Rochefort, L. (1996) *Sphagnum* regeneration on bare peat surfaces: field and greenhouse experiments. *Journal of Applied Ecology,* **33,** 599-608.

Charman, J.D., Aravena, R., Bryant, C.L., and Harkness, D.D. (1999) Carbon isotopes in peat, DOC, CO2, and CH4 in a Holocene peatland on Dartmoor, southwest England. *Geology,* **27**, 539-542.

Chasar, L.S., Chanton, J.P., Glaser, P.H., Siegel D.I. and Rivers, J.S. (2000) Radiocarbon and stable carbon isotopic evidence from transport and transformation of dissolved organic carbon, dissolved inorganic carbon, and CH_4 in a northern Minnesota peatland. *Global Biogeochemical Cycles*, **14**, 1095-1108.

Christ, M.J. and David, M.B. (1994) Fractionation of dissolved organic carbon in soil water: Effects of extraction and storage methods. *Communications in Soil Sciences and Plant Analysis*, **25**, 3305-3319.

Christ, M.J. and David, M.B. (1996a) Dynamics of extractable organic carbon in spodosol forest floors. *Soil Biology and Biochemistry*, **28,** 1171-1179.

Christ, M.J. and David, M.B. (1996b) Temperature and moisture effects on the production of dissolved organic carbon in a spodosol. *Soil Biology and Biogeochemistry*, **28,** 1191-1199.

Clymo, R.S. (1984) The limits of peat bog growth. *Phylosophical Transactions of the Royal Society , London, Series B,* **303**, 605-654.

Cronan, C.S. (1985) Comparative effects of precipitation acidity on three forest soils: carbon cycling responses. *Plant and Soil*, **88**, 101-112.

Cronan, C.S. (1990) Patterns of organic acid transport from forested watershed to aquatic ecosystems. *Organic Acids in Aquatic Systems* (eds. E.M. Perdue, E.T. Gjessing), John Wiley and Sons, Chichester.

Dai, K. H., Johnson, C.E., and Driscoll, C.T. (2001) Organic matter chemistry and dynamics in clear cut and unmanaged hardwood forested ecosystems. *Biogeochemistry*, **54**, 51-83.

Day,S. personal communication

Devito, K.J., Waddington, J.M., and Branfireun, B.A. (1997) Flow reversal in peatlands influenced by local groundwater systems. *Hydrological Processes*,**11**, 103-110.

David, M.B. and Vance, G.F. (1991) Chemical character and origin of organic acids in streams and seepage lakes of central Maine. *Biogeochemistry*, **12**, 17-41.

Easthouse, K.B., Mulder, J., Christophersen, N., and Seip, M. (1992) Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, Southern Norway. *Water Resources Research*, **28**, 1585-1596.

Environment Canada (1993) *Canadian Climate Normals, 1961-1990. Québec.* Atmospheric Environmental Services, Canadian Climate Program, Environment Canada, Ottawa.

Fenner, N., Freeman, C., Hughes, S., and Reynolds, B. (2001) Molecular weight spectra of a rewetted Welsh peatland and possible implications for water quality. *Soil Use and Management,* **17**, 106-112.

Fraser, C.J.D., Roulet, N.T., and Moore, T.R. (2001) Hydrology and dissolved organic carbon biogeochemistry in a large peatland. *Hydrological Processes,* **15**, 3151-3166.

Freeman, C., Evans, C.D., and Monteith, D.T. (2001) Export of organic carbon from peat soils. *Nature*, **412**, 785.

Frimmel, F.H. (1998) Impact of light on the properties of aquatic natural organic matter. *Environment International*, **24**, 559-571.

Girard, M., Lavoie, C., and Thériault, M. (submitted for publication) The spontaneous regeneration of a highly disturbed ecosystem: mined peatland of southern Quebec

Gödde, M., David, M.B., Christ, M.J., Kaupenjohann,M. and Vance, G.F. (1996) Carbon mobilization from the forest floor under red spruce in the northeastern U.S.A. *Soil Biology and Biochemistry*, **28**, 1181-1189.

