

UNIVERSITY OF CALGARY

Biogeochemical Exchange of Carbon After Peatland Restoration: Carbon Dioxide Fluxes and
Dissolved Organic Carbon Export and Chemistry

by

Yoseph Caelo Atreyu Zuback

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF GEOGRAPHY

CALGARY, ALBERTA

JANUARY, 2013

© Yoseph Caelo Atreyu Zuback 2013

Abstract

This study looks at an abandoned peatland ten years after a restoration which was undertaken to return the peatland to its natural ecological function of carbon storage.

This thesis examines the export of organic carbon in water (dissolved organic carbon), its chemical properties, and carbon dioxide (CO₂) flux in different vegetation communities and environmental conditions, ultimately seeking to understand how restoration has affected the carbon exchange in the restored peatland, vs. an abandoned peatland, and a nearby natural peatland.

DOC export was higher at the abandoned site over the course of the year, DOC chemical properties suggested slowing decomposition at the restored site, and restoration has roughly halved atmospheric carbon export, now ten years after restoration.

Table of Contents

Abstract.....	ii
Table of Contents	iii
List of Tables	vi
List of Figures	vii
List of Equations.....	ix
List of Plates.....	x
List of Abbreviations.....	xi
1 Introduction	12
1.1 Background.....	12
1.2 Peatland Carbon Balance.....	13
1.2.2 Controls on CO ₂ Flux	14
1.2.3 Controls on DOC Export.....	15
1.2.4 Effects of discharge on DOC.....	18
1.3 Effects of Peat Extraction on Peatland Carbon Biogeochemistry	18
1.3.1 Effects of Extraction on CO ₂ Exchange	18
1.3.2 Effects of Extraction on DOC Export and Chemistry.....	19
1.4 Effects of Restoration.....	20
1.4.1 Effect on CO ₂ Exchange	20
1.4.2 Effect of Restoration on DOC Export and Chemistry.....	21
1.4.3 Unknowns & Objectives.....	22
1.5 Study Site Overview	23
2 CO ₂ Dynamics.....	25
2.1 Methods.....	25
2.1.1 Vegetation Biomass (Fuel Rule)	25
2.1.2 Collar placement.....	26
2.1.3 Modelling GEP.....	26

2.1.4 Modelling Respiration	29
2.1.5 Statistics	30
2.2 Results	30
2.2.1 General comments	30
2.2.2 GEP	31
2.2.3 Respiration.....	32
2.3 Discussion	32
2.3.1 Monthly trends	32
2.3.2 Seasonal carbon balance.....	33
2.3.3 Site carbon balances.....	34
2.4 Chapter Summary	34
3 DOC In-situ & GEP	35
3.1 Instrumental Methods	35
3.1.1 Photospectrographic Ratios.....	37
3.2 Chemical Methodology.....	38
3.2.1 Pentose	38
3.2.2 Hexose.....	38
3.3 Results	39
3.3.1 Quality and Chemistry Results	39
3.3.2 CO ₂ and DOC concentrations.....	41
3.3.3 CO ₂ Production and Hexose.....	41
3.4 Discussion	41
3.4.1 DOC Concentration	41
3.4.2 Effect of low water tables and vegetation on DOC chemistry	42
3.5 Chapter Summary	45
4 DOC Export; Storms and Baseflow	46
4.1 Methods:	46

4.1.1 Water Sampling.....	46
4.1.2 Storm Sampling.....	46
4.1.3 Concentration Calculations	47
4.2 Results	47
4.2.1 DOC concentration.....	47
4.2.2 DOC Chemistry	48
4.2.3 DOC Export.....	48
4.2.4 Storm hydrology	49
4.3 Discussion	50
4.3.1 DOC Export and Chemistry.....	50
4.3.1 E2:E3	52
4.4 Chapter Summary	53
5 Conclusion.....	54
5.1 Summary of Findings	54
5.2 Improvements and Future Research	55
5.2.1 Snow water equivalents.....	55
5.2.2 Sugars and decomposition.....	56
5.2.3 Correcting E4:E6 field protocols.	56
5.2.3 Further research for DOC.....	56
6 Figures and Tables.....	58
Bibliography.....	80
Appendix A:.....	96
Appendix B	97
Appendix C.....	98
Appendix D	99
Appendix E.....	102

List of Tables

Table 1: Reported range of carbon dioxide flux and DOC export from peatlands. Notable is the amount of variance in natural peatlands. A summary of literature suggests that carbon dioxide storage ranges from -411 to 312 g CO ₂ m ⁻² y ⁻¹ . Ovenden (1990) provides a narrower normal for Canadian peatlands of 8-30g C m ⁻² y ⁻¹ of storage. Similarly DOC export ranges broadly 1.1 - 43 g m ⁻² y ⁻¹	58
Table 2: Precipitation, 2010 compared to the 30-year climate average, with calculated percent difference between 2010 and 30-year average. July and August are abnormally dry, some 46% dryer and 89.5 percent dryer respectively, while September is abnormally wet at more than double the climate average precipitation.....	62
Table 3: Number of collars at each site which have statistical correlations (Pearson's, P<0.05) to denoted environmental variables.	64
Table 4: Monthly calculated variation in CO ₂ flux components as a numerical complement to Figure 5.....	67
Table 5: Chemistry and quality summary, Red text denotes a Kruskal-Wallis statistic (H), while black text denotes an ANOVA (F). Bolded text is to highlight statistical differences between pair wise comparisons.....	69
Table 6: Sorting collars for linear regressions of GEP to DOC concentration, with ANOVA performed on regression vs. measured values showing no significance between GEP and DOC with any group of collars examined.....	71
Table 7: Calculated discharge from the abandoned site and restored site according to Verhoff's equation (Equation 9).....	71
Table 8: Chemical properties of export DOC. Export properties were significantly different between the restored site and abandoned sites for pH, E2:E3, Hexose, Pentose, Pentose to Hexose, and DOC concentrations.....	72
Table 9: Storm flow lag from the abandoned and restored sites.	77
Table 10: Sugars and sugar ratios from specified depths of soil at the restored site.....	78

List of Figures

- Figure 1: Site overview map. Ditches are spaced parallel every 30m. While the abandoned site has ditches that actively dry the site, the restored site has only artifact ditches that serve as habitat for bog species. The site is inclined to the east where the water discharges from both sites. Dikes have been built on the restored section to cache precipitation and snow melt. 60
- Figure 2: The top panel shows the BDB complex ranging from east to west roughly 2km. On the eastern side is a undisturbed natural open bog, while on the far west side fields have been left abandoned for control study sites, with restored site adjacent to the abandoned site. The bottom panel shows the locations selected for collars at the natural site. 61
- Figure 3: NEE, Respiration, and GEP from data gathered at $PAR > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, statistical difference (ANOVA, $P < 0.05$) denoted by difference in lettering. 63
- Figure 4: Seasonal modelled data for six collars presented over the hour of day. Collars are chosen to represent sites that show the range of variability among collars. 65
- Figure 5: Seasonal modelled data for all collars (grouped by site) presented by month. 66
- Figure 6: Hours of sunlight over the months in Figure 5. Sunlight hours drop as summer ends and the autumnal equinox in September is passed. 66
- Figure 7: Changes to water table depth below ground level (two sites) over the field season. Points show individual well measurements. The solid line shows the moving average as the season progresses as compared to a -40cm datum at each site. 68
- Figure 8: DOC to absorbance regression for water drawn from the site export points for both abandoned and restored site discharge. 70
- Figure 9: DOC to absorbance regression for water drawn from wells, 70
- Figure 10: Restored site discharge with panels for DOC concentration, E2:E3, SUVA, and pH. Numbers in the two top panels show the position of 5 recorded storm events recorded. 73
- Figure 11: Abandoned site discharge with panels for DOC concentration, E2:E3, SUVA, and pH. Numbers in the two top panels show the position of 5 recorded storm events recorded. 74

Figure 12: A large storm event's effect on DOC export at the restored site, shown here as cumulative export of DOC (as a percent of the total during this storm system) , corrected for changing DOC concentration..... 75

Figure 13: DOC concentration from export waters compared to rainfall. Rainfall represented across the season masks relative volume, and impact, of a storm event. By showing as cumulative rainfall large events can be easily distinguished from medium or small events with short but intense rainfall..... 76

Figure 14: The percentage of DOC that is exported during times of high discharge (as a cumulative percentage of 14-days of discharge) relative to the DOC exported during lower flow periods during a 14-day storm system at the restored site. This chart shows that high flow periods denoted as the amount of flow occurring only 5% of the time exports 15% of the DOC, and that 50% of the total export occurs in the top 26% discharge amounts. 77

Figure 15: Changing E2:E3 seasonally at an abandoned and restored, excavated peatland shown with cumulative recorded precipitation. 78

List of Equations

Equation 1: Carbon balance equation.....	13
Equation 2: GEP calculation for modelling CO ₂ fixation.....	27
Equation 3: Soil Temperature Factor for GEP.....	27
Equation 4: Water Table Factor for GEP	27
Equation 5: Vegetation Biomass Factor for GEP.....	28
Equation 6: Respiration calculation for modelling CO ₂ production.....	29
Equation 7: TOC methodology	36
Equation 8: Absorbitivity constant; the relationship between absorbance and DOC concentration.....	37
Equation 9: Verhoff's Equation (Verhoff <i>et al.</i> , 1980)	47

List of Plates

Plate 1: BDB field 1: <i>Eriophorum vaginatum</i> (centre arrow) dying back after its vigorous colonization of the site early after restoration. <i>Polytrichum</i> sp., a pre- <i>Sphagnum</i> spp. colonizer, grows from the dying <i>Eriophorum</i>	79
--	----

List of Abbreviations

BDB	Bois-des-Bel, Québec, the site of this study
bgl	Water table levels as measured below ground level.
DOC	Dissolved organic carbon, carbon suspended or dissolved below 0.45µm size
EMR	Electromagnetic radiation
GEP	Gross ecosystem production, a measure of photosynthetic carbon dioxide use
NEE	Net ecosystem exchange, net carbon dioxide change over time
PAR	Photosynthetically active radiation, EMR between 400 nm and 700 nm wavelength
SUVA	Specific UV absorbance, a value derived from spectrophotometer measurements and DOC concentration
TOC	Total organic carbon, all organic carbon <i>i.e.</i> not just dissolved organic carbon
UV	Ultraviolet light, EMR ranging between 10 nm and 400 nm wavelength.
UWP	Ultrapure Water™, A water purity classification designated by the SEMI group.
Veg	Vegetation biomass
VIS	Visible light, EMR between 380 and 740 nm wavelength
WT	water table, measured as depth below water table

1 Introduction

1.1 Background

Peat mosses (*Sphagnum* spp.) are able to colonise areas with high water tables and as they die the high water tables and internal chemistry of these plants can slow their decay and cause them to accumulate. Peatlands (including tropical non-*Sphagnum* peatlands) together store approximately 30% of the world's soil carbon (Gorham, 1991; Batjes, 1996) equivalent to 455 billion tonnes of carbon and cover 3.46 million km² of the earth (Batjes, 1996). In fact, Canada's land area is estimated at 14% peatlands (Zoltai & Pollett, 1983). In addition, every year peatlands are estimated to store 0.076 more Pg (Pg = 10¹⁵ g) of carbon (Clymo, 1984).

Peat is an important mineral and biological resource that is utilised for fuel and horticultural uses. Extraction of peat for horticultural use involves removing surface vegetation, and draining the peatland (Waddington & Price, 2000). Once the peatland is no longer economical for extraction they are often left abandoned (Waddington & Price, 2000). These drained peatlands usually have a depth of peat still left, and this dry aerated peat mineralizes at a higher rate than natural peatlands (Waddington *et al.*, 2002). Globally, mineralization of peat is estimated to release 0.0085 Pg C every year (Clymo, 1984; Waddington *et al.*, 2002).

To mitigate carbon losses restoration is now being applied to peatlands. Abandoned, extracted peatlands have had restoration treatments applied from simply blocking drainage ditches, to introducing vegetation and manually flattening the site profile. These methods combined (Quinty & Rochefort, 2003) have shown positive results in establishing *Sphagnum* spp. (Lucchese *et al.*, 2010), regulating water levels (Shantz & Price, 2006), and increasing levels of vegetative productivity (Petroni *et al.*, 2001; Waddington *et al.*, 2010). Despite these promising results this early data does not answer several key questions following restoration: (1) what are the long term changes to carbon fluxes? (2) when will carbon flux patterns return to a natural state? (3) will hydrologic export of carbon stabilize? (4) and how does restoration compare to abandonment in the long term?

To answer these questions this study compares the CO₂ fluxes and the hydrologic carbon export at a peatland restored for 10 years to an abandoned and an undisturbed natural site.

1.2 Peatland Carbon Balance

The amount of organic carbon (C) contained in a particular soil (Equation 1) is a balance between the rate of deposition of plant residues in or on the soil and of the sorption of dissolved organic carbon (DOC) in the cation exchange sites of the soil, the rate of mineralization of the residue carbon by soil biota, and the export of DOC and particulate organic carbon. Carbon balance looks only at the changes to the inputs and outputs to the system (Equation 1)

Equation 1: Carbon balance equation

$$\text{Carbon Export (-) or Storage (+)} = CO_2D + CO_2R + CO_2P + CH_4N + DOC + DIC$$

Where: CO₂D is the CO₂ released from decomposition
CO₂R is the CO₂ released from plant respiration
CO₂P is the CO₂ fixed from the atmosphere by autotrophic organisms
CH₄N is the net release of CH₄ which is a balance between CH₄ oxidised, to the CH₄ produced.
DOC is the net dissolved organic carbon export
DIC is the net dissolved inorganic carbon export
(Source: Gorham, 1991)

The peatland carbon balance is controlled by the conditions established in the peatlands. For instance, anoxic conditions (Freeman *et al.*, 2001) resulting from high water tables make peatlands a significant cache of carbon. This is because decomposition of vegetation is slowed, and much of the decaying biomass preserved. The specific amount stored annually can greatly vary as in Table 1.

As an example of carbon storage in a natural bog we can use measurements taken at Mer Bleue (Roulet *et al.*, 2007). Mer Bleue is a 28 km² hummock-hollow alternating shrub bog where 6-years of CO₂ net ecosystem exchange and regular DOC export was measured. The net ecosystem exchange (NEE) or the net flux of CO₂ at Mer Bleue was a storage of 40.2 ±

40.5 g CO₂-C m⁻² y⁻¹, while the DOC export was 14.9 ± 3.1 g m⁻² y⁻¹. (Roulet *et al.*, 2007). Reviews (Table 1) suggest that NEE ranges from 313 (net release) to -411 g C m⁻² y⁻¹ (net storage) (Saarnio *et al.* 2007, Strack *et al.* 2008) with Ovenden (1990) providing a narrower normal for Canadian peatlands of 8-30 g C m⁻² y⁻¹ of storage. Similarly, DOC export ranges broadly (1.1 - 43 g m⁻² y⁻¹, Table 1). These large variations have been explained by environmental controls on CO₂ flux, and controls on DOC export.

1.2.2 Controls on CO₂ Flux

CO₂ flux, including both gross ecosystem photosynthesis (GEP) and respiration, may be controlled by several environmental variables including soil temperature, water table, photosynthetically active radiation (PAR), and vegetation biomass. These four environmental variables give a range of variances in CO₂ fluxes in mathematical models (Blodau, 2003). However these controls are selected as explanatory variables by their strong correlations to field data (Riutta *et al.*, 2007).

Temperature is a measure of kinetic energy of molecules. As temperature increases, activation energy for a given reaction becomes less of an energetic burden to overcome, and thus, as temperature increases, reaction rates increase. This was seen to be true in ecological contexts by Lafleur *et al.* (2005) who measured higher total respiration with increasing soil temperatures. Besides immediate changes in rates of respiration, temperature also has important seasonal variation that has implications for photosynthesis and carbon fixation. Griffis *et al.* (2000) saw temperature increases result in longer growing seasons, and with plants able to stay alive longer they contribute more to GEP yearly sums.

Water table is one of the most significant controls on peatland carbon balances. Gorham (1991), and Riutta *et al.*, (2007) saw water table eclipse temperature as an explanatory variable for annual carbon balances. The most important peat accumulator in many northern peatlands, *Sphagnum* (Ovenden, 1990; Rochefort, 2000), is non-vascular, relying on the wicking action of its leaves to hydrate its cells (Nichols & Brown, 1980). This makes the importance of water table as an explanatory variable fairly clear: *Sphagnum* is extremely sensitive to water availability (Titus & Wagner, 1984; Schipperges & Rydin,

1998). In fact Waddington *et al.* (1998) saw highest productivity in a subarctic fen when the water table was merely 2 cm below the ground surface. Water table also has important effects on degradation; decomposition is faster under oxic conditions compared to anoxic conditions, and because of this, deeper water table creates a larger oxic zone, which in turn increases heterotrophic respiration (*e.g.* Moore & Dalva, 1993).

Plants' ability to photosynthesize is dependent on their exposure to photosynthetically active radiation (PAR). Pigments in the plant's cells are able to take energy from the PAR range (400-700 nm) of electromagnetic radiation and store it as energy by fixing CO₂ in a Calvin-Benson Cycle which ultimately yields hexose sugars (McCree, 1981). *Sphagnum* spp. were seen to reach their GEP maximum at a relatively low PAR level of 700 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ (Titus & Wagner, 1984). Ultimately vascular vegetation is important to peatland GEP values as they are able to fix much more carbon than *Sphagnum* at light levels higher than 700 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ when *Sphagnum* spp. have already reached their peak GEP rates (Frolking *et al.*, 1998).

Vegetation type affects CO₂ exchange in several ways; certain plants are more productive, some respire copiously, and others still decompose much faster. At rich fen sites with vigorous vegetation Frolking *et al.*, (1998) saw greater NEE at high light levels than at poor fens or *Sphagnum* dominated bogs. Moore *et al.*, (2005) and Moore & Basiliko (2006) reported differences in respiration based on different substrates, and differences in the decomposability between plant species. For instance *Sphagnum* litter's exponential decay constants averaged -0.02 y^{-1} for hummock species, and -0.08 y^{-1} for hollow and lawn species, while sedges averaged -0.28 y^{-1} (Moore *et al.*, 2005). Different parts of plants also differ in their decomposition rate. For example, Zech *et al.* (1997) reports that root xylem, epidermis, and leaf veins are rich in lignin, which decomposes slowly.

1.2.3 Controls on DOC Export

Decomposition is a concern also for carbon exported in water. Peatlands are a major contributor to global DOC levels in oceans (Thurman, 1985). This represents a future source of CO₂ because though not a greenhouse gas itself, DOC can be oxidised to CO₂ (Billet *et al.*, 2004). DOC export can be a significant factor in the carbon balance of a peatland,

changing the final tally from a sink of carbon to a net source (Waddington & Roulet, 2000; Roulet *et al.*, 2007).