Gonet, S.S. and Debska, B. (1998) Properties of humic acids developed during humification process of post-harvest plant residues. *Environment International*, **24**: 603-608.

Gorham, E., Underwood, J.K., Martin, F.B., and Ogden, J.G. (1986) Natural and anthropogenic causes of lake acidification in Nova Scotia, *Nature*, **324**, 451-453.

Gorham, E. (1991) Northern peatlands: role in the carbon cycle and probable responses to climatic warming. *Ecological Applications*, **1**, 182-195.

Gron, C., Torslov, J., Albrechtsen, H.-J., and Jensen H.M. (1992) Biodegradability of dissolved organic carbon in groundwater from an unconfined aquifer. *Science of the Total Environment*, **20**, 241-251.

Gu, B., Mehlhorn, T.L., Liang, L., and McCarthy, J.F. (1996) Comparative adsorption, displacement, and transport of organic matter on iron oxide: II. Displacement and transport. *Geochemica et Cosmochemica Acta*, **60**, 2977-2992.

Guggenberger, G., Zech W., and Schulten H. (1994) Formation and mobilization of dissolved organic matter: evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. *Organic Geochemistry*, **21**, 51-66.

Glatzel, S., Kalbitz, K., Dalva, M., and Moore, T. (2002) Dissolved organic matter properties and their relationship to carbon dioxide efflux from restored peat bogs submitted to *Geoderma*

Heathwaite, A.L. (1995) The impact of disturbance on mire hydrology. In Hydrology and Hydrochemistry of British Wetlands, John Wiley & Sons Ltd., pp. 401-417.

Hem, J.D. (1985) Study and interpretation of the chemical characteristics of naturalwater (3d ed.): U.S. Geological Survey Water Supply Paper 2254, 263 p.

Hinton, M.J., Schiff, S.L., and English, M.C. (1997) The significance of storms for theconcentration and export of dissolved organic carbon from two Precambrian Shield catchments *Biogeochemistry*, **36**, 67-88.

Hinton, M.J., Schiff, S.L., and English, M.C. (1998) Sources and flow paths of dissolved organic carbon during storms in two forested watersheds of the Precambian shield. *Biogeochemistry*, **41**, 175-197.

Hobbs, N.B. (1986) Mire morphology and the properties and behavior of some British and foreign peats. *Quarterly Journal of Engineering Geology*, **19**, 7-80.

Hongve, D. (1999) Production of dissolved organic carbon in forested catchments. *Journal of Hydrology*, **224**: 91-99.

Hornberger, G.M., Bencala, K.E. and McKnight, D.M. (1994) Hydrological controls on dissolved organic carbon during snowmelt n the Snake River near Montezuma, Colorado, *Biogeochemsitry*, **25**, 147-165.

Hughes, S., Reynolds, B., Brittain, S.A., Hudson, J.A., and Freeman, C. (1998) Temporal trends in bromide release following rewetting of a naturally drained gully mire. *Soil Use and Managament*, **14**, 248-250.

Ingram, H.A.P. (1978) Soil layers in mires: function and terminology. *Journal of Soil Sciences*, **29**, 224-227.

Ingram, H.A.P. (1983) Hydrology. Ecosystems of the world, Vol.4A, Mires: Swamp, bog fen and moor, Elsevier Sciences, New York.

Jonsson-Ninniss, S. and Middleton, J. (1991) Effect of peat extraction on the vegetation in Wainfleet Bog, Ontario. *Canadian Field-Naturalist*, **105**, 505-511.

Kabitz, K. and Geyer, S. (2002) Different effects on peat degradation on dissolved organic carbon and nitrogen *Organic Geochemistry*, **33**, 319-326.

Kaiser, K., Guggenberger, G., Haumaier, L., and Zech, W. (2001) Seasonal varioations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine an European beech stands in northeastern Bavaria, Germany. *Biogeochemistyr*, **55**, 103-143.

Kaiser, K., Guggenberger, G., Haumaier, L., and Zech, W. (2002) The composition of dissolved organic matter in forest soil solutions: changes induced by seasons and passage through the mineral soil. *Organic Geochemistry*, **33**, 307-318.