Chemically, DOC is given an operational definition of organic carbon that passes through a 0.45 µm filter. However, all DOC is not equal, as some DOC mineralizes easily (labile DOC), and some DOC is, or becomes, highly recalcitrant over time. Labile DOC is considered fresh, newly derived from vegetation. Vegetation has two interfaces to deliver labile DOC to the peat. The first is through surface litter, and the second is through roots, via root exudates (Nelson *et al.*, 1994). An organic carbon ages, and is repeatedly utilized for energy, removing side chains and increasing the relative percentage of aromatic functional groups, it becomes recalcitrant (Almendros *et al.* 1990, Baldock *et al.*, 1992; Baldock & Preston, 1995; Zech *et al.*, 1997). These two extremes on a gradient of DOC lability, from very labile to very recalcitrant, have different solubilities. Labile organics are generally smaller and polar and are more able to become dissolved; recalcitrant carbon, with its hydrophobic aromatic groups (Qualls & Haines, 1991), generally remains in sorption spots in the soil (Dunnivant *et al.*, 1992). Essentially, fresh, labile DOC is likely to decay quicker, recalcitrant DOC is older, and all DOC comes from vegetation.

A major control on organic carbon entering solution is pH. Falling pH has been seen to decrease DOC concentration as having high H⁺ concentrations forces hydrophobic non-polar DOC out of solution, precipitating to suspensions, or flocculating into the soil (Jardine *et al.*, 1989). An increase of pH of 0.5 has been seen to increase the amount of mobilised organic carbon by 50% (Tipping & Woof, 1990). Bogs are acidic (3.5 > pH > 4.2, IPCC), thus holding a pool of DOC in sorption sites in the soil (Thurman, 1985; Jardine *et al.* 1989; Peterson, 1990; Kennedy *et al.*, 1990; Evans *et al.*, 2006).

Peatlands can be acidic for three primary reasons. Firstly, as bogs are only fed by atmospheric precipitation (ombrotrophic), there is no groundwater inflow to carry away organic acids and hydrogen ions, as well as no influx of geologic materials to neutralize the acids present in bogs (Charman, 2002). Second, the decay of vegetative material in bogs releases organic acids (Gorham *et al.*, 1984). Third, peatlands generally have high cation exchange capacities (CEC) where cations are taken in from solution and hydrogen ions

replace them, lowering pH. *Sphagnum* has been seen to be efficient at removing cations from solution. Up to 30% of the dry mass of *Sphagnum* exchange sites are in the form of carboxyl groups (COO⁻) in the sugars *Sphagnum* creates (Clymo & Hayward, 1982).

Seasonal differences exist in DOC export from peatlands (McDowell & Wood, 1984). First, DOC concentration is partially controlled by contact time between soil and solution (McDowell & Wood, 1984; Easthouse *et al.*, 1992; Michalzik & Matzner, 1999). In spring, a large volume of water rapidly passes through the soil, resulting in less contact time in the soil leading to lower DOC concentration. In summer, deep water tables and longer contact times during subsurface flow increase DOC concentrations (McDowell & Wood, 1984; Bourbonniere 1989). Important to note is that there is an inverse relationship between DOC concentration and water fluxes in peatlands. That is to say increasing water volume decreases DOC concentration (Pastor *et al.*, 2003). However, a change in DOC concentration does not necessarily affect DOC export as much as discharge volume does (Jardine *et al.*, 1990), specifically, during storm events (Hinton *et al.*, 1997). Essential the seasonal trend in DOC concentration mimics the seasonal water availability in the peatland.

The second reason for seasonal differences in DOC export in peatlands is the effect of temperature on the energetics of organic carbon dissolution. The temperature response of DOC is tiny relative to that of soil CO₂ respiration to temperature (Strack *et al.*, 2008). The trend is that as temperature increases, DOC concentration increases as well (Bourbonniere, 1989; Waddington & Roulet, 1997; Moore & Dalva, 2001). Additionally, freeze/thaw cycles increase DOC concentration (relative to the water content of the soil before freezing) (Zsolnay, 1996) with part of the increase in DOC concentration coming from microbial cell disruption (DeLuca *et al.*, 1992), and part due to increased surface area (Kalbitz *et al.*, 2000).

Last, DOC concentration may be controlled by vegetative productivity (Neufeld *et al.*, 2010), a control examined in this study. It can vary with litter type (Strack *et al.*, 2008); and it has been linked to level of soil respiration (Burford & Bremner, 1975) both of which vary seasonally.

1.2.4 Effects of discharge on DOC

Peatlands are seen as dynamic ecosystems where the accumulation of peat results from hydrological conditions which in turn are reinforced by the peat properties and accumulation, through the peat's effect on flow patterns of water (Wright *et al.*, 1992). As water passes through an organic soil, *i.e.* a bog, its concentration of DOC increases (Cronan & Aiken, 1985; Moore, 1989; Moore & Jackson, 1989; Marin *et al.*, 1990; Dalva & Moore, 1991; Qualls & Haines, 1991; Koprivnjak & Moore, 1992; Dosskey & Bertsch, 1994) and as discharge increases the DOC concentration falls (McDowell & Fisher 1976, Fiebig *et al.* 1990, Brown *et al.* 1999). Bog discharge often flows into fens (Wright *et al.*, 1992), with exported DOC maintained in the soil column or metabolised by microbes and released to the atmosphere (Pastor *et al.*, 2003). In natural peatlands water table affects both export of DOC and DOC production. Water table levels control the region of the peat profile that is aerobic, a control on DOC concentration (Moore & Dalva, 2001), and the discharge (by raising the water to levels where hydraulic conductivity is higher), which changes the total mass of DOC exported (independent of concentration; Boelter & Verry, 1977; Brooks, 1992)

1.3 Effects of Peat Extraction on Peatland Carbon Biogeochemistry

1.3.1 Effects of Extraction on CO₂ Exchange

Any disturbance to a peatland can have drastic effects, and extraction, the removal of vegetation and the drying of the peat, leads to conditions that a peatland ecosystem cannot recover from on a time scale of 100's of years. Extraction has two impacts on carbon balance. First, any peat extracted may decompose. Horticultural peat continues to decay, and this decay accounts for 70% of the greenhouse gas emission in the lifecycle of peatland extraction (Cleary *et al.*, 2005). Secondly, once extracted the remnant peatland may be a net source of carbon due to lack of productive vegetation, and a deep water table allowing oxidation of the residual peat. At an abandoned peatland, estimates of CO₂ flux, prior to restoration, were a source of 520 g C m⁻² y⁻¹ (Petroni *et al.*, 2001). With a lifetime of abandonment being 20 years to 100 years, in historical peat excavations, the loss of carbon is significant.

1.3.2 Effects of Extraction on DOC Export and Chemistry

Extraction in peatlands increases DOC export (Glatzel *et al.*, 2003; Waddington *et al.*, 2008) through increased discharge. Discharge in extracted peatlands is intentionally sped up. Across a site parallel ditches will be dug, spaced every 30 meters (Waddington & Price, 2000)(Figure 1). Between these the bare peat is worked into a slope towards the ditches. In natural peat systems water would have to travel laterally perhaps hundreds of meters with a loss of one meter elevation, whereas in extracted peatlands the distance between any point in the peat and the drainage ditch is 15 meters, with a loss of two meters of elevation. These hydrological conditions not only dry the peat, but they prevent water from being retained. Spikes in discharge at extracted sites are expected to be higher following precipitation than at a restored site with blocked drainage ditches that has been recolonized by bog vegetation (Shantz & Price, 2006).

The second way DOC export is increased, besides through discharge, is that the concentration of DOC in the water is changed. There are four reasons why extraction can increase DOC concentrations. First, peatland disturbance itself, in removing the surface vegetation, and creating a slope in the fields towards ditches, creates a new interface for carbon to become dissolved (Lundquist *et al.*, 1999). Second, dry conditions induced by drainage ditches leave conditions harsh for microbial colonies that would otherwise decompose DOC (Lundquist *et al.*, 1999) so net production of DOC increases and this leaves more DOC available to be exported. Third, wetting and drying cycles in the peat result in increased turnover (Lundquist *et al.*, 1999) and disruption of microbial biomass (*i.e.* cell lysis/death) (Christ & David, 1994) and condensation of microbial products (Lundquist *et al.*, 1999) which are exported as DOC. Fourth, deeper infiltration of rainwater raises pH, a situation where organic carbon is more likely to enter solution (Christ & David, 1996).

In addition to higher DOC concentration, the chemistry of DOC is also altered in extracted peatlands. Specific UV absorbance (SUVA), a measure of aromaticity, calculated with UV absorbance divided by DOC concentration, can show significant differences between measurements comparing extracted peatlands and those rewetted for 20 years (Höll *et al.*, 2009). Abandoned sites have SUVA values consistent with less aromatic DOC molecules, and DOC molecules smaller in overall size (Höll *et al.*, 2009). In contrast, Glatzel *et al.*,

(2003) between undisturbed and extracted peatlands, did not observe any significant change in SUVA values, which indicate humic acid content, humification index, or aromaticity in general.

1.4 Effects of Restoration

Restoration of bogs seeks to create a carbon sink by re-establishing natural hydrological conditions, and recolonization of *Sphagnum* moss (Gorham & Rochefort, 2003; Waddington & Warner, 2001; Rochefort, 2000). Hydrology, in brief, is stabilized by blocking ditches and levelling the peatland site. Then vegetation is introduced from a nearby donor site and covered with a straw mulch (Rochefort *et al.*, 2003). However, the results of these "restorations" are unknown in the long term, and the results that have been published are both positive, by establishment of a carbon sink function (Bortoluzzi *et al.* 2006, Tuittila *et al.* 2004, McNeil & Waddington 2003, Waddington & Warner 2001, Tuittila *et al.* 1999), and uncertain with regard to long-term effects of restoration (Gorham & Rochefort, 2003; Feldmeyer-Christe *et al.*, 2001).

1.4.1 Effect on CO₂ Exchange

Restoring peatlands reduces CO₂ emissions due to both wet, reducing conditions and increased vegetation cover. Some bogs have become carbon sinks following establishment of a thick carpet of *Sphagnum spp.* (Strack *et al.*, 2008). Previous investigations have been too short to evaluate the long-term effects of restoration on the carbon flux and DOC export. Petrone *et al.* (2001) saw temperature as the only notable control on respiration after restoration at BDB; yet this occurred only in the first year after restoration treatment. Waddington *et al.* (2010) looked at BDB only in the first three years after restoration, yet started to see significant differences between the abandoned site and the restored site. Samaritani *et al.* (2011) also looked at a site post-restoration before it was fully vegetated. These studies leave us asking what are the long-term results of peatland restoration.

Long-term results may have important differences compared to these short-term review studies. Joosten & Augustin (2006) reviewed contemporary studies on peatland rewetting, and broke restoration into three phases of carbon balance. They suggest that it is only in the third phase, postulated as 51 years after restoration, that positive results are achieved

(CO₂ and CH₄ sink function in the peatlands). Long-term studies should be pursued based on estimates of length of time to naturalization, and the uncertainties raised by short-term studies.

1.4.2 Effect of Restoration on DOC Export and Chemistry

Restoration may increase anoxia in the peatland which alters DOC concentration as seen in three studies. Rewetting produces anoxia, and this is known to decrease DOC adsorption in soils (Kaiser & Zech, 1997). Anoxia also induces microbial anaerobic decomposition which releases a higher proportion of water-soluble intermediate organic carbon as metabolites (Mulholland *et al.*, 1990). Laboratory results, as well, show that anoxic waterlogged soils release higher levels of water-extractable organic carbon than controls (Kalbitz *et al.*, 1997). However, even if concentration increases due to anoxic conditions, the hydrologic changes made during restoration should lower discharge, possibly lowering the amount of DOC export.

Waddington *et al.* (2008) looked at the export of DOC from BDB before and in the two years after restoration. In 1999, the wettest of the three years, Waddington *et al.* (2008) measured DOC export at the abandoned site and the "restored" site (the latter awaiting treatment). The DOC export was 10.3 g C m⁻², and 4.8 g C m⁻², at the abandoned and to-be-restored sites respectively. In 2000 and 2001, two drier years, the DOC export for the abandoned site, and for the restored site both dropped to 6.2 g C m⁻², and 3.5 g C m⁻², respectively. Meanwhile a restoration involving only blocking ditches was modelled to decrease export (Wilson *et al.*, 2011) depending on drain spacing (Worrall *et al.*, 2010; Armstrong *et al.*, 2010). Also, long-term rewetting studies in Europe suggest that DOC concentrations become lower than abandoned sites in the time range of 20 years (Höll *et al.*, 2009). These studies still leave us to question what a comprehensive donor vegetation restoration does to DOC export.

DOC compositional assessments following restoration have been performed. DOC fractionation, into humic and fulvic acids (Strack *et al.*, 2011) recorded exported DOC composition (humic acid fractions) not significantly different between abandoned sites and restored sites. Yet Glatzel *et al.* (2003) suggested that restoration led to a increases of DOC

concentration. This was reported to be due to an increased source of dissolved organic matter from anoxic conditions, and the authors suggested that root exudates could be a primer for increased DOC concentrations. In this case still, the DOC composition was not altered after restoration (Glatzel *et al.*, 2003). We are again left wondering what the effects of restoration are in the long term.

1.4.3 Unknowns & Objectives

Time scales to achieve a carbon sink status in restored peatlands are poorly studied highlighting the need for long-term studies. Chemical changes, and changes in DOC concentration in-situ are not understood especially in restored peatlands and how this compares to abandoned and natural peatlands is unclear.

In order to address these knowledge gaps this study looks at a site restored 10-years ago. The first chapter aims for greater precision models on long-term CO₂ balances in peatlands following rewetting/restoration based on CO₂ flux and DOC data collected a decade after restoration.

I address long-term changes in CO₂ fluxes due to restoration efforts in chapter two. This part of the study evidences whether ten years is the time frame to return the BDB restored site to a negative carbon balance (*i.e.* storing carbon). This was completed by measuring CO₂ as part of a site carbon balance to make a comparison between a restored site (restored 10 years prior to the study), a nearby natural site, and an abandoned site.

The third chapter deals with DOC concentration and chemistry, and the fourth chapter examines DOC export from the peatland. In-situ DOC concentration and chemistry was measured, quantifying changes long after restoration was performed. Also, this study seeks evidence to corroborate studies suggesting carbon dioxide fixation by productive vegetation has a link to DOC concentration and chemistry in-situ (Gödde *et al.*, 1996) or to the contrary that there may be no such link. Chapter four deals with DOC export from the site and the effect of storms on DOC concentration, export, and discharge. This study's objective is to determine the effect of restoration on discharge, storm discharge lag time, and DOC export ten years after restoration. In these chapters DOC is thoroughly investigated with special attention on long-term effects compared to previous short-term

studies, and lesser understood relationships such as DOC quality and soil carbohydrates, or DOC concentration and moisture regimes.

1.5 Study Site Overview

Bois-des-Bel (BDB) Quebec (Figure 1, Figure 2) is a NSERC and CSPMA funded research site in the Bas-St. Laurent region of Quebec approximately 11km northeast of Rivière-du-Loup (N47.9671°, W69.4285°).

The BDB research site is part of a 200ha treed and open bog complex. Bogs are normally elevated portions of peatland complexes where peat has accumulated and raised the surface level (and local water table) above the regional water table (Pastor *et al.*, 2002). Horticultural extraction commenced at BDB in 1972, and an 11.5 ha section was drained and vacuum harvested, and operationally abandoned in 1980. The abandoned peatland has eleven 300 m long fields separated by parallel drainage ditches 30 m apart. These fields are surrounded by a thick *Picea mariana* treed bog that transitions into open bog in places within the complex.

In late 1999 an ecological recovery project was undertaken, 19 years after abandonment post-extraction. As part of the restoration effort the 11.5 ha were separated into three sites. The first site, two fields or 1.8 ha, was left abandoned to be a control field for future studies. The second site of 7.5 ha was actively restored according to the guidelines of Quinty & Rochefort (2003) with a buffer field between the first and second sites (*cf.* Figure 1).

Active restoration has several steps. To stabilise water levels several peat dikes were constructed to contain snowmelt waters in four terraces with the highest elevation at the west end (Figure 1), and a mildly lower elevation at the east end in which direction all the ditches empty. These drainage ditches were blocked at their southeast ends to stop further drainage rather than levelled. These now artefact ditches were retained as habitat for open water bog fauna with open water area further supplemented with the construction of eight small ponds (Figure 1). Live donor material from a nearby bog was spread on the top of the 1.5 m of peat remaining on the 30m wide fields, where 0.75 ha of material was spread over 7.5 ha, a 1:10 ratio. A protective straw mulch cover (3000 kg ha⁻¹) was sprayed on the donor material; by adding a straw mulch as a protective cover, surface humidity increased,

thus improving soil moisture and tension (Price *et al.*, 1998), making the dry peat surface more habitable for the donor material that cannot survive extreme water stress (esp. *Sphagnum spp.*). Finally, to stimulate *Sphagnum* nurse species *Polytrichum strictum* colonization, 15g m⁻² phosphorus fertilizer was applied (Groeneveld *et al.*, 2007). Though restoration treatment has been applied, for simplicity the restoration treatment site, will be referred to as restored in this study.

Bois-des-Bel (BDB) Quebec is 5 km from St. Arsène weather station. St. Arsène has a 30-year average (1971-2000) annual precipitation of 962.9 mm. Bois-des-Bel received 885.6mm in 2010, and compounding this drier year was the unequal distribution of precipitation. This resulted in a severe water deficit compared to the 30 year climate average in July and August (Table 2). Average annual temperature is 3.2°C ± 0.8 with average of 17.8°C ± 5.0 in July and -12.6°C ± 3.4 in January (Environment Canada, 2000). In 2010 ,the annual average temperature was 6.3°C, with July average of 18.5°C, and a January average of -7.5°C.

2 CO₂ Dynamics

2.1 Methods

CO₂ exchange was measured with the closed chamber technique (Tuittila *et al.*, 1999; Griffis *et al.*, 2000). An acrylic chamber was designed for this experiment measuring 60 cm x 60 cm and 30 cm high. The chamber had an electric fan installed inside to mix headspace air while a field researcher sampled CO₂ concentration and recorded incident temperature. To gather data the chamber was placed on the ledge of a metal sampling collar placed into the peat the preceding summer. By filling the ledge with water, the acrylic chamber formed an air-tight seal with the ground for sampling air inside the chamber. An EGM-4 infrared gas analyser (PPSystems) was connected to two sealed connectors inside of the acrylic chamber with PVC tubing to sample chamber air for CO₂ concentration (ppm). The CO₂ flux was calculated from the linear change in CO₂ concentration recorded every 15 seconds for 105 seconds within the chamber. Additionally, environmental data including incident PAR and air temperature were recorded every 15 seconds with the CO₂ concentration, and soil temperature was sampled from 2 cm to 20 cm below ground level using a thermocouple thermometer. Water table level was recorded from a perforated plastic tube installed adjacent to the collar to a depth of approximately 115 cm, at every sampling. Once a week a measure of vegetation volume was recorded using the fuel rule technique outlined below.

2.1.1 Vegetation Biomass (Fuel Rule)

Davies *et al.* (2008) developed a visual estimation technique to derive a calculated index of volume of vegetation. Statistically significant regressions were found between vegetation volume, and biomass of vegetation clippings in a peatland in the same region as BDB (Strack & Srivastava, 2010).

A 1.5 m four sided ruler was made from a square-cut rod painted with 10 cm bands, 5 cm bands, and 2 cm bands on three of its sides respectively. By placing the rule in the collar, a field researcher recorded the percent of each band that was obscured with vegetation. The ruler was rotated so at least five coloured bands were obscured by vegetation; if the 10 cm bands were not at least partially obscured up to 50 cm, the 5 cm band was used; if 25 cm were not partially obscured on the 5cm banded side, the 2 cm bands were used. Collars

were evaluated for vegetation volume using this technique biweekly May to October. The applicability of this technique was evaluated by collecting and weighting biomass and regressing this on the vegetation volume derived from the Davies *et al.* (2008) method ($r^2 = 0.711$, $F = 29.570$, $p < 0.001$).

With CO₂ concentration, PAR, soil temperature, air temperature, vegetation volume, and water table level collected on a weekly basis, I was able to construct an extrapolation for CO₂ flux throughout the measurement season. But to ensure the extrapolated seasonal values matched the site variability I had to ensure collar placements represented the BDB site.

2.1.2 Collar placement

To estimate site wide carbon dioxide flux, collar placement reflected site vegetation community variation. Collar placement varied by bog microtopography *i.e.* hummocks and hollows, sites that were visibly wet vs. drier sites. Collars were placed in the abandoned site based on differences in surrounding vegetation in three distinct areas: treed, open growth, and bare peat. The restored site collars were placed based on differences in water regime, with half in wetter areas, and half on drier lawns or hummocks. Collars were also placed in artefact (not functioning) ditches, and in artificially landscaped ponds. This strategy aimed to achieve a measure of the range of variation across the site, not to estimate the carbon balance for specific vegetation communities. In the end 34 collars were placed in the BDB complex, 14 of which were on restored fields, an additional three on ditches, and three on pools; another six were placed on the abandoned site of BDB; eight were installed on a nearby natural site. The eight natural site collars were placed in May of 2010, and the other 26 in August 2009. With appropriate, representative collar placement I was able to create an extrapolation for GEP and for respiration from the CO₂ concentrations and environmental variables recorded.

2.1.3 Modelling GEP

GEP was modelled with environmental factors compared to field recorded GEP. Field measurements, however, only recorded net change in CO₂ concentration (ppm). This change, net ecosystem exchange (NEE) has two component parts. The first is consumption

of CO₂ by the plants, and the second is production of CO₂ through respiration. Respiration was recorded as the change in CO₂ concentration under zero light, when there could be no contribution to NEE from GEP, leaving only respiration. By taking the difference of the NEE and respiration from the field measurements, taken under ambient or shaded light, field GEP measurements were calculated. With these field GEP measurements, parameters from literature adapted from recent peatland work (Riutta *et al.*, 2007) were used to derive empirical models of seasonal GEP from the following equations:

Equation 2: GEP calculation for modelling CO₂ fixation

$$GEP = P_{max} \times \left(\frac{PAR}{k+PAR} \right) * T_f * WL_f * VB_f \quad (\text{Riutta } et \text{ al.}, 2007)$$

Where: GEP = gross ecosystem photosynthesis (g CO₂ m⁻² day⁻¹)
P_{max} = level of PAR required for maximal photosynthesis (μmol photons m⁻² s⁻¹)
PAR = recorded PAR levels (μmol photons m⁻² s⁻¹)
k = PAR correction factor

This equation has three embedded equations (Riutta *et al.*, 2007):

Equation 3: Soil Temperature Factor for GEP

$$T_f = e^{-0.5 * \left(\frac{Soil\ T - optimum}{tolerance} \right)^2} \quad (\text{Riutta } et \text{ al.}, 2007)$$

Where: T_f = Soil Temperature Factor
Soil T = Recorded Soil Temperature (°C)
optimum = Soil temperature of greatest GEP (°C)
tolerance = deviation from optimum where GEP is 61% of its maximum (°C)

Equation 4: Water Table Factor for GEP

$$WT_f = e^{-\frac{WT\ level - optimum}{tolerance}} \quad (\text{Adapted from: Riutta } et \text{ al.}, 2007)$$

Where: WT_f = Water Table Factor

WT_{level} = Recorded Water Table Level (cm below ground level (bgl))

$optimum$ = Water table of greatest GEP (cm bgl)

$tolerance$ = deviation from optimum where GEP is 61% of its maximum (cm bgl)

Equation 5: Vegetation Biomass Factor for GEP

$$VB_f = 1 - e^{-\alpha * volume} \quad (\text{Riutta } et \text{ al., 2007})$$

Where: VB_f = Vegetation Biomass Factor

α = Vegetation correction factor

$Volume$ = Biomass volume (Davies *et al.*, 2008)

Equation 2 was used to generate seasonal GEP. Maximum, *optimum* GEP calculated using the PAR factors in Equation 2 are multiplied by environmental factors calculated in equations Equation 3 to Equation 5. Having these equations from Riutta *et al.* (2007) I entered them into Microsoft Excel beside the field recorded environmental and GEP data. These cells with Equation 2 were designated to calculate GEP and compare them with the field recorded GEP. Each of the field recorded GEP and modelled GEP Equation 2 columns drew its variables from the same constant cells. These constant cells were empty but associated with given optimums and tolerances not yet calculated. Microsoft Excel's solver function was started to iterate 10,000 times to vary the values of optimum, tolerance, and other factors to achieve the lowest sum of squares for the modelled GEP. This was repeated for each collar to calculate all parameters. With these modelled parameters, weather station data and seasonal vegetation models could be entered into the PAR, temperature, water table and biomass variables in Equation 2 to Equation 5 to calculate GEP outside of weekly field measurements. Seasonal GEP sums were calculated from the 30 minute weather station data and modelled seasonal vegetation biomass.

Vegetation biomass seasonal models were derived from the field recorded biomass estimated by the fuel rule technique. Biomass was modelled for each collar to determine fall declines, and summer peaks in vegetation for each collar. Weather station variables (PAR, soil temperature, and water level) were recorded twice per hour from May 25th to

October 28th. These data were used in conjunction with the modelled parameters in Equation 2 to Equation 5 to determine GEP at each collar from May 25th to October 28th. Each 30 minute period returned a GEP value that was summed for a "seasonal GEP" of the length of weather station measurements (155 days).

2.1.4 Modelling Respiration

Respiration models for each collar were calculated using the same iterative manipulation of modelled constant factors as GEP (Equation 2 -Equation 5) but with the following equation:

Equation 6: Respiration calculation for modelling CO2 production

$$Respiration = R_{10} \left[b_1 \left(\frac{1}{10^{\circ}C - -46.02^{\circ}C} - \frac{1}{T - -46.02^{\circ}C} \right) \right] \times \left[1 - e^{\left(-\frac{WL - b_2}{b_3} \right)} \right]^{-1} + b_4 Veg$$

(Riutta *et al.*, 2007)

where: R_{10} = Respiration at 10°C, when Veg is zero,

and WT is non-limiting (g CO₂ m⁻² day⁻¹)

b_1 = activation energy divided by the gas constant

T = Soil temperature (°C) at 5 cm bgl.

WL = Water Table Level (cm bgl)

b_2 = Water level (cm bgl) at the centre of the fastest change along the WL range.

b_3 = This is the slope determining the speed and direction of change in respiration along the WL range.

b_4 = Change in respiration per biomass unit

Respiration modelling for each collar was similar to modelling for GEP modelled parameters. Microsoft Excel solver function was used to iteratively modify the parameters for Equation 6. With parameters calculated (by minimizing sum of squares between calculated respiration and recorded field respiration) seasonal respiration (May 25th to October 28th) was calculated using environmental factors recorded every half hour at the

field weather station. With both seasonal respiration and seasonal GEP modelled for each collar, a seasonal NEE was calculated from the sum of GEP and respiration.

2.1.5 Statistics

Differences in means between the restored, abandoned and natural sites were compared using one way analysis of variance (Sigmaplot 11.0) on pair wise comparisons of the three sampling sites with α set to 0.05, leaving a cut-off for statistically significant differences at $p < 0.05$. Parametric statistical tests were only referred to if they fulfilled the requirements of the tests (*e.g.* normality of residuals). In cases of non-normal variance a non-parametric Kruskal-wallis ranks sum analysis was used to determine significant differences between groups (Sigmaplot 11.0). Pearson's r correlation (Sigmaplot 11.0) was used to evaluate correlations between measured environmental variables and all the measured carbon dioxide fluxes (GEP, respiration and NEE.) Differences among sites were also evaluated based on variations between sites in means, standard deviations, and ranges.

2.2 Results

2.2.1 General comments

Modelled results were graphed against their field measured values to give a measure of under or over estimation in the models. In this test the slopes of the lines-of-fit rarely deviated far from a value of one. When models did deviate they underestimated values. Underestimation occurred in the highest respiration values. To correct this we could not remove these models due to further unspecified underestimation. Because of further underestimation these collars were retained in the site wide calculations despite their drawbacks.

When the collars are separated and the seasonal model is separated by the time of day we can see the average daily trend over the season (Figure 4). Dry sparsely vegetated collars like "C10C" have low but constant total respiration throughout the day as modelled across the season. Highly vegetated collars, like C10A, have higher peaks (-48 g C m^{-2}) and a respiration curve that swings upward through the day, as temperature increases.

Besides looking at daily aggregates, I investigated how the system reacts by month (Figure 5). As noted in Table 2, July and August were extremely dry months. July precipitation was 46.3% below 30-year averages, and August precipitation was 89.5% below average (Table 2). July was the only month that the natural site did not store CO₂. In August there was a drop in NEE at the abandoned site, due to an upswing in GEP (Appendix B). All the while CO₂ export trends towards a July peak at the restored site.

The abandoned site, when averaging the seasonal (June to October) modelled sums for each collar, was a source of CO₂ to the atmosphere of 295.6 g C m⁻² (±199.8 g C m⁻²). The restored site was a seasonal source of 119.7 g C m⁻² (±78.0 g C m⁻²) based on modelled values, including area covered by ditches and pools (113.1 g C m⁻² y⁻¹ without ditches and pools included).

2.2.2 GEP

Models were created for each of the collars to generate GEP numbers to span the meteorological records at the BDB site. Models did not necessarily utilise each of the model parameters. Many GEP models, for example, only required PAR; occasionally adding water table to the model did not ultimately minimise the regression sum of squares. Additional statistics were run to evaluate the effect of environmental parameters.

For instance, a Pearson's correlation was run between weekly measured values and recorded environmental variables. Site wide tables are given in Appendix D. Pearson R values for GEP largely resembled environmental differences associated with the collar microtopography, the specifics of which are detailed here. Across the restored site collars, the four parameters investigated for correlation to GEP were: PAR, soil temperature, water table, and vegetation biomass (Appendix D). With PAR above 1000 μmol m⁻² s⁻¹ the GEP correlations remain for PAR, but no other parameters correlate to GEP (Appendix D).

Looking on a collar by collar basis at the restored site (Table 3), GEP correlated to PAR at 13 collars (at all restored collars but R8A), and to soil temperature at five collars. All of these particular five collars were dryer lawn or hummock collars, suggesting that water table might be the limiting factor leaving changes in temperature of little effect (Appendix D). Broadly speaking GEP models seemed to fit environmental specifics in the

microtopography of the collars. Seasonal GEP modelled levels had no significant difference between any of the three sites (ANOVA $F=2.405$, $P=0.093$, $\alpha=0.95$, Figure 3).

2.2.3 Respiration

Respiration was compared to three environmental variables for correlation: Soil temperature, water table levels, and vegetation biomass; with correlation of: 0.309 ($P<0.001$), 0.0257 ($P=0.67$), 0.15 ($P=0.0111$), respectively. Looking at the effect of temperature, which was assumed to be a major control of respiration, on respiration at individual collars found almost no significant correlations ($P<0.05$) at individual collars but did find significant correlations ($P<0.05$) with each site as a whole. Water table's effect on respiration was significantly correlated ($P<0.05$) with nearly all the natural and restored collars. Vegetation biomass was significantly correlated to nearly all the restored site collars.

2.3 Discussion

2.3.1 Monthly trends

NEE was calculated for month to month comparison (Figure 5, Table 4). It was thought monthly sunlight hours (Figure 6) would take a significant role for monthly CO_2 flux, but the calculated NEE does not mimic sunlight trends closely (*cf.* Figure 5 vs. Figure 6). Contrary to the month over month export at the restored and abandoned sites, the natural site was able to store CO_2 (shown as negative values) in each of the modelled months other than July (Figure 5). Export of CO_2 at the natural site might be explained by the abnormal summer precipitation patterns. In 2010 BDB had 46.3 percent less precipitation than climate normals in July, and 89.5 percent less in August (Table 2). This provides an opportunity to see the effect water stress takes on CO_2 balance in abandoned, restored, and natural peatlands. In July respiration increased overall at the abandoned site, but had a dramatic drop as the water stress deepens. This makes sense based on previous field research indicating drying under aerobic conditions limits CO_2 release from respiration (Blodau & Moore, 2003). This was also observed in laboratory simulations (Goldhammer & Blodau, 2008). The restored site has falling water tables in August but the water table falls deeper at the abandoned site (Figure 7). The differences in water table levels may play into

respiration declines due to microbial die off, and lowering respiration more intensively at the hydrologically unstable abandoned site. These broad month-by-month comparisons, which appear controlled in part by water table, lead us to the seasonal carbon balances.

2.3.2 Seasonal carbon balance

In 2002, Waddington *et al.* (2010) measured a growing season carbon balance of $-19.9 \pm 5.0 \text{ g C m}^{-2} \text{ d}^{-1}$ at the restored site. In this respect our 2010 seasonal carbon balances are slightly unexpected, the restored site for instance has a net loss of 113.1 g C m^{-2} , more loss than the abandoned site in 2002 ($76.1 \pm 19.0 \text{ g C m}^{-2} \text{ d}^{-1}$) (Waddington *et al.*, 2010).

Eriophorum vaginatum is a peatland colonizer that expanded quickly in the restored site as recorded by Waddington *et al.* (2003). In 2010, *Eriophorum* was observed to be in the midst of a die-back (Plate 2). *Eriophorum* may have provided an early boost to CO₂ fixation at the restored site early in restoration, while providing microhabitat (observe *Polytrichum* spp. growing from *Eriophorum* litter in Plate 2) suitable for species that are more naturally prevalent in bogs. A similar pattern of rapid CO₂ uptake initially following restoration followed by reduced CO₂ uptake or even a shift to a CO₂ source has been reported in Finland with a dieback of *Eriophorum* cited as a possible cause (Yli-Petays *et al.*, 2007). Observed dieback of *Eriophorum* at BDB may have led to reduced productivity and contributed to the restored site acting as CO₂ source during the study period. With this dieback, modelled carbon balances are showing net release of carbon, though this release has been mitigated with roughly one third the carbon loss of an abandoned peatland.

Though species composition may be playing a role, water deficits likely also affected the measurements taken in this study. The restored site in particular may have remained a CO₂ source due to the particularly dry conditions observed in July. Natural peatlands have been seen to be sources of CO₂ in dry years (Waddington & Price, 2000; Roulet *et al.* 2007; Koehler *et al.*, 2009). Furthermore, several studies (Titus *et al.*, 1983; Titus & Wagner, 1984; Rydin & McDonald, 1985; Murray *et al.*, 1989; Gerdol *et al.* 1996; McNeil & Waddington, 2003; Blodau *et al.*, 2004) have found decreasing water levels reduced CO₂ uptake by photosynthesis. Furthermore, *Sphagnum* photosynthesis may take 20 days to recover from water stress (McNeil & Waddington, 2003).

2.3.3 Site carbon balances

Natural peatland NEE has been reported to range between $341 \text{ g C m}^{-2} \text{ y}^{-1}$ source and $-411 \text{ g C m}^{-2} \text{ y}^{-1}$ sink (Table 1) with northern peatlands averaging net storage of $-25 \text{ g C m}^{-2} \text{ y}^{-1}$ (Gorham, 1991). We can see the restored site has recovered ($119.7 \text{ g C m}^{-2} \text{ y}^{-1}$) compared to the abandoned site ($295.6 \text{ g C m}^{-2} \text{ y}^{-1}$) yet it has not reached an average, carbon storing peatland state. Important to mention is that the area designated to be restored had its carbon dioxide flux measured before restoration and the difference in respiration between sites manifested itself even before restoration (Waddington *et al.*, 2003) with the restored site recording higher respiration than the abandoned site. Considering the innate higher respiration at the restored site before restoration treatment the difference in CO_2 exchange between the restored and abandoned site, as measured in this study, are encouraging for restoration progress.

In this study I noticed thick hummocks had formed in places in BDB higher than recorded in a systematic peat depth profiling study (Lucchese *et al.*, 2010). In Lucchese *et al.*'s (2010) opinion, the excavated peatland, eight years after restoration, had not yet been restored in an ecohydrological framework. The authors did not find that peat accumulated to the degree that the accumulated peat contained seasonal water table level variation, *i.e.* an acrotelm. Ten years after restoration the seasonal balance suggested that the accumulation of peat on the surface may not be entering the catotelm where organic matter decay is slower (Clymo, 1984).

2.4 Chapter Summary

Weekly CO_2 measurements were combined with environmental variables to generate seasonal models of CO_2 exchange. Seasonal models show that the abandoned site was a source of 295.6 g C m^{-2} . The restored site is still a net source of carbon (119.7 g C m^{-2}), however, the reduction is the source compared to the abandoned site suggests that restoration has mitigated CO_2 loss. The specific conditions in 2010, namely the dry summer, may have masked further fixation of carbon. Lastly, ongoing changes in vegetation cover may also play a role in changing BDB from a net sink of carbon in 2002, to a net source in 2010.

3 DOC In-situ & GEP

Previous work investigating DOC in peatland ecosystems has led to a number of hypotheses to be dealt with in this chapter. DOC has been seen to correlate to CO₂ fixation on an hourly time range (Fenner *et al.*, 2004; 2007) but not at a seasonal or monthly time scale (Glatzel *et al.*, 2003). I hypothesise that DOC measurements will correlate to GEP. Increased GEP may lead to increased photosynthate and root exudates that could increase DOC concentrations in-situ. Bergmann *et al.* (1999) saw a relationship between hexose and CO₂ production, and this study will extend this work by investigating hexose and pentose in the BDB abandoned and restored peatland.