Kalbitz, K. and Knappe, S. (1997) Influence of soil properties on the release of dissolved organic matter from the topsoil. *Z. Pflanzenernaehr. Bodenkd.*, **160**, 475-483.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., and Matzner, E. (2000) Controls on the dynamics of dissolved organic Matter in soils: A review. *Soil Science*, **165**, 277-304.

Kerkes, J., Beauchamp, S., Tordon, R., Tremblay, C., and Pollock, T. (1986) Organic vs. anthropogenic acidity in tributaries of the Kejimkujik watersheds in western Nova Scotia, *Water Air Soil Pollution,* **31**, 207-214.

Keys, D. (1992) Canadian peat harvesting and the environment. *North American Wetlands Conservation Council*, Ottawa, Issue paper no. 1992-3. pp. 29

Kirschbaum, M.U.F. (1995) The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. *Soil Biology and Biochemistry*, **27**, 753-760.

Klove, B. and Bengtsson, L. (1999) Runoff generation in a plough-drained cutover fen in Central Finland. *Journal of Hydrolgoy*, **218**, 157-168.

Lappalainen, E. (1996) General historical review on world peatland and peat resources *Global peat resources* (eds E. Lappalainen),International Peat Society, Jyväskylä.

Lavoie, C. and Rochefort, L. (1996) The natural revegetation of a harvested peatland in southern Quebec: a spatial and dendrochronological analysis. *Écoscience*, **3**, 101-111.

Leenheer, J.A. (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science and Technology*, **15**, 578-587.

Leenheer, J.A. and Huffman, E.W.D. (1979) Analytical method for dissolved-organic matter fractionation. *U.S. Geological Survey Water Resources Investigations*, Denver, CO.

Lundin, L. (1998) Hydrochemistry of natural, cut-over and rewetted peatland sites. *Peatland Restoration and Reclamation: proceedings of the 1998 International Peat Symposium* (eds T. Malterek, K. Johnson, and J. Stewart) pp. 139-143. International Peat Society, Duluth.

Lundin, L. and Bergquist, B. (1990) Effects on water chemistry after drainage of a bog for forestry. *Hydrobiologia*, **196**, 167-181.

Marin, L.E., Kratz, T.K. and Bowser, C.J. (1990) Spatial and temporal patterns in the hydrogeochemistry of a poor fen in northern Wisconsin. *Biogeochemistry*, **11**, 63-76.

Marschner, B. and Bredow, A. (2002) Temperature effects on release and ecologically relevant properties of dissolved organic carbon in sterilized and biologically active soil samples. *Soil Biology and Biochemistry*, **34**, 459-466.

McDowell, W.H and Wood, T. (1984) Soil processes control dissolved organic carbon concentration in stream water. *Soil Sciences*, **137**, 23-32.

Meredith, A., Hullar, J., Fry, B, Peterson, B.J., and Wright, R.T. (1996) Microbial utilization of estuarine dissolved organic carbon: a stable isotope tracer approach tested by mass balance. *Applied and Environmental Microbiology,* **62**, 2489-1493.

Metcalfe, R.A. and Buttle, J.M. (2001) Soil partitioning an surface store controls on spring runoff from a boreal forest peatland basin in north-central Manitoba, Canada. *Hydrological Processes*, **15**, 2304-2324.

Mitsch, W.J, and Gosselink, J.G. (1986) Wetlands. 1st edn. Van Nostrand Reinhold, New York.

Molot, L.A. and Dillon, P.J. (1996) Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. *Global Biogeochemical Cycles*, **10**, 483-492.

Moore, T.R. and Dalva, M. (2001) Some controls on the release of dissolved organic carbon by plant tissues and soils *Soil Science,* **166**,1-9.

Moore,T.R , Roulet, N.T., and Waddington, J.M. (1998) Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands. *Climatic Change*, **40**, 229-245.

Mulholland, P.J., Dahm, C.N., David, M.B., Di-Toro, D.M., Fisher, T.R., Kogel-Knabner, I, and Meybeck,J.L. (1990) What are the temporal and spatial variations of organic acids at the ecosystem level? *Life Sciences Research Report 48* (eds. E.M. Perdue, E.T. Gjessing), John Wiley and Sons, Chichester.