3.1 Instrumental Methods

Wells were bored through the peat moss and recently accumulated peat (0.2-0.4 m) and into the remaining residual peat following Bois-des-Bel's horticultural peat extraction (1.5-1.6 m). Wells were made of 2 inch PVC pipe with drilled 5mm perforations along its subsurface length with a bottom reservoir of 10 cm and an end cap to protect the reservoir of water that accumulated. Wells were sheathed with nylon stockings to prevent peat entering the well *en masse*. To understand the effects of carbon flux on DOC chemistry and concentration, wells were placed at all the gas flux collars, except at the natural site where three pairs of collars share a single well per pair (Figure 2).

Each well had its water level recorded once a week during carbon flux measurements while DOC was sampled bi-weekly. The day before collection accumulated water was siphoned out with 1.5 cm diameter plastic tubing. Twenty-four hours later all the water that accumulated in the wells was removed from the well with a foot pump into a 1 L bottle. The bottle was shaken vigorously to emulsify the water samples. From this, a subsample of 100 mL was taken. DOC is known to decompose after collection, so to prevent compositional changes, or to minimize them, DOC samples were transported in a cooler with ice packs, and refrigerated at 4°C until filtration.

Determining DOC concentration required three steps: first, 15 mL to 30 mL of the samples were filtered with a 0.4 µm borosilicate glass fibre filter (Macherey-Nagel GF-5), 25 mm filter paper on a standard vacuum filtration apparatus. In cases of high particulate load

each sample was filtered multiple times, or prefiltered through a 1.5 µm borosilicate glass fibre filter paper. While samples underwent filtering the remaining unfiltered sample was tested for pH (HANNA®, HI98130)

Second, a spectrophotometer was used to measure absorbance of 400 nm wavelength light by the water sample (compared to Ultrapure Water™ (UPW) blank). Chemical properties such as E2:E3 and E4:E6 ratios, and a measure of aromaticity (SUVA) were calculated by measuring absorbance at 365 nm:250 nm, 465 nm:665 nm, and 254 nm, respectively, using a UV/VIS Spectrophotometer (Perkins-Elmer 3B Lambda). Quartz cuvettes with a 1 cm path length and 1.2 mL volume, designed for wavelengths between 90 and 2500 nm, were used.

Third, a subset of samples were chosen to be analysed on Shimadzu TOC analyser (Environmental Sciences Program, University of Calgary), these samples had an additional 15 mL vacuum-filtered and then acidified with 1 mL HCl, to a pH < 1. Acidifying these samples prevented microbial changes to the DOC while in transport to Calgary from Quebec. The TOC analyser effectively determines the DOC concentration at the time of sampling. Though the machine is called a total organic carbon analyser, all the samples analysed on this machine were filtered to remove non-dissolved organic carbon, leaving only DOC to be detected. TOC was analysed using the Shimadzu 680 C combustion catalytic oxidation method as below:

Equation 7: TOC methodology

$$TOC = Total\ Carbon \left(Sample\ Combustion \xrightarrow[CO_2\ release]{} NDIR\ Detection \right) - Inorganic\ Carbon \left(Sample\ Sparging \xrightarrow[CO_2\ isolation]{} NDIR\ Detection \right)$$

(Shimadzu Ltd, 2011)

Once the concentration of DOC had been determined for DOC samples with known absorbances, the absorbtivity constant for the BDB peatland was determined (Equation 8) and used to convert absorbances to DOC concentration.

Equation 8: Absorbivity constant; the relationship between absorbance and DOC concentration

$$\text{absorbivity} = \frac{\text{Absorbance at 400 nm} * \text{Cuvette optical path length}}{\text{mg carbon}}$$

(Thurman, 1985)

Results from TOC derived DOC concentrations to absorbance at 400 nm fit within a 95% confidence interval (Figure 8, Figure 9), and samples had the best regressions when split between in-situ DOC samples (Figure 8), and export DOC samples (Figure 9).

3.1.1 Photospectrographic Ratios

Absorbance ratios, such as E4:E6 (Kononova, 1966), can be used to indicate chemical characteristics of DOC. E4:E6 is an absorbance ratio (665 nm to 465 nm) used to detect differences in humic materials. One difference E4:E6 can detect is different quantities of fulvic acids and humic acids. This could be important as there is a clear chain of progression in thermal transformations of humic material from fulvic acids to humic acids to humin, and finally to the maximally recalcitrant black carbon (Almendros *et al.*, 1990). As a chain of thermal transformations mimics recalcitrance, the E4:E6 should correlate to recalcitrance. There is some discussion as to how to interpret E4:E6; Kononova (1966) wrote that E4:E6 was related to the electronic pi-bond condensation of an aromatic carbon network. A large E4:E6 ratio under this theory indicates predominance of aromatic C structures, while a large E4:E6 in Chen *et al.*'s (1977) determination indicated larger molecular size and weight, with a higher C:O ratio indicating fewer side chains.

SUVA (Specific UV Absorbance) is calculated by taking absorbance of a sample at 254 nm and dividing by DOC concentration to control for increased absorbance due to the concentration of DOC. The measure has been correlated to aromatic concentration in a sample (Bourbonniere, 2009). E2:E3, an absorbance ratio measured at 250 nm to 365 nm, has been negatively correlated to molecular mass as has E4:E6. However E2:E3 does not have the depressing effect of side chains that E4:E6 has (Zhao *et al.*, 1996). These ratios were measured on each weekly export sampling and each biweekly in-site water sampling.

3.2 Chemical Methodology

3.2.1 Pentose

In addition to absorbance ratios I have tried to characterise the chemistry of the DOC in several ways. First, I measured the ratio of pentose to hexose. Pentoses are largely from plant-based sources. By measuring pentose and giving a ratio of pentose to hexoses we get a measure of how much of the carbon is sourced from plants vs. microbes and decomposers (Gupta 1967, Stevenson 1982). Pentose concentrations were calculated using the standard Bial's orcinol test (Chantigny *et al.*, 2008a). This experiment had two reagents. The first reagent, 0.1 g iron chloride (FeCl_3), was dissolved in 100 mL of 32% hydrochloric acid (HCl). The second reagent, 1g of orcinol ($\text{CH}_3\text{C}_6\text{H}_3\text{-1,3-(OH)}_2$; 3,5-dihydroxytoluene), was dissolved in 100 mL of 95% ethanol. I took 1 mL of a DOC sample and placed it in a test tube with 1 mL of iron chloride reagent. Here the acid dehydrated the pentoses to form furfural. At this point I added 1 mL of orcinol reagent. The furfural present reacted with the orcinol, and the furfural-orcinol complex attracts Fe^{3+} ions colouring the solution blue. Lastly before measuring in a spectrometer, 2 mL of ethanol was added and the sample mixed by hand swirling the vials. At this point 1 mL of the reacted sample was placed into a cuvette for the spectrophotometer and read against a blank (blanks were UPW that followed all the preceding steps) at 660 nm. A calibration curve was prepared using a prepared standard solution of ribose diluted to various concentrations (2.5, 5, 10, 20, 30, 50, and 100 mg L^{-1} ribose) with UPW.

3.2.2 Hexose

Hexose concentrations were calculated using the standard anthrone reaction (Chantigny *et al.*, 2008b). Hexose was added to 0.200 g anthrone dissolved in 100 mL 98%v/v H_2SO_4 . 2 mL of this reagent was added to 1 mL of DOC sample which was then mixed for 15 minutes. The acid reacts with all sugars and produces furfuraldehyde derivatives. Anthrone reacts with the resulting chemicals producing a blue/green colour with an intensity relative to the concentration of sugars. The solution was heated in a water bath for 20 minutes at 95°C. Heating makes pentose furfuraldehyde-anthrone complexes react with excess anthrone and makes them yellow or colourless derivatives out of the range of the 625 nm wavelength optimally absorbed by blue/green compounds. The samples were then cooled

on ice packs and read in a spectrophotometer at 625 nm. The hexose concentration to absorbance regression was calibrated from reactions of known concentrations of D-glucose and laboratory blanks of UPW.

Hexose and pentose concentrations were calculated for a subset of samples once per month from May to July. Samples were taken from filtered in-situ and export water samples.

3.3 Results

3.3.1 Quality and Chemistry Results

The concentration of DOC in-situ had the highest mean at the restored site (

Table 5), and the lowest mean in the natural site, while the abandoned site had samples that crossed the entire range of both the natural and restored sites. Each of the sites was significantly different from one another (ANOVA: F= 4.219, p=0.043 Abandoned to

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural to Abandoned
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Restored; F=72.293, p<0.001 Restored to Natural; F=5.28, p=0.026 Natural to Abandoned;

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural to Abandoned
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6

mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Table 5).

pH had no significant difference between the abandoned and restored site (ANOVA F=0.218, P=0.641), though there is a significant difference between the natural site to the abandoned (F=23.609, P<0.001), and to the restored site (F=25.11, P<0.001;

Table 5).

DOC absorbance ratios of E2:E3 and E4:E6 had contradictory results in the natural site

	Abandoned to				Restored to				Natural		Natura
	Abandoned		Restored		Restored		Natural		Natural		Aband
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

(when one parameter goes down the other should go up) though these results were not statistically significant, which may be due to uncorrected pH (*cf.* § 3.4.2, paragraph two).

The restored site's E4:E6 was slightly depressed (

	Abandoned to				Restored to				Natural		Natura
--	--------------	--	--	--	-------------	--	--	--	---------	--	--------

	Abandoned		Restored		Restored		Natural		Natural		Aband
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Table 5) compared to abandoned site's levels. Natural levels (recorded at the natural site) of E4:E6 were higher than both the restored site and abandoned site (

Table 5). Statistical tests (ANOVA) did not mark any of the sites as significantly different from each other (

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natura
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Table 5) with regard to E4:E6. Averaging all the restored collars together has a negative seasonal trend ($r^2=0.5218$), while individual collars (R2A, R2B) can have positive trends (r^2 0.6228). The abandoned site shows a very weak positive seasonal trend (r^2 0.0513), though individual collars (C10B, C11A) had stronger seasonal correlations (r^2 0.4314, 0.4075).

E2:E3 for the natural site was the highest of the three, however we predicted that as E2:E3

increases, E4:E6 decreases. Again this may be due to incorrect pH correction (*cf.* § 3.4.2). Regardless, the E2:E3 at the natural site was significantly different from both the abandoned and restored site. E2:E3 were however nearly identical, with no statistical difference, between the abandoned and restored site.

Restored and abandoned sites had very similar mean values of SUVA (

Table 5), but variance was much higher at the latter. Statistical significance tests saw significant differences between the abandoned site and restored site, and the restored and the natural site (Kruskal-Wallis: H= 11.913, p<0.001 Abandoned to Restored; H=17.23,

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
	pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

p<0.001 Restored to Natural;

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
	pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92

:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Table 5).

Hexoses when in soil are largely derived from microbial decomposition (DeLuca & Keeney, 1993) which gives us a measure of microbial activity, but also of recalcitrance as the chemical method employed to measure hexose cannot access recalcitrant carbon. Here the values are similar for each of the sites but with much variation. The abandoned site, is an extreme example of this, ranging from more than 15 mg/L to 2 mg/L all while having a similar mean as the rest of the sites near 3 mg/L. Further investigation with a Pearson's R correlation test gave no correlation ($p > 0.05$) to environmental variables. However, significant differences ($F=2.885$, $p=0.045$,

Table 5) were recorded between the abandoned and restored site.

Pentose, largely coming from vegetation, had significant differences (

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹											
$\alpha:\alpha$											
pH	5.00	2.109	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	11.913	<0.001	175.56	220.941	173.23	<0.001	162.78	99.982	0.588
$\alpha:\alpha$	33.31	30.663	2.879	0.045	60.06	65.563	38.39	<0.001	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

Table 5) between sites. High levels can indicate slowing decomposition in the soil column (Gupta 1967, Stevenson 1982). The natural site and the restored site both had high levels compared to the abandoned site, the variation was greatest at the natural site while the restored and abandoned site had similar variation. Significant differences (

Table 5) were observed between the abandoned and natural sites (F=2.92, p=0.046), and comparing the abandoned and restored site (F=2.967, p=0.089) at a lower 90% confidence

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
	pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

level.

Pentose to hexose ratios were not significantly different (

Table 5) between the restored site and the natural site, but were significantly different between the abandoned site and both the restored and natural sites.

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
	pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

3.3.2 CO₂ and DOC concentrations

DOC can be derived from root exudates and plant photosynthate. This provides a ready source of decomposable organic matter that increases CO₂ release. As part of this process

photosynthate has been implicated as a control in hourly DOC production in ^{13}C studies (Fenner *et al.*, 2004; Fenner *et al.* 2007). However this linkage did not extend to production of CO_2 on long time scales; seasonal and monthly DOC concentrations were not found to correlate to CO_2 efflux (Glatzel *et al.*, 2003). These results can be attributed to not all DOC coming from plants, and not all DOC decomposing readily to CO_2 .

Furthermore, photosynthetic productivity is related to CO_2 uptake, when there is more photosynthesis, more CO_2 is bound into sugars. Photosynthetic production as GEP was examined, thus, for possible correlations to DOC concentrations in this study. When daily GEP averages were used as an independent variable to calculate DOC concentration in the top 100cm of soil it returned insignificant results at BDB (Table 6) without considerable sorting. With all the collars taken together the r^2 is 0.002. Sorting by vegetation, or by water regime both had poor regressions. Even running single collars by themselves yielded poor results ("Treed peat", Table 6). Monthly GEP to DOC concentrations had strong linear regressions but the statistics may not be reliable due to low sample size and heteroscedastic variances. That being said, abandoned site average GEP vs. DOC concentration had r^2 of 0.936 ($F=14.718$ $p=0.162$). The natural site returned an r^2 of 0.151 ($F=0.178$, $p=0.746$), and the restored site returned an r^2 of 0.988 ($F=82.058$, $p=0.070$)

3.3.3 CO_2 Production and Hexose

Bergmann *et al.* (1999) saw a relationship where glucose (a hexose sugar) led to higher CO_2 production. The hexoses measured in this study however, did not form a significant relationship between CO_2 production on a daily ($P=0.433$) or weekly ($P=0.382$) time scale.

3.4 Discussion

3.4.1 DOC Concentration

DOC concentration was significantly different at each site. Waddington *et al.* (2008) found at the BDB site from 1999 to 2001, that the abandoned site had higher concentrations than a natural site, and the restored site had still higher concentrations. Two mechanisms for high DOC concentrations following restoration were proposed in that preliminary study: 1). that straw mulch used to protect donor plants from desiccation was creating a labile substrate for DOC production, and 2). that water table fluctuations had a greater amplitude

at the restored site (Shantz & Price, 2006), and until these fluctuations are isolated to an acrotelm layer DOC concentrations could be expected to be larger.

In this thesis too DOC concentrations were higher at the restored site (significantly higher) than the abandoned site. However, with no remnant of the straw mulch the explanation may have to do with water table levels. Another possible link between the DOC concentration and the restored site is vegetative productivity. Regressions between these produced poor results except at the abandoned site with small grouping based on vegetative cover. DOC is refreshed by labile carbon, with modern sources providing the majority of DOC (Neff *et al.*, 2006), but essentially all the carbon in the soil column can come into play in the production of DOC, especially late in the season (Neff *et al.*, 2006), and due to this pH can play a significant role.

The pH of pore water at the restored and abandoned site was 5.78 and 5.98. pH is believed to be a controlling factor in the release and solubility of organic carbon (Kalbitz *et al.*, 2000). As pH rises it allows organic carbon cations that were forced to precipitate, to dissolve. *Sphagnum* moss is known to provide a source of acidity to peatlands (Charman, 2002). The absence of *Sphagnum* at the abandoned site and colonization at the restored site should result in lower pH at the latter and thus reduced DOC export. As lower pH should reduce the amount of dissolved organic carbon at the restored site, the higher measured in-situ concentrations suggest that rapid production must be occurring. It is also possible that this interplay between production and precipitation resulted in the lack of strong correlation between CO₂ exchange and DOC concentration.

3.4.2 Effect of low water tables and vegetation on DOC chemistry

Lower E4:E6 has been linked to drain blocking in peatland restoration studies (Wallage *et al.*, 2006). More recent studies have linked drain blocking to higher E4:E6 ratios (Wilson *et al.*, 2011), however the BDB site, though having different values, did not have significant differences between the restored site and the abandoned site, ten years post restoration. Above are three results all different with regard to E4:E6. Resolving this conflict requires an examination of studies into the nature of E4:E6 and a understanding of the processes at work in the BDB peatland.

Moore (1987) reported that the E4:E6 ratio had a strong increasing seasonal trend, this was corroborated at a few collars; however, on a site wide basis, seasonal trends were marginal, or negative. As E4:E6 has been used as a correlate of recalcitrance, with larger numbers being more recalcitrant, Moore's (1987) results are harder to rationalize. Over the growing season, why would recalcitrance increase as plants deposit more fresh labile material to the soils? In my sampling regime DOC was taken from more than 100cm of the soil profile. While the surface of the peat may have highly labile material, when this surface area dries it is exclusively the recalcitrant remnant peat contributing to the DOC samples. In the abandoned site shrubby collars do show this trend, with the largely bare peat collars having a flat trend across the season (with larger variability in the early season). Having seasonally consistent values of E4:E6 led to weak seasonal trends for the abandoned site. But again, results show that certain vegetation communities can have strong positive seasonal trends, while this is not the rule across the collars. In addition to these seasonal trends, experimental error may have played a part in the calibration of our E4:E6 data. Information provided by E4:E6 includes largely particle size (or weight) (Chen *et al.*, 1976), and independent fulvic and humic acid concentrations between 100 to 500 ppm are known to be affected by pH (Chen *et al.*, 1976). The original suggestions for using E4:E6 as an analytical measure (Kononova, 1966) suggested confining the range of pH to between 7 and 8 by adding 0.05N NaHCO₃. As this was not done for this study differences in pH may contribute to the inconclusive results of the E4:E6 ratio for this study and the three contradictory results between Wilson *et al.* (2011), Wallage *et al.*, (2006) and this study.

This narrative of a low water table selectively releasing only older or more recalcitrant carbon could possibly be corroborated by data collected from SUVA measurements, sugars, and from E2:E3 ratios. Aromatics (*via* SUVA measurements) curiously showed no significant difference between the abandoned and natural sites, whereas the restored site was significantly different from both and was the highest average aromatic absorbance mean. Neff *et al.* (2006) reported that DOC flux is in large part from modern sources (from ¹⁴C measurements), however the mechanism of DOC generation transitions from surface layers (aromatic lignin derived monomers) to deeper, previously stabilized carbon after spring melt is over (Neff *et al.*, 2006). A transition of DOC production to deeper peat might

happen to a lesser degree at the restored site, which leaves the higher aromatic levels due to another mechanism such as near surface labile DOC being consumed much faster at the restored site.

Rapid consumption of DOC should be observed in changes in sugar concentrations. Fructose (a pentose sugar) to all pentose ratio, has been well correlated to decomposition constants in mosses (Turetsky *et al.*, 2008), but otherwise analytical uses of pentoses and hexoses have been limited in peatlands. The pool of free sugars in soil can be read as decomposability as it reflects the rate of decomposition versus uptake (Gupta 1967, Stevenson 1982). Levels of pentose were significantly different at the three sites, compounded by not only the differences in the ultimate vegetative sources, but also likely in the rates of decomposition in the soils. Looking at a index of supplied sugars vs. decompositional sugars (pentose:hexose) at the three sites as a measure of decomposition gives 33.31 ± 30.66 at the abandoned site, and 60.00 ± 63.56 at the restored site which had no statistical difference to the natural site 60.31 ± 33.61 (

Table 5).

Considering the high quantities of free pentose measured at the restored site, if labile DOC

	Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural
	Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H
pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6
mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538
α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7
α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4
mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35
mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92
:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41
mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28

is being consumed faster at the restored site, the contributions of labile DOC to the soil could be even higher, and masked by consumption. Another possible reason is the plant communities involved at the restored site differ from the other sites and could have more

phenolic compounds (phenolic acids, tannins, quinones, humic and fulvic acids) (Gallet & Lebreton, 1995) that have higher levels of aromatics even before decomposition. *Sphagnum* spp. may be a significant contributor: a natural collar dominated by *Sphagnum* spp. (95-100% coverage) had a SUVA value higher than the restored site mean. Also, the many sedges currently dying back (*cf.* Plate 2) at the restored site could provide a significant source of lignin. Grasses as they grow do not contribute growth laterally, and have no lateral vascular structures only independent elongated vascular bundles. Bundles across the width of a leaf grow the length of the leaf *vs.* in the rings of woody plants. These bundles are sheathed in sclerechyma cells that are rich in lignin. In each of the bundles that compose a single leaf, xylem tissue is generated at the centre. Xylem is a unique tissue in vascular plants composed of hydrophobic lignin covalently bonded to hydrophilic hemicelluloses in a way that allows bands of lignin to efficiently move water. With all the xylem tissue surrounded by sclerechyma, and therefore (on both counts) lignin, sedge decomposition could lead to higher aromatic levels (Prescott *et al.*, 2000, Höll *et al.*, 2009).

Thirdly, E2:E3 is correlated to molecular weight, where a high ratio is interpreted as a low molecular weight. E4:E6 is similar to E2:E3, however E4:E6 ratio can be increased by reducing the number of side chains on the bulk molecule. A lower number of side chains would indicate high recalcitrance. When we look at the E2:E3 and E4:E6 numbers we see that E2:E3 is higher in the restored, while E4:E6 is higher at the abandoned. This is understandable as newly produced organic carbon would be less recalcitrant (*i.e.* a lower E4:E6 ratio). The higher E2:E3 number might be because higher water table at the restored site may allow water movement through a soil layer with more labile material. Aromaticity as a measure of hydrophobicity aids this explanation, as a lower aromaticity allows larger molecules to become dissolved.

3.5 Chapter Summary

Looking at in-situ DOC concentrations and chemistry allowed me to explain larger trends happening in the peatland reflected at a molecular level. We can see through pentose to hexose ratios that decomposition is slowing at the restored site, and is now significantly different than the abandoned site. Differences in the hydrology between the sites manifests itself in observed differences in E4:E6 ratios and may reflect slowing decomposition,

deeper water tables as the season progresses, or differences in plants contributing phenolic compounds to the soil. Correlations between gross photosynthesis and DOC concentration were also examined, but were found to be insignificant at BDB. This suggests that differences in vegetative productivity between the sites are not the main drivers of net DOC production. This may be due to the water table being low enough to reduce the influence of newly sourced labile DOC on the total DOC pool. Secondly, hexose sugars were not seen to contribute to alterations in CO₂ efflux on short time scales.

4 DOC Export; Storms and Baseflow

4.1 Methods:

4.1.1 Water Sampling

At the study site each of the two zones, restored and abandoned, are surrounded by ditches that feed a continuous water flow into two outlets, one for the abandoned site, and one for the restored site. These two exit points have V-notch weirs installed where volume of the water discharged is a function of the height of the flowing water on the "V" shape of the V-notch weir (Shantz and Price, 2006). Water was collected every week, or if precipitation was expected measurement regimes were changed to include a pre-storm sampling.

Samples of 100 mL was taken from outflow from the V-notch weir at the restored site, and from a large conduit at the abandoned site where water discharged. Samples were filtered and measured for chemical properties (pH, sugars, ratios), and concentrations according to the same methods as outlined in Chapter 3.

4.1.2 Storm Sampling

Discharge was measured at each DOC sampling, during storm events and an additional three times a week at each weir. A 100 ml graduated cylinder was used, or during extremely large flow a Rubbermaid™ 54 gallon bin was used to collect discharge while using a stopwatch. Every measurement of discharge was averaged over three runs. Time was recorded to provide a discharge amount to create a regression between discharge and recorded water level. Water level was measured and recorded using a level-logger (Solinst Levelogger™). Atmospheric pressure was subtracted from the overall recorded pressure and difference was averaged over a four hour period to create a stage-discharge relationship for high flow and flow less than 100 mL/s.

Storm events and snowmelt are the major types of discharge prompting events in bogs, accounting for substantially more discharge than base flow. Precipitation events export more DOC than base flow (Clark *et al.*, 2007). In order to investigate storms DOC export, during storms DOC was collected before peak rainfall, and every four hours afterwards, up to 16 hours after the peak rainfall. Events longer than three days were measured twice a day.

Regular precipitation occurs throughout the year at the study site with a mean annual precipitation of 926 mm with 27% falling as snow (Waddington, 2010). Snowmelt is the most important discharge event of the year; however, storm events also have considerable influence on DOC concentrations and export. In spring, snowmelt volume can be very high and the weir cannot be installed and measured (i.e. water flow over the top of the weir or washes it out completely). Previously, to gauge water export researchers used a dilution experiment to infer how much water was escaping. However, in this study a salt dilution was not performed. As a result DOC exported by snowmelt was estimated based on scaling Waddington *et al.*'s (2008) measurements from 2001 according to snow depth preceding melting.

4.1.3 Concentration Calculations

DOC concentration could not be regressed to pressure across the season due to regression residuals failing statistical requirements (non-constant variance, non-normal) so Verhoff *et al.*'s (1980) widely cited (Koehler *et al.*, 2009; Billet *et al.*, 2010; Worall *et al.*, 2009) calculation method (Equation 9) was used to calculate cumulative DOC export from the restored and abandoned sites' weirs.

Equation 9: Verhoff's Equation (Verhoff *et al.*, 1980)

$$\left(\frac{K \sum_{i=1}^n (C_i Q_i)}{\sum_{i=1}^n Q_i} \right) Q_r$$

Where:

C_i = instantaneous concentration of DOC (mg/L)

Q_i = instantaneous discharge (L/s)

Q_r = average discharge (L/s)

K = time correction factor (s/day)

4.2 Results

4.2.1 DOC concentration

The abandoned site DOC concentration ranged between 75.25 to 134.79 mg/L, with a mean of 100.62 ± 15.21 mg/L. The restored site DOC concentration ranged between 49.20 to

129.29 mg/L with a mean of 86.31 ± 20.92 mg/L. There is no seasonal trend in DOC concentrations at the abandoned ($r^2= 0.003$, $F= 0.169$, $p=0.683$) or restored sites ($r^2=0.009$, $F=0.457$, $p=0.502$). However, a negative trend appears to exist between discharge and DOC concentration. Discharge versus DOC concentration relationships have been positively correlated in watersheds with few wetlands (McDowell & Fisher 1976, Fiebig *et al.* 1990, Brown *et al.* 1999). However the seasonal relationship in the BDB peatland has a negative correlation (

Figure 10 and Figure 11), which corresponds to similar results in peatlands (Freeman *et al.*, 2004).

At the restored site, regressing discharge on DOC returns r^2 of 0.9968 ($p<0.0001$) during the September 27th/October 9th storm event. This is one example of how shorter events results in a strong correlation between DOC concentration and discharge.

Hudson *et al.*, (2003) reported that temperature does not positively correlate to DOC concentrations in a 21 year field study. However models created for peatlands using monthly mean temperatures, and rainfall (Worrall *et al.*, 2008) have performed well. In this study temperature was positively correlated to export DOC concentration at the abandoned site ($r=0.764$, $P<0.001$) and to a lesser extent at the restored site ($r=0.557$, $P<0.001$).

4.2.2 DOC Chemistry

The abandoned and restored sites have many significant differences in the chemistry of the discharge water and exported DOC (Table 8). The pH of the discharge was 6.18 ± 0.42 and 5.94 ± 0.59 at the restored and abandoned sites, respectively. E2:E3 was higher at the restored site implicating reduced recalcitrance; however, no difference was noted in the SUVA or E4:E6 measurements. Also sugars, and DOC concentrations at each site were significantly different with higher sugars at the restored site (ANOVA: Hexose $F=6.733$, $p=0.011$; Pentose $F=99.311$, $p<0.001$, Table 8), and DOC concentration was higher at the abandoned site weir (ANOVA: $F=15.801$, $p<0.001$).

4.2.3 DOC Export

Total DOC export for May through October was 28.8 g C m⁻² at the abandoned site and 5.0 g C m⁻² (Table 7) at the restored site as calculated from Verhoff's equation (Equation 9).

At the restored site, regressing discharge on pressure returned a r² of 0.9968 (p<0.0001) with the formula $f = ax^b$ during the September 27th/October 9th storm event. DOC concentration regressed well with discharge (r² 0.6275, p=0.0037), with most of the variance coming with low level discharge.

4.2.4 Storm hydrology

The seasonal hydrograph shows a few early season peaks, but these are overshadowed by very large events in October with a peak discharge of 30.2 L/s. A good cross section of storms of various magnitudes were sampled for DOC export. Storm event samples were taken (

Figure 10) on Julian day 175 and 199, storms with 34.3 mm, and 1.3 mm of precipitation, respectively. Also recorded, the events on Julian day 271, 274, and 280 were 43.9 mm, 97.0 mm, and 36.3 mm of precipitation respectively.

At the restored site the lag from the start of precipitation to peak discharge was not standard, changing as the site reached its saturation point (Table 9). After a dry summer, lag time to peak discharge was shorter at the restored site by almost three hours. It was not until approximately 90 mm of rain fell that the sites were equivalent for lag time. After this time the restored site followed the trend recorded by Shantz & Price (2006) where lag time was longer at the restored site than at the abandoned site.

As discharge increased DOC concentration dropped in every case at both sites. As the storm progressed the DOC concentration would rise, and after the storm it would increase further. Highlighted in

Figure 10 and Figure 11 on the right middle panel is DOC concentration through a large storm system. The lowest DOC concentration occurs shortly after peak discharge was recorded, whereas the highest DOC concentration measured in the system is during late summer base flow before Julian day 271 and 274.

A reduction in DOC concentration with increasing discharge does not greatly reduce DOC export (Figure 12). This is seen in the first derivatives of the cumulative percent of DOC exported that are highest at the peaks of discharge, and taper off towards base flow. The loss of carbon in this storm event of 36.32 mm is calculated at 2.17 g C m⁻².

4.3 Discussion

4.3.1 DOC Export and Chemistry

In this study DOC concentration in discharge changed over time; however, this change seemed to follow rainfall patterns versus a seasonal trend (Figure 13) and a Pearson's correlation shows no significance between progression of the year, and DOC concentration (Julian day and DOC concentration, $R=-0.0599$, $P=0.679$). In Figure 13, we look at the central panel; between droplines 1 and 2 we can see that there is no precipitation. It is during this time that there is an increase in DOC concentration in both the abandoned and restored sites (as seen in the top and bottom panels respectively). This is a trend repeated between lines 6 and 7. This trend of increasing DOC concentration during lack of precipitation is complemented by the reverse trend when there is precipitation. After rainfall, in the days before dropline 6, there is a fall in DOC concentrations in both the abandoned site and restored sites. As the precise timing of DOC concentrations increasing coincide with no rain, and DOC concentrations dropping coincide with rainfall, we rationalise that precipitation is a control on DOC concentrations in export waters (Hinton *et al.*, 1997).

While knowing the amount of DOC exported is important to quantify the carbon balance and understand water quality coming from abandoned and restored peatlands, we want to understand how water moves through these ecosystems and how restoration affects this movement and subsequent DOC export. Lag time may provide some insight into the hydrological response to the peatland to precipitation events. One of the effects of restoration taken into consideration when drafting hypotheses was whether a layer of uncompressed peat could accumulate in ten years that would significantly affect water flow via changed (higher) hydraulic conductivity (Shantz & Price, 2006), and thus lag times. Hypothetically, it was rationalized that water would move transversely through the

restored site's uncompressed peat faster than transversely through the abandoned site's peat. Moreover, the expected higher hydraulic conductivity at the restored site, due to uncompressed peat (*i.e.* an *acrotelm*), would lead to more of the rainfall penetrating the restored peatland's *acrotelm*, compared to the compressed peat at the abandoned peatland. The abandoned site would thus not have as much water infiltration and would quickly discharge precipitation into drainage ditches leading to shorter lag times compared to the restored site. Contrary to this hypothesis, in 2010 after extended periods of dryness the time from peak rainfall to peak discharge (*i.e.* lag-time) was shorter at the restored site, than at the abandoned site (Table 9, Julian day 267). This outcome may be due to the overall lower water table positions at the abandoned site (Figure 7) that left much more pore space available for rain to infiltrate. Indeed, longer lag times at the abandoned site following dry periods could certainly be due to precipitation recharging the deeper unsaturated zone at the abandoned peatland, and the water table drawdown after a long dry period is simply a more significant export control *versus* the expected peat compression at the abandoned site and the resultant low hydraulic conductivity. Contrary to shorter lag times at the restored site following dry spells, after rain, as both sites reach saturation, the lag time relationship reverses. After rainfall (*i.e.* antecedent wet conditions) the restored site has *increasingly* longer lag times (*cf.* Table 9, antecedent wet Julian day 273 *versus* antecedent very wet Julian day 289). Similarly, in 2002 Waddington *et al.* (2008) reported that restoration had led to higher water tables, which resulted in higher discharge and shorter lag time at the restored site. This is the same pattern as 2010 when there are antecedent dry conditions at the restored site. Following up these results we found when rainfall followed antecedent wet conditions the situation was reversed with the abandoned site reaching peak discharge sooner than the restored site. I propose this difference could have stemmed from difference in peat properties between the restored and abandoned sites, namely that the accumulation of fresh organic matter at the restored site and the compressed peat at the abandoned site, the former impeding water discharge, and the latter discharging water quickly when wet, and storing water when dry.

But the rationale of "impeding water discharge" goes further. As the sites become wetter, independent systems of stored water, such as the terraces of BDB separated by peat dikes,

could become connected. When stored water becomes connected the contributing area to the restored site's discharge increases. With a larger contributing area, the water being exported travels farther and thus takes longer to reach the outlet. This leads to longer lag times, which is what we observe when the restored site is wet, and these systems of water would be connected. Furthermore, these longer lag times during antecedent wet conditions (*cf.* Table 9) could increase contact time between the water and the soil likely increasing DOC concentrations, and picking up larger molecules that would be left from regular faster flow, this was observed to occur between Sept. 30 and Oct. 9th at both the restored and abandoned sites with changes in chemical properties (*e.g.* E2:E3) of exported DOC. This is further discussed below.

4.3.1 E2:E3

Previous research (Austnes *et al.*, 2010) has reported an E2:E3 ratio that increases as the season progresses, the implication being that the DOC has decreasing molecular weight. Figure 15 displays the E2:E3 ratios recorded at BDB across the year April to October. Austnes *et al.* (2010) trend was observed in BDB with E2:E3 ratios following the cumulative precipitation, and not falling during the dry summer.

Figure 10 and Figure 11 show E2:E3 during a large autumn storm event indicating that E2:E3 decreases with lower discharge *i.e.* increased molecular weight associated with longer lag times. However, as hydrological systems would be connected, as rationalized above, no change in molecular weight of DOC is detected (in antecedent wet vs. antecedent dry conditions). Are E2:E3 levels under the influence of a biogeochemical control or a hydrological control? The non-detection of a change in E2:E3 with changing lag times could be due to the zone in which water moves as the site discharges. Table 9 shows increasing lag time with wet antecedent conditions at the restored site. As discussed above, this may result from an increase in contributing area as the site wets up. This suggests that the restored site during dry times may act as independent systems, and wetting links them together. Increasing lag times suggest a larger and larger portion of the restored site is contributing to storm discharge as the site becomes wetter and these independent systems

are connected. The E2:E3 measurement suggests that the restored site is exporting lighter, less aromatic molecules when discharge is high. This suggests an interaction between hydrologic and biogeochemical controls since as the site wets up, flow is through the near surface where fresh material is available due to growth of vegetation. The difference seen in export between the abandoned and restored site but not in in-situ could be that in-situ measurements average the entire soil column while export is more likely to mobilize the smaller, more labile molecules if they are available, and it is moving through the surface layers where smaller, more labile carbon is available.

4.4 Chapter Summary

Discharge has a negative relationship with DOC concentration. Regardless, DOC export increases with increasing discharge. Dry periods show increasing DOC concentrations and rainfall is followed by a fall in DOC concentrations. The restored site was calculated to export less DOC than the abandoned site. I propose that separate independent caches of water become connected as the site water table rises enough to hydrologically link them. Lag times compellingly suggest this is the case; however, chemical evidence was not found to support this, possibly due to the restored site lacking high molecular weight DOC that would be transported in slow moving water.

5 Conclusion

5.1 Summary of Findings

This study used measurements, gathered weekly, to model GEP and respiration for BDB. The model created has the abandoned site losing 295.6 g C m⁻² June to October. Over the same period the restored site lost carbon (113.1 g C m⁻²) yet this CO₂ loss, compared to the abandoned site, is mitigated by restoration at this point in time, ten years hence. This source of CO₂ at the restored site was unexpected as Waddington *et al.* (2010) determined that the site was a carbon sink only two years after restoration. This fits in with the narrative that ongoing changes in vegetation cover (*viz. Eriophorum*) may also play a role in shifting BDB from a net sink of carbon in 2002, to a net loss in 2010. As well the dry conditions in the growing season of 2010 may have masked further fixation of carbon that may be occurring in wet years.

By examining chemical differences in the water samples from natural, restored, and abandoned sites I was able to examine hypotheses on the link between, productivity of vegetation and DOC concentration (not established by this study), as well as hexose concentrations on CO₂ production (not established on short time scales by this study).

DOC concentration drops as discharge increases; however, ultimately increasing discharge still exports more DOC. DOC concentration was seen to mimic rainfall cycles, dropping with rainfall and rising during dry periods. The restored site was calculated to export less DOC than the abandoned site. Chemical evidence suggests that the restored site may be separate independent caches of soil water until the site is wet enough to link these systems together. This being the case lag times increase at the restored site as the site becomes more wet, and E2:E3 ratio decreases as additional labile carbon is mobilized from in-situ to the export weirs.