National Wetlands Working Group (1987) The Canadian wetland classification system. *Ecological Land Classification Series*, Inland Waters/Land directorate, Environment Canada, Ottawa.

Nelson, P.N., Baldock, J.A., and Oades, J.M. (1993) Concentration and composition of dissolved organic carbon in streams in relations to catchment soil properties. *Biogeochemistry*, **19**, 27-50.

Petrone, R.M., Waddington, J.M. and Price, J.S. (2001) Ecosystem scale evapotranspiration and net CO_2 exchange from a restored peatland. *Hydrological Processes*, **15**, 2839-2845.

Price, J.S. (1997) Soil moisture, water tension, and water table relationship in a managed cutover bog. *Journal of Hydrology*, **202**, 21-32.

Price, J.S. (1998) Methods of restoration of a cutover peatland, Quebec, Canada. *Peatland Restoration and Reclamation: Proceedings of the 1998*

International Peat Symposium (eds. T.Malterer, K. Johnson, and J. Stewart), pp. 149-154.

Price, J.S. Rochefort,L. and Quinty, F. (1998) Energy and moisture considerations on cutover peatlands: surface microtopography, mulch cover and *Sphagnum* regeneration. *Ecological Engineering*, **10**, 293-312.

Price, J.S. and Waddington, M.J. (2000) Advances in Canadian wetlands hydrology and biogeochemistry. *Hydrological Processes*, **14**, 1579-1589.

Price, J.S. and Woo, M. K. (1988) Studies of a subarctic coastal marsh, I. Hydrology. *Journal of Hydrology*, **103**, 275-292.

Robert, E.C., Rochefort,L. and Garneau, M. (1999) Natural revegetation of two block-cut mined peatlands n eastern Canada. *Journal of Botany*, **77**, 447-459.

Roulet, N.T. and Woo, M.K. (1986) Hydrolgoy of a wetland in the continuous permafrost region. *Journal of Hydrology*, **89**, 73-91.

Sachse, A., Babenzine, D., Ginzel, G., Gelbrecht, J., and Steinberg, C.E.W. (2001) Characterization of dissolved organic carbon in a dystrophic lake and an adjacent fen *Biogeochemistry*, **54**, 279-296.

Salonen, V. (1987) Relationship between the seed rain and the establishment of vegetation on two areas abandoned after peat harvesting. *Horticultural Ecology*, **10**, 171-174.

Schiff, S.L., Arawena, R., Trumbore, S.E., Hinton, M.J., Elgood, R., and Dillon, P.J. (1997) Export of DOC from forested catchments on the Precambrian

Shield of Central Ontario: Clues from ^{13}C and ^{14}C *Biogeochemistry*, **36**, 42-65.

Schilstra, A.J. (2001) How sustainable is the use of peat for commercial energy production? *Ecological Economics*, **39**, 285-293.

Schindler, D.W. and Curtis, P.J. (1997) The role of DOC in protecting fresh-waters subjected to climatic warming and acidification from UV exposure. *Biogeochemistry*, 36, 1-8.

Schlotzhauer, S.M. and Price J.S. (1999) Soil water flow dynamics in a managed cutover peat field, Quebec: Field and laboratory investigations. *Water Resources Research*, **35**, 3675-3683.

Shantz, M. and Price, J.S. personal communication

Shannon, G.M. and Woo, M.K. (1997) Spring and summer hydrology of a valley-bottom wetland, Ellesmere Island, Northwest Territories, Canada. *Wetlands*, **17**, 321-329.

Sommerfeld, R.A., Moiser, A.R., and Musselman, R.C. (1993) CO_2, CH_4 and N_2O flux through a Wyoming snowpack. *Nature*, **36**, 140-143.

Swanson, D.K. and Grigal, D.F. (1988) The simulation model of mire patterning *Oikos*, **53**, 309-314.

Tarnocai, C. (1998) The amount of organic carbon in various soil orders and ecological provinces in Canada: *Soil processes and the carbon cycle,* (eds R. Lal, J.M. Kimble, R.F. Follet, B.A. Stewart) CRC press, Boca Raton. pp. 81-92.