Results in this study suggest there are ways in which the restored site is becoming naturalized. For instance, the pentose to hexose ratio, as a measure of uptake of metabolites to the soil vs. decomposition, is much more similar at the restored site to the natural peatland than the abandoned site. In other ways the restored site of this study does not appear to agree with previous work at the BDB site; Waddington *et al.*, (2010) found

net carbon storage a few years after restoration treatment. In this study the restored site was releasing carbon. *Eriophorum vaginatum* is known to rapidly colonize after restoration (Lavoie *et al.*, 2003), and BDB is no exception. Waddington *et al.* (2010) noted extensive *Eriophorum vaginatum* colonization at the site. Vegetation at each of the collars suggest it may be dying back (Appendix E) and this is what we observed in this study (Plate 2). However there was no correlation between percent coverage of *Eriophorum vaginatum* and GEP or NEE ($R=-0.144$, $p=0.581$; $R=-0.0421$, $p=0.873$, respectively).

Also evaluating the restoration method, specifically digging pools and leaving ditches, the ditches lost less carbon than the average of non-aqueous collars but this loss may remain at these levels as long-term trends of restoration improve the carbon storage of the restored site. Therefore it is too early to definitively decide whether ditches and pools are of utility from a carbon storage perspective.

5.2 Improvements and Future Research

5.2.1 Snow water equivalents

Unfortunately mother nature makes fools of us all, and despite my plans to be at BDB to capture snowmelt, the snow was entirely melted by my first days at the field. Regardless, based on previous research some ballpark figures can be calculated. Near 30% of the annual precipitation passes as snow melt. Even with the lowest of the annual DOC concentrations, snow melt discharge still accounted for 88.7% of the unrestored sites, and 70.3% of the restored sites annual DOC export from Bois-de-Bel in 2001 (Waddington *et al.*, 2008). Snow melt alone accounted for 43.6 g C m⁻², while at the restored site 8.3 g C m⁻² was exported by snow melt in 2001 (Waddington *et al.*, 2008). In 2001 the amount of snowfall, was 150 mm (snow water equivalents; SWE) for the unrestored, and 137 mm SWE for the restored site in March, 2001 (Waddington *et al.*, 2008). Snow on the ground March 24, 2010 was 67 cm (estimated as 67 mm SWE). Taking this into account to scale the discharge from the 2001 to 2010 levels for the abandoned site snowmelt DOC export could have been as high as 19.43 g C m⁻² for the unrestored site, and 4.05 g C m⁻² for the restored site. Further studies should include previous salt-dilution experiments, together with DOC sample collection for a more accurate estimate of DOC export during snowmelt.

5.2.2 Sugars and decomposition

Throughout this study sugars have been used as a measure of decomposition. Another BDB research team (Macrae & Wells, unpublished) suggested decomposition rate of litter at the surface at the restored site had increased. To complement these conclusions piezometers (wells drawing water from a limited cross section of soil) could have been used more extensively on the site, and sugar chemistry could have been performed on specific depths in the soil profile to understand where decomposition was occurring. This was attempted, but unfortunately only two sets of samples were performed at each of the four depths (50 cm, 75 cm, 100 cm, and 125 cm). Performing analytical chemistry on sugars in the field had unique limitations, and an improvement on this study would be using a well-equipped lab to measure sugars in more samples, and to install multiple piezometers at each site. Even with two samples we see a trend in sugars in the soil column (Table 10). The highest pentose to hexose ratio at the restored site (samples drawn from beside collar R6C, Figure 1) were 45.90 at 50 cm below the surface, and this ratio trended downwards until reaching a low of 15.80 at 125 cm. Deep peat has a low hexose concentration suggesting low microbial activity, and a low pentose to hexose ratio here suggesting low levels of sugar infiltration below 100 cm. Further studies should install piezometer nests at many depths, and at both the restored site, and the abandoned site, so a comparison in decomposition rates can be made.

5.2.3 Correcting E4:E6 field protocols.

As mentioned previously E4:E6 measurements have been used extensively and correctly measuring E4:E6 (*i.e.* making measurements of E4:E6 at neutral pH) is critical for larger regional comparisons.

5.2.3 Further research for DOC

Future research is required on the relationship between DOC and environmental factors through laboratory studies. DOC fractionation, and phenolic molecule concentration experiments could be useful in determining the significance of chemical changes that occur as water moves through a peatland and could add a richer understanding to the processes that occur as extracted peatlands are becoming restored and naturalized. DOC sources could be studied with ¹³C enriching of plants (for litter and root exudates), and microbial

communities. No assessment has taken place regarding soil fauna and DOC production, and this also may be worthy of investigation.

BDB also represents a subset of hydrological conditions. Future studies could investigate further the importance of local hydrological conditions in restoration efforts by measuring DOC dynamics at a range of restored peatlands.

6 Figures and Tables

Table 1: Reported range of carbon dioxide flux and DOC export from peatlands. Notable is the amount of variance in natural peatlands. A summary of literature suggests that carbon dioxide storage ranges from -411 to 312 g CO₂ m⁻² y⁻¹. Ovenden (1990) provides a narrower normal for Canadian peatlands of 8-30g C m⁻² y⁻¹ of storage. Similarly DOC export ranges broadly 1.1 - 43 g m⁻² y⁻¹.

Peatland type and location	Reference	
<i>Location</i>	<i>g CO₂ m⁻² yr⁻¹</i>	<i>Authors</i>
Raised bog (Canada)	-7 to -411	Roulet <i>et al.</i> , 2007
Raised bog (Canada)	-85 to 67	Lafleur <i>et al.</i> , 2001; Frohking <i>et al.</i> , 2002
Raised bog (Sweden)	-7 to -37	Waddington & Roulet, 2000
Raised bog (Siberia)	-79 to 132	Arneth <i>et al.</i> , 2002
Open bog (Baltic Russia)	-80	Alm <i>et al.</i> , 1999
Bog complex (Siberia)	48	Schulze <i>et al.</i> , 2002
Patterned blanket bog (Ireland)	-179 to -223	Sottocornola & Kiely, 2005
Sphagnum-sedge-pine fen (Finland)	-359	Alm <i>et al.</i> , 1997
Subarctic peatland (Russia)		
Wet hollow	-62	Heikkinen <i>et al.</i> , 2002
Intermediate hollow	-158	
Wet lawn	-147	
Intermediate lawn	-110	
Hummock	11	
Subarctic peatland (Finland)		
Palsa top	-19 to -53	Nykänen <i>et al.</i> , 2003
Palsa margin	-62 to -154	
Thermokarst wetland	-71 to -94	
Subarctic peatland (Alaska)		
Palsa top	312	Wickland <i>et al.</i> , 2006
Palsa margin	191	
Thermokarst wetland	134	
<i>Adapted from Strack et al. 2008 and Saarnio et al. 2007)</i>		
	<i>g DOC m⁻² y⁻¹</i>	
Subarctic (Quebec) DOC	1.1-4.9	Moore, 1987
Boreal Bog, (Quebec) DOC	1.3-4.8	Moore, 1988
Wetland (RUS, NA, NZ) DOC	0.18-14.2	Hope, 1994
Moors (EU) DOC	0.8-9.0	
Kettle Beg (MN, USA) DOC	0.9-4.3	Urban <i>et al.</i> , 1989
Upland Bog (Western	1.9	

Ontario) DOC		
Bog (MS, USA)	8.6	McKnight <i>et al.</i> , 1985
Bog (Southeast Ontario)	14.3	Roulet <i>et al.</i> , 2007
BDB Cutover site	6.2-10.3	Waddington <i>et al.</i> , 2008
BDB Restored site	3.5-4.8	

Peatland Restoration Study Site
Bois-Des-Bel, Québec

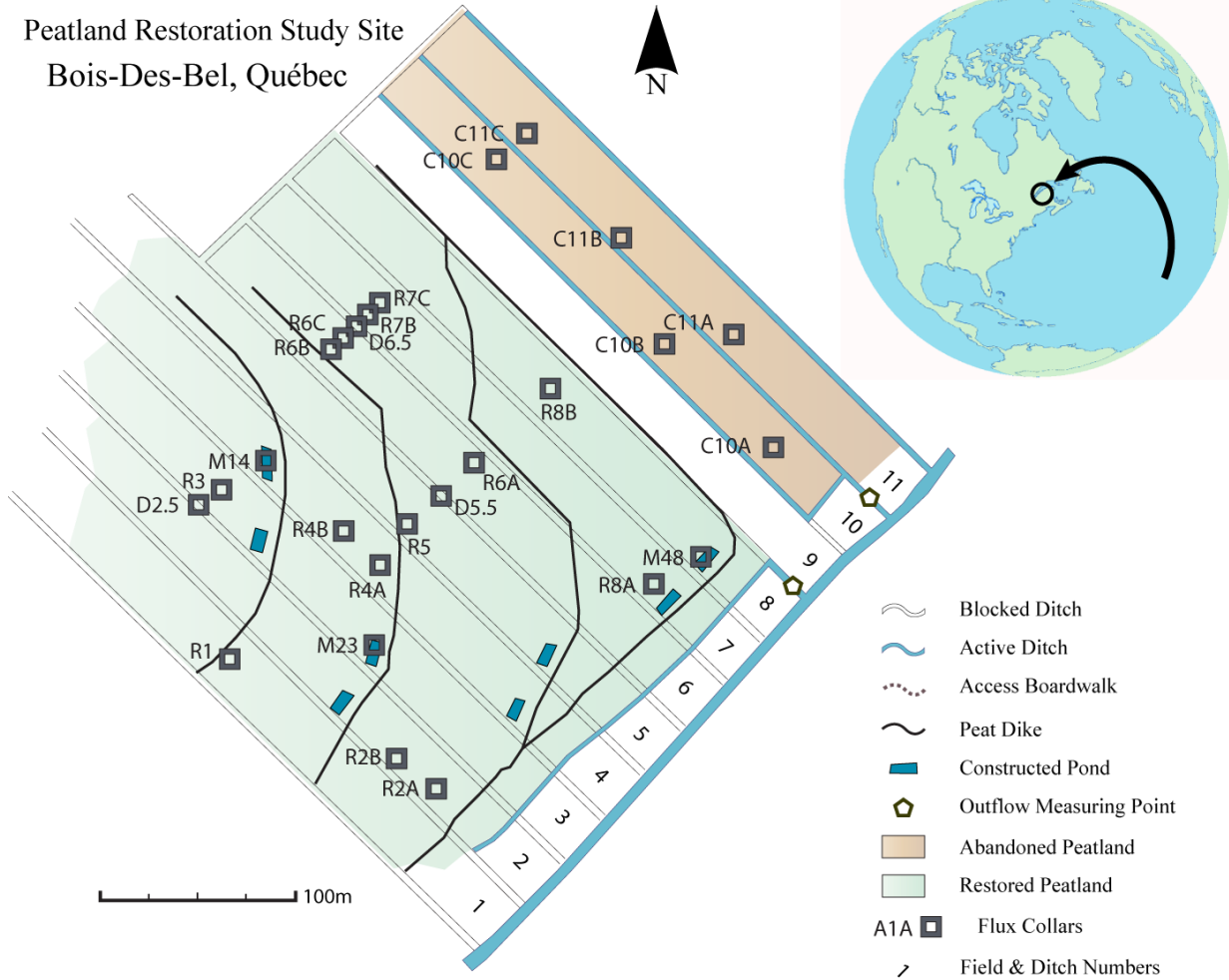


Figure 1: Site overview map. Ditches are spaced parallel every 30m. While the abandoned site has ditches that actively dry the site, the restored site has only artifact ditches that serve as habitat for bog species. The site is inclined to the east where the water discharges from both sites. Dikes have been built on the restored section to cache precipitation and snow melt.

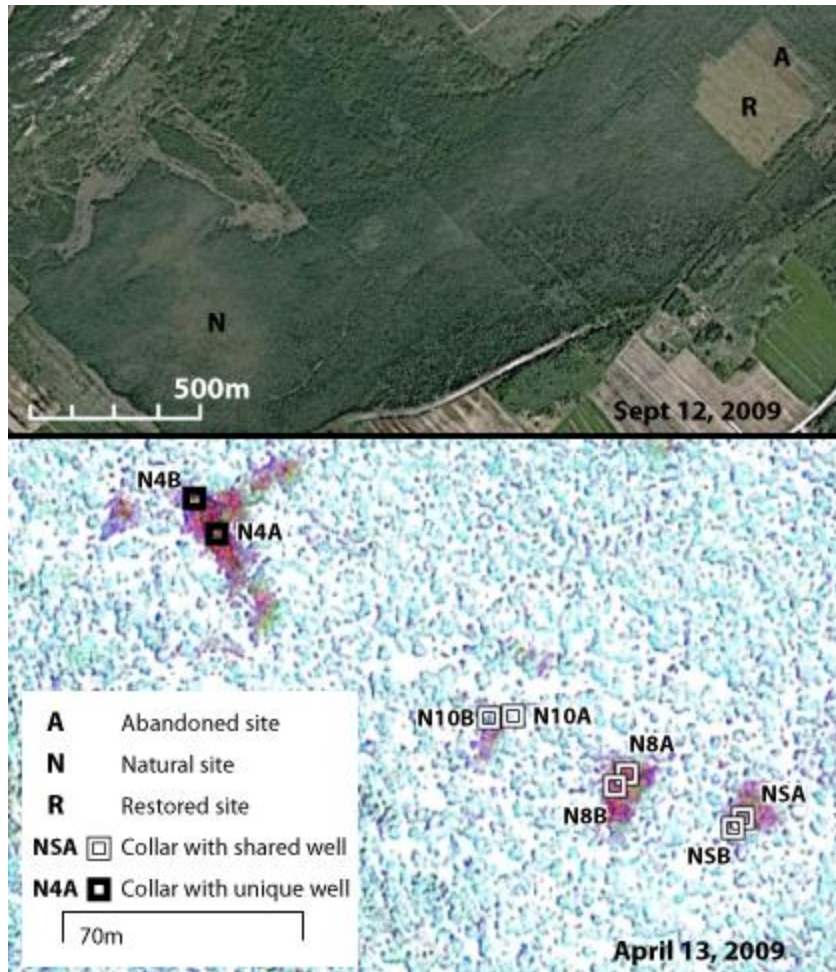


Figure 2: The top panel shows the BDB complex ranging from east to west roughly 2km. On the eastern side is a undisturbed natural open bog, while on the far west side fields have been left abandoned for control study sites, with restored site adjacent to the abandoned site. The bottom panel shows the locations selected for collars at the natural site.

Table 2: Precipitation, 2010 compared to the 30-year climate average, with calculated percent difference between 2010 and 30-year average. July and August are abnormally dry, some 46% dryer and 89.5 percent dryer respectively, while September is abnormally wet at more than double the climate average precipitation.

Month	2010 Records (mm)	30 Year average (mm) 1971-2000	% Difference
May	63.1	89.6	-29.6
Jun	88.2	87.1	1.3
Jul	49.4	92.0	-46.3
Aug	10.2	97.5	-89.5
Sep	193.5	89.5	116.3
Oct	94.6	80.7	17.2

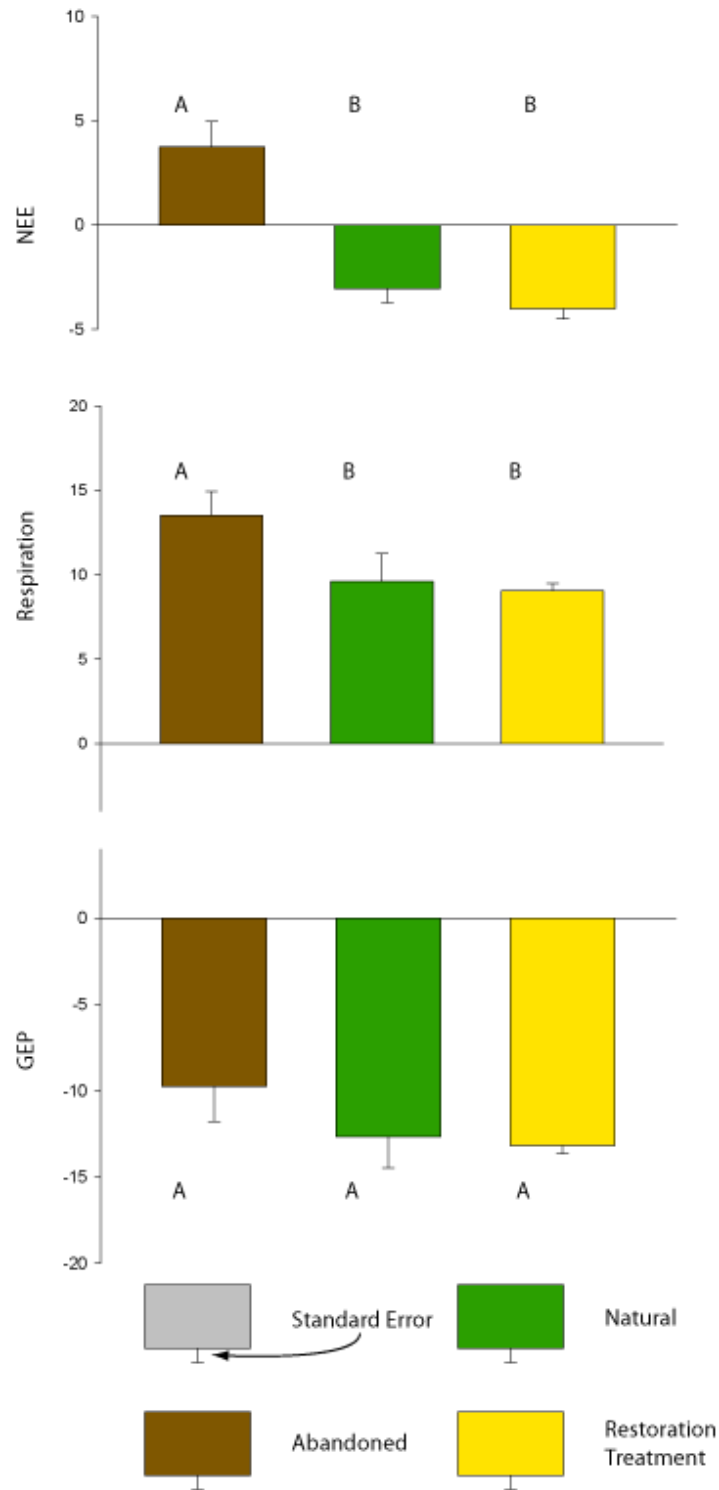


Figure 3: NEE, Respiration, and GEP from data gathered at PAR > 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$, statistical difference (ANOVA, $P < 0.05$) denoted by difference in lettering.

Table 3: Number of collars at each site which have statistical correlations (Pearson's, $P < 0.05$) to denoted environmental variables.

<i>R</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>PAR</i>	<i>soil</i>	<i>WT</i>	<i>Veg</i>
NEE		12	14	11	8	7	5
Rtot			6	2	12	13	11
GEP				13	5	4	2
<i>A</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>PAR</i>	<i>soil</i>	<i>WT</i>	<i>Veg</i>
NEE		4	6	4	2	3	1
Rtot			5	1	6	2	4
GEP				6	3	1	4
<i>N</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>PAR</i>	<i>soil</i>	<i>WT</i>	<i>Veg</i>
NEE		5	8	8	0	1	0
Rtot			6	0	6	8	2
GEP				8	3	3	2

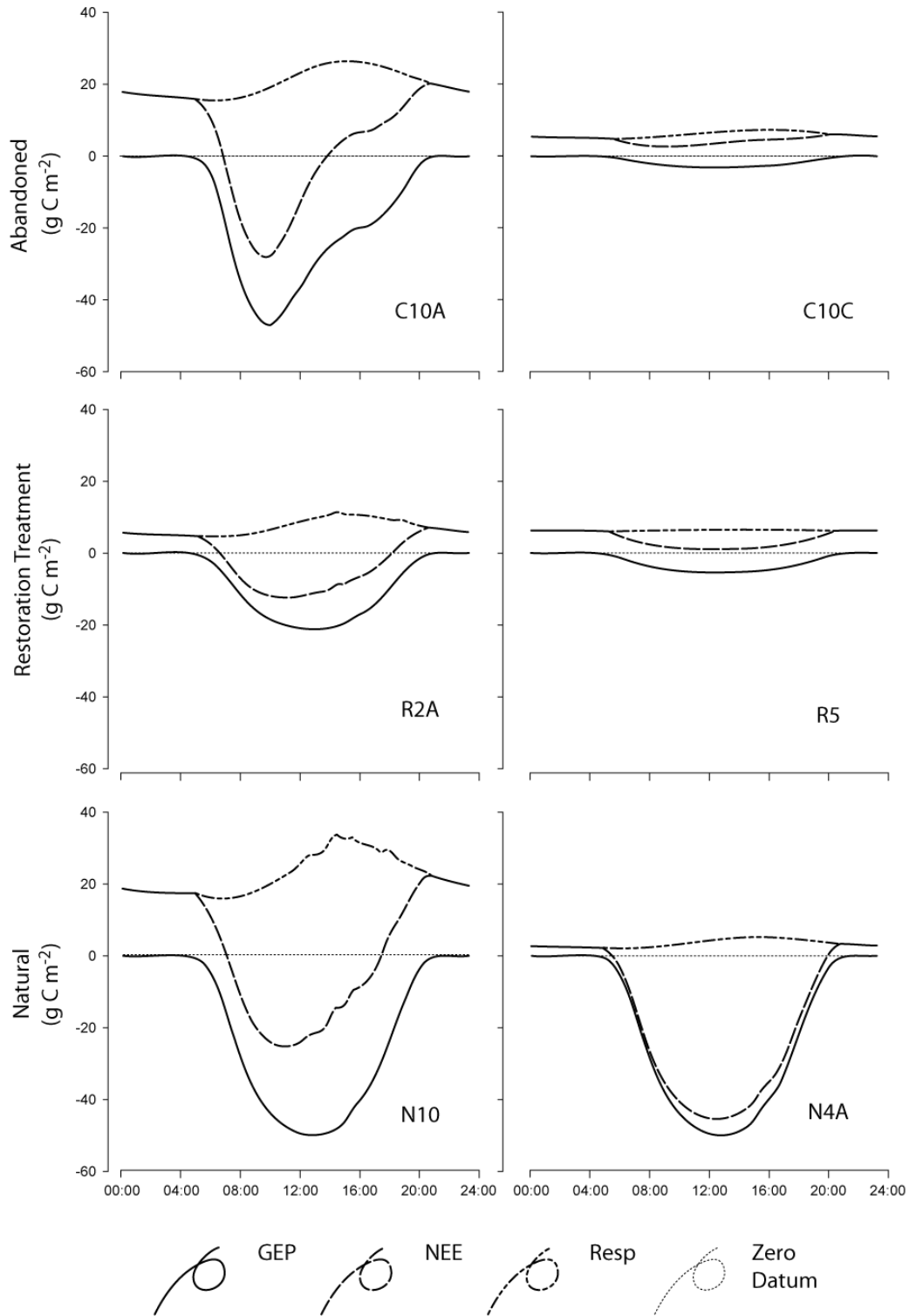


Figure 4: Seasonal modelled data for six collars presented over the hour of day. Collars are chosen to represent sites that show the range of variability among collars.

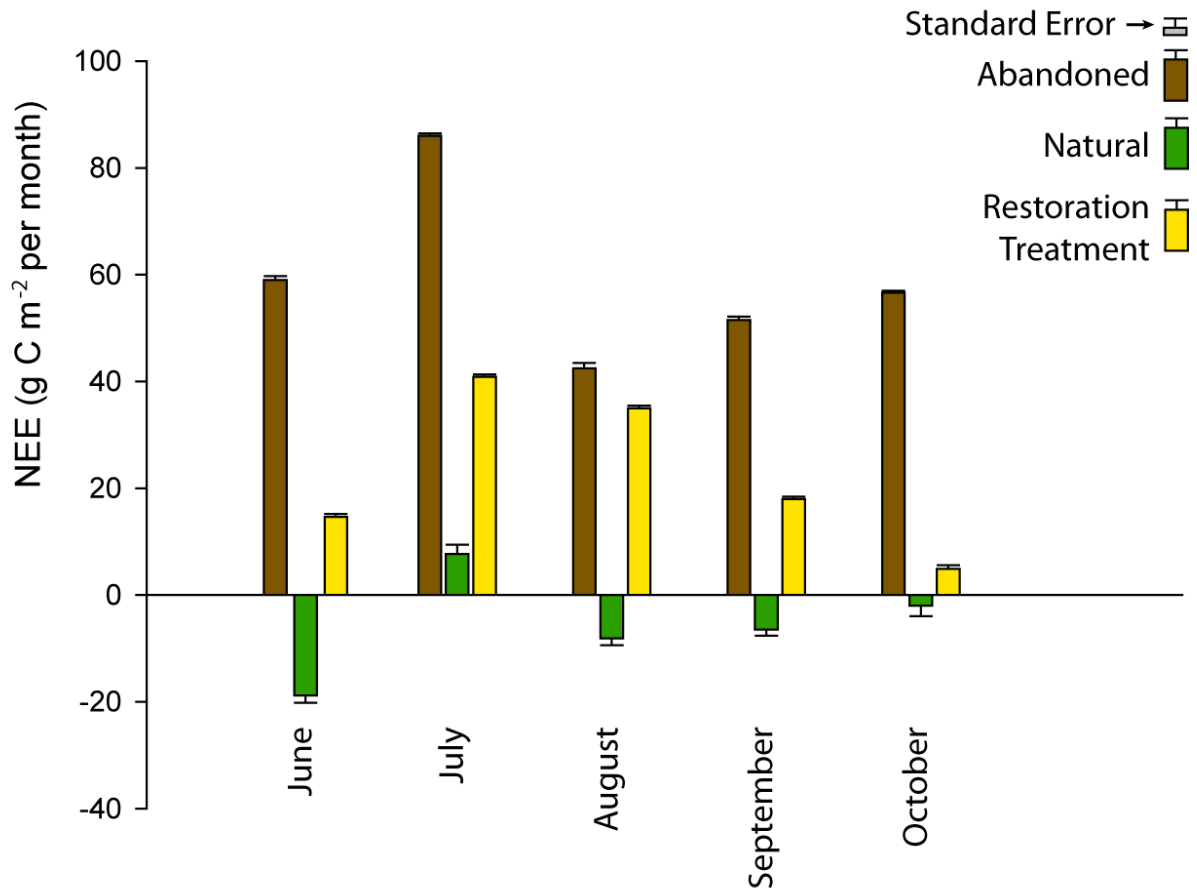


Figure 5: Seasonal modelled data for all collars (grouped by site) presented by month.

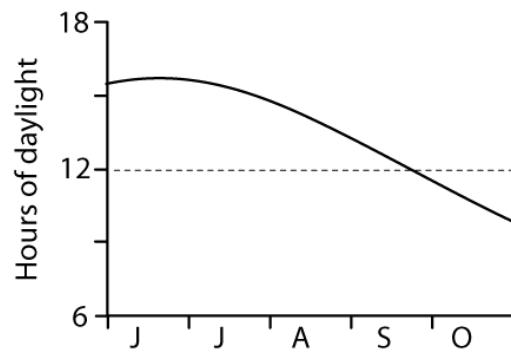


Figure 6: Hours of sunlight over the months in Figure 5. Sunlight hours drop as summer ends and the autumnal equinox in September is passed.

Table 4: Monthly calculated variation in CO2 flux components as a numerical complement to Figure 5.

		June	SD	July	SD	August	SD	September	SD	October	SD
Abandoned	GEP	-51.5	±7.2	-47.2	±5.2	-80.3	±10.7	-49.4	±7.9	-18.4	±3.8
	Resp	110.6	±2.1	133.1	±1.8	122.8	±1.8	98.2	±1.7	77.8	±1.4
	NEE	59.1		85.9		42.5		48.7		59.4	
Natural	GEP	-114.8	±15.5	-136.5	±16.0	-136.0	±16.5	-86.0	±13.8	-60.2	±12.6
	Resp	96.0	±6.7	144.2	±14.7	127.9	±6.2	79.0	±4.7	58.7	±14.2
	NEE	-18.8		7.7		-8.1		-7.0		-1.5	
Restored site	GEP	-45.4	±6.1	-53.9	±6.3	-53.6	±6.5	-34.2	±5.5	-23.5	±4.9
	Resp	60.0	±1.9	94.7	±2.6	88.6	±2.6	51.4	±2.0	29.2	±4.5
	NEE	14.7		40.8		35.0		17.2		5.7	

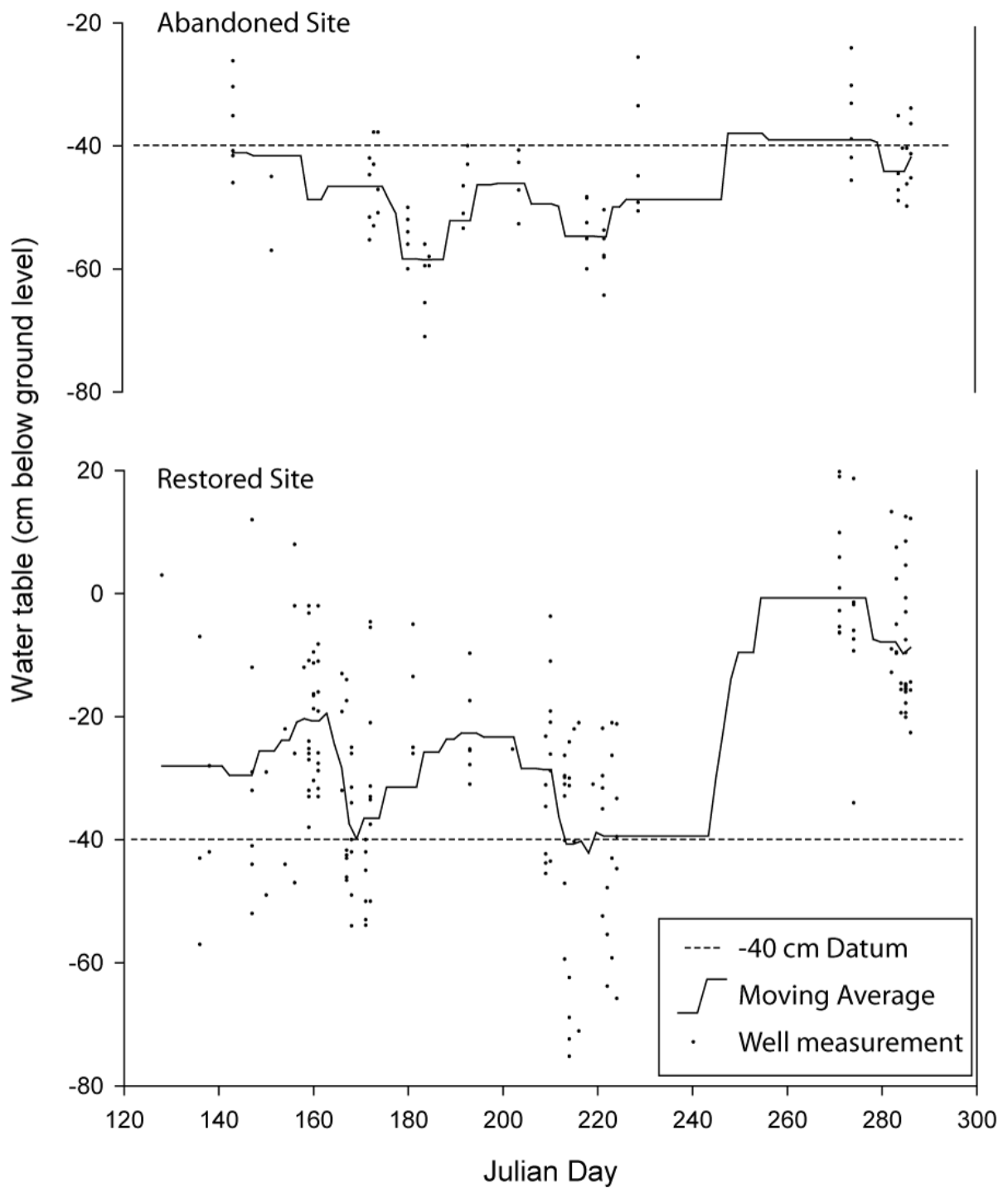


Figure 7: Changes to water table depth below ground level (two sites) over the field season. Points show individual well measurements. The solid line shows the moving average as the season progresses as compared to a -40cm datum at each site.

Table 5: Chemistry and quality summary, Red text denotes a Kruskal-Wallis statistic (H), while black text denotes an ANOVA (F). Bolded text is to highlight statistical differences between pair wise comparisons.

		Abandoned		Abandoned to Restored		Restored		Restored to Natural		Natural		Natural to Abandoned	
		Mean	SD	F or H	p	Mean	SD	F or H	p	Mean	SD	F or H	p
	pH	6.05	1.101	0.218	0.641	5.95	1.055	25.11	<0.001	4.46	0.942	23.6	<0.001
SUVA254	mg C cm ⁻¹	0.0397	0.0319	11.913	<0.001	0.0876	0.0177	17.23	<0.001	0.0419	0.0148	0.538	0.463
E2:E3	α:α	3.00	0.765	0.499	0.482	3.10	0.606	38.39	<0.001	4.09	0.282	28.7	<0.001
E4:E6	α:α	5.60	2.139	0.473	0.493	5.38	0.97	2.868	0.094	6.04	2.422	0.4	0.528
Hexose	mg/L	4.84	6.305	2.885	0.045	2.98	1.237	0.987	0.324	2.61	0.23	1.35	0.252
Pentose	mg/L	101.1	77.078	2.967	0.089	175.56	220.941	0.0349	0.852	162.78	99.982	2.92	0.046
P:Hex	:	33.31	30.663	2.879	0.045	60.06	65.563	0.0001	0.99	60.31	33.612	3.41	0.021
DOC	mg/L	59.57	25.491	4.219	0.043	66.84	9.695	72.293	<0.001	44.09	7.543	5.28	0.026

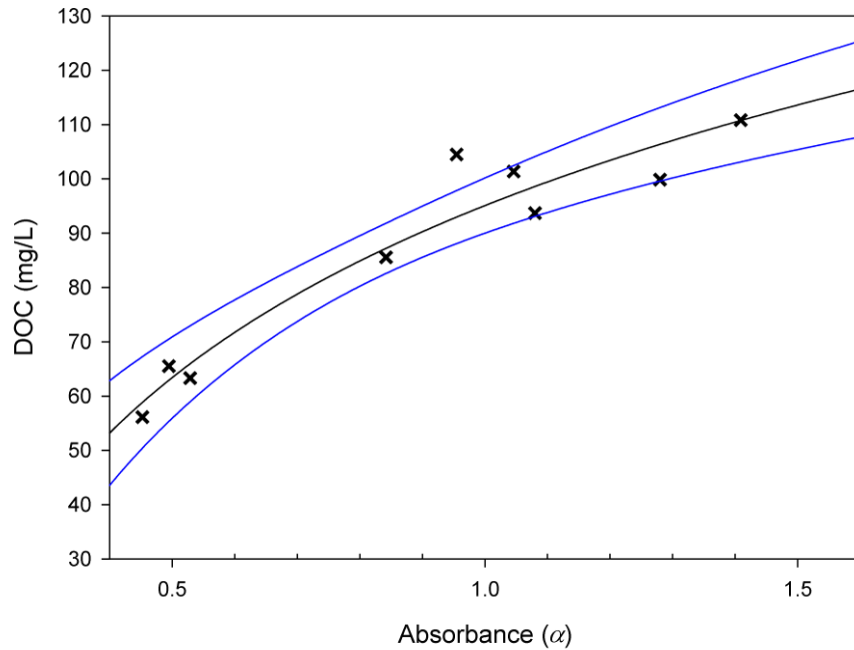


Figure 8: DOC to absorbance regression [$45.69 \times \log_e(\text{Absorbance}) + 95.086 = \text{DOC concentration}$], $r^2=0.9262$, for water drawn from the site export points for both abandoned and restored site discharge.

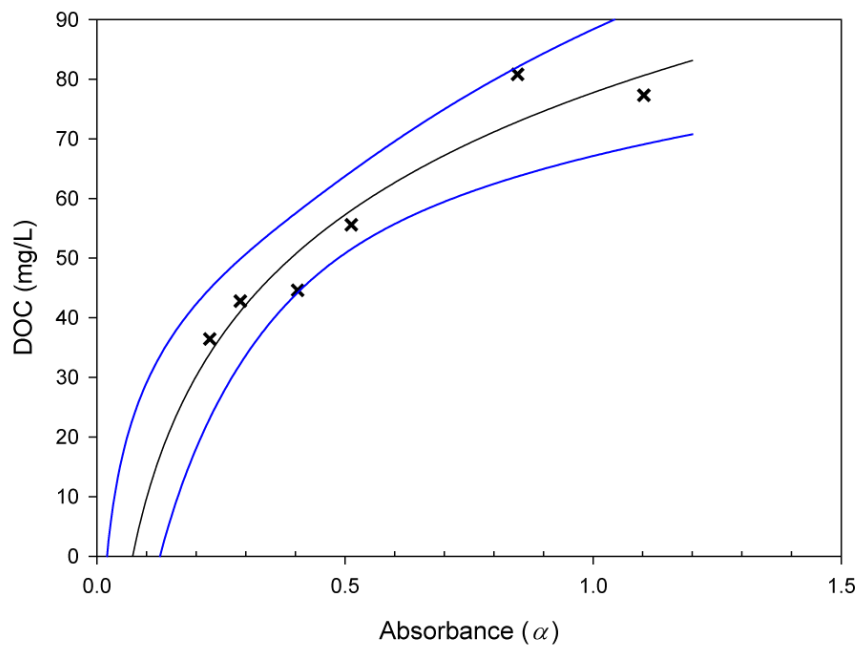


Figure 9: DOC to absorbance regression [$29.561 \times \log_e(\text{Absorbance}) + 77.745 = \text{DOC concentration}$], $r^2= 0.926$, for water drawn from wells.