Tipping, E. (1981) The adsorption of aquatic humic substances by iron oxides. *Geochemica et Cosmochemica Acta*, **45**, 191-199.

Tipping, E. (1998) Modelling the properties and behaviour of dissolved organic matter in soils. *Mitteilgn. Dtsch. Bodenk. Gesellesch.*, **87**, 237-252.

Thurman, E.M. (1985) *Organic Geochemistry of Natural Waters.* Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht

Urban, N.R., Eisenreich , S.J. and Gorham, E. (1986) Proton cycling in bogs: geographic variation in northeastern North America. In Hutchinson T.C. and Meena, K.M. *Effects of Acidic Depostion on Forest , Wetland and Agricultural Ecosystems.* Spring-Verlag, New York.

Van Seters, T.E., and Price, J.S. (2001) The impact of peat harvesting and natural regeneration on the water balance of an abandoned cutover bog, Quebec. *Hydrological Processes,* **15**, 233-248.

Vance, G.F. and David, M.B. (1991) Chemical characteristics and acidity of soluble organic substances from northern hardwood forest floor, central Maine U.S.A., *Geochemica Cosmochemica Acta,* **55,** 3611-3625.

Von Waldow, H. and Price, J.S. (2002) *Hydrology of a recently restored cutover peatland in eastern Quebec.* M Sc. Thesis. Waterloo University.

Waddington, J.M., Greenwood, M.J., Petrone, R.M., and Price, J.S. (submitted) Mulch decomposition impedes recovery of net carbon sink function in a restored peatland. *Ecological Engineering*

Waddington, J.M. and McNeil, P. (2002) Peat oxidation in an abandoned cutover peatland. *Canadian Journal of Soil Sciences*, **82**, 279-286.

Waddington, J.M., Rotenberg, P.A., and Warren, F.J. (2001) Peat CO_2 production in a natural and cutover peatland: implications for restoration. *Biogeochemistry*, **54**, 115-130.

Waddington, J.M. and Roulet, N.T. (1997) Groundwater flow and dissolved carbon movement in a boreal peatland, *Journal of Hydrology*, **191**, 122-138.

Waddington, J.M. and Warner, K.D. (2001) Atmospheric CO_2 sequestration in restored mined peatlands. *Ecoscience*, **8**, 359-368.

Warner, B.C, and Rubec, C.D.A. (997) The Canadian wetland classification system. *National Wetlands Working Group*, Wetland Research Centre, University of Waterloo, Waterloo, Ontario.

Wessen, B., Berg, B. (1986) Long-term decomposition of barley straw: chemical changes and ingrowth of fungal mycelium. *Soil Biology and Biochemistry*, **18**, 53-59.

Whitehead, G.S. (1999) *The hydrological processes influencing the natural recolonisation of Sphagnum in a cutover bog after 25 years of abandonment, Quebec.* M Sc. Thesis. University of Waterloo.

Wind-Mulder, H.L., Rochefort, L., and Vitt, D.H. (1996) Water and peat chemistry comparison of natural and post-harvested peatlands across

Canada and their relevance to peatland restoration. *Ecological Engineering,* **7**, 161-181.

Woo, M.K. (2002) Wetlands: A hydrological perspective. in the Physical Geography of North America, Oxford University Press, New York.

Woo, M.K. and diCenzo (1988) Pipe flow in Jams Bay coastal wetlands. *Canadian Journal of Earth Sciences*, **26**, 625-629.

Woo, M.K. and diCenzo (1989) Hydrology of small tributary streams in a subarctic wetland. *Canadian Journal of Earth Sciences*, **26**, 1557-1566.

Zoltai, S.C. (1988) Wetland environments and classification. Wetlands of Canada. (ed. C.D.A. Rubec), pp. 4-26. Polyscience Publicatins Inc., Montreal, Quebec.

Zsolnay, A., Baiger, E., Jimenez, M. Steinweg, B., and Saccomandi, F. (1999) Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. *Chemosphere*, **38**, 45-50.