Table 6: Sorting collars for linear regressions of GEP to DOC concentration, with ANOVA performed on regression vs. measured values showing no significance between GEP and DOC with any group of collars examined.

	r ²	F	p
All collars	0.002	0.199	0.656
Abandoned	0.160	3.992	0.059
Forb	0.602	1.513	0.435
Shrub	0.327	2.919	0.138
Bare peat	0.122	0.697	0.442
Treed peat	0.073	0.236	0.661
Natural	0.006	0.079	0.784
Hollow	0.035	0.329	0.580
Hummock	0.562	2.564	0.250
Restored	0.002	0.098	0.755
Hollows	0.000	0.009	0.926
Hummocks	0.020	0.582	0.452

Table 7: Calculated discharge from the abandoned site and restored site according to Verhoff's equation (Equation 9).

		Abandoned	Restored
Rain Export (g C m ⁻²)	2001	6.2	3.5
	2010	9.4	0.9
Total Export (g C m ⁻²)	2001	49.8	7.6
	2010	28.8	5.0

Table 8: Chemical properties of export DOC. Export properties were significantly different between the restored site and abandoned sites for pH, E2:E3, Hexose, Pentose, Pentose to Hexose, and DOC concentrations.

	Abandoned Export		Restored Export		ANOVA	
	Mean	SD	Mean	SD	F	p
pH	5.94	0.59	6.18	0.42	5.427	0.022
E2:E3	2.31	0.68	2.80	0.91	9.745	0.002
SUVA	0.0258	0.0204	0.0290	0.0203	0.636	0.427
E4:E6	6.87	1.40	6.36	1.50	3.187	0.077
Hexose (mg/L)	2.7	0.3	3.1	1.0		0.011
Pentose (mg/L)	86.7	48.9	159.1	20.0	99.311	<0.001
Pen:Hex	31.5	15.5	49.1	11.5	43.476	<0.001
DOC (mg C/L)	100.62	15.21	86.32	20.92	15.801	<0.001

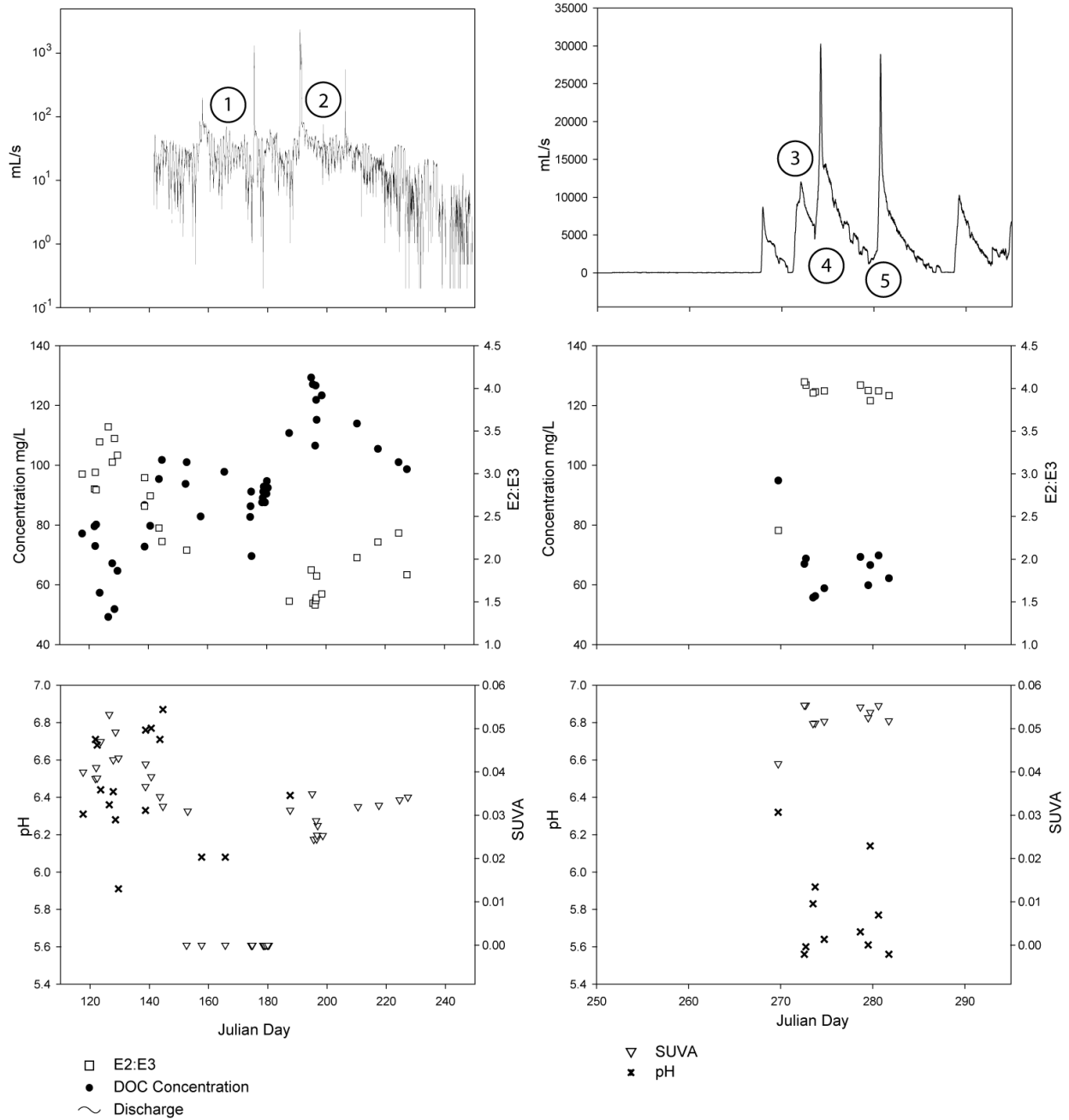


Figure 10: Restored site discharge with panels for DOC concentration, E2:E3, SUVA, and pH. Numbers in the two top panels show the position of 5 recorded storm events recorded.

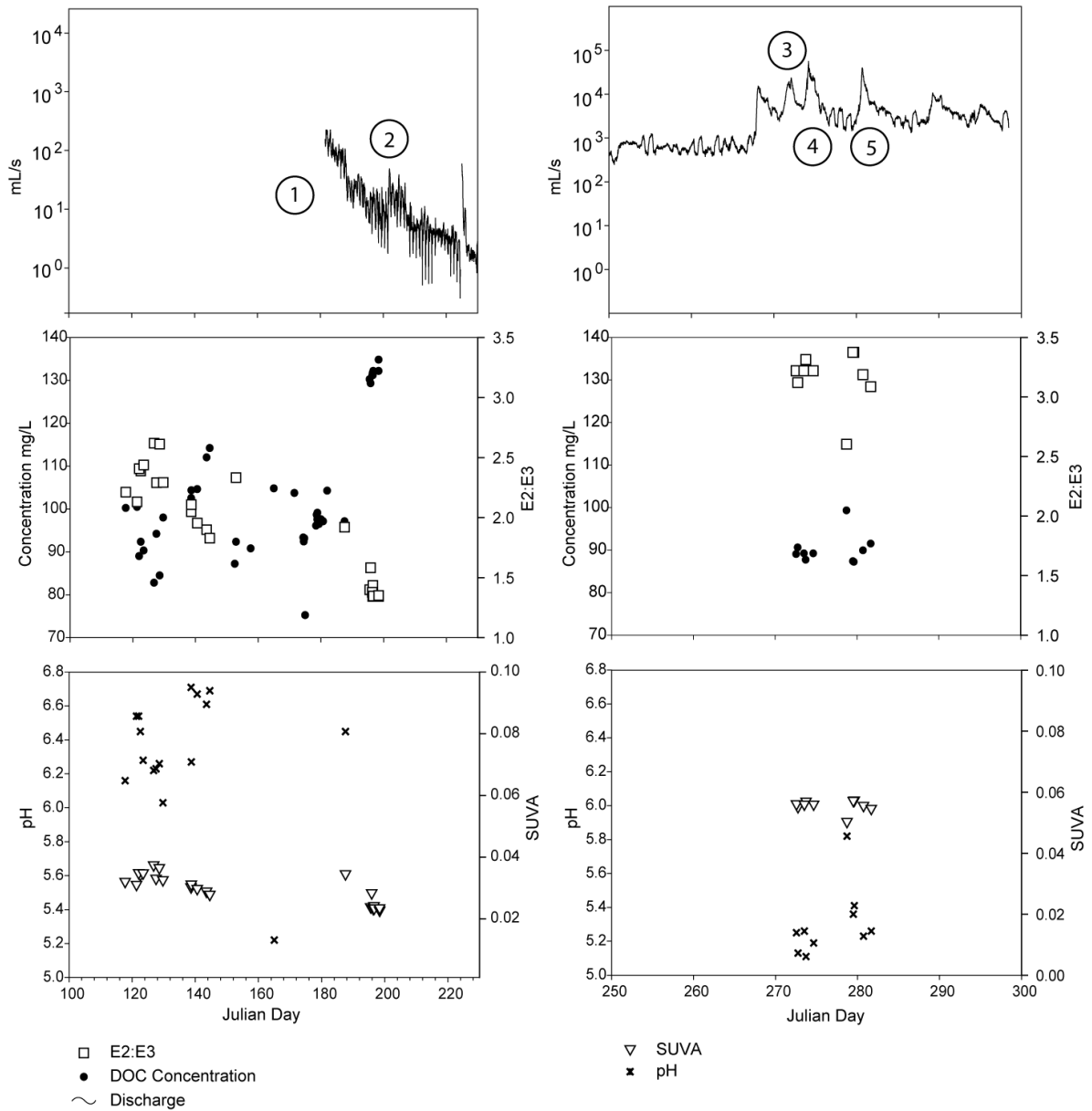


Figure 11: Abandoned site discharge with panels for DOC concentration, E2:E3, SUVA, and pH. Numbers in the two top panels show the position of 5 recorded storm events recorded.

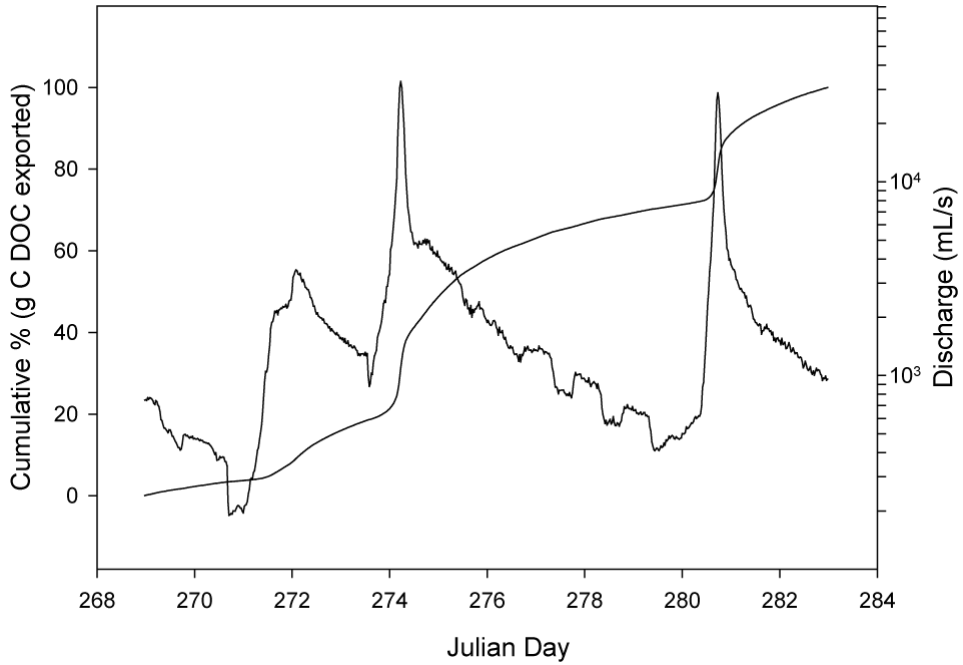


Figure 12: A large storm event's effect on DOC export at the restored site, shown here as cumulative export of DOC (as a percent of the total during this storm system) , corrected for changing DOC concentration.

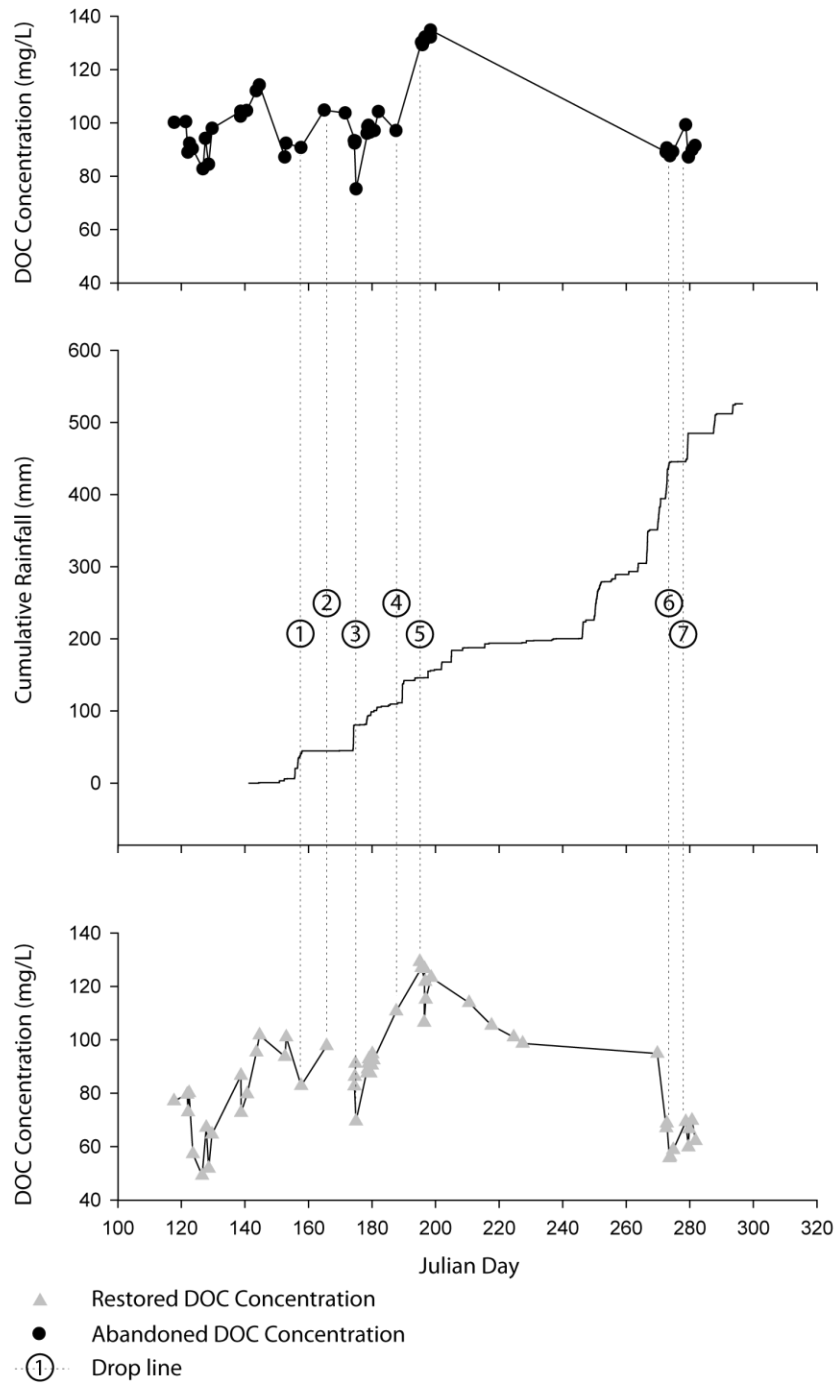


Figure 13: DOC concentration from export waters compared to rainfall. Rainfall represented across the season masks relative volume, and impact, of a storm event. By showing as cumulative rainfall large events can be easily distinguished from medium or small events with short but intense rainfall.

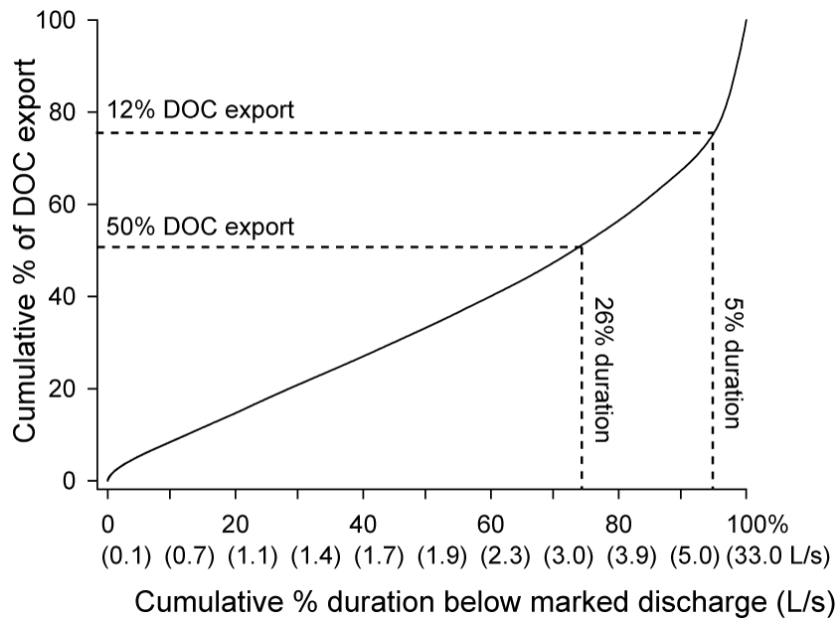


Figure 14: The percentage of DOC that is exported during times of high discharge (as a cumulative percentage of 14-days of discharge) relative to the DOC exported during lower flow periods during a 14-day storm system at the restored site. This chart shows that high flow periods denoted as the amount of flow occurring only 5% of the time exports 15% of the DOC, and that 50% of the total export occurs in the top 26% discharge amounts.

Table 9: Storm flow lag from the abandoned and restored sites.

Date/ Precipitation	Site	Lag time to peak discharge (hrs)	Difference (minutes)
267	A	17.08	
45.97mm	R	14.09	-179.4
271	A	27.99	
43.94mm	R	27.90	-5.4
273	A	19.36	
53.09mm	R	19.63	16.2
280	A	20.77	
36.32mm	R	21.29	30.9
289	A	16.27	
26.92mm	R	17.37	66.0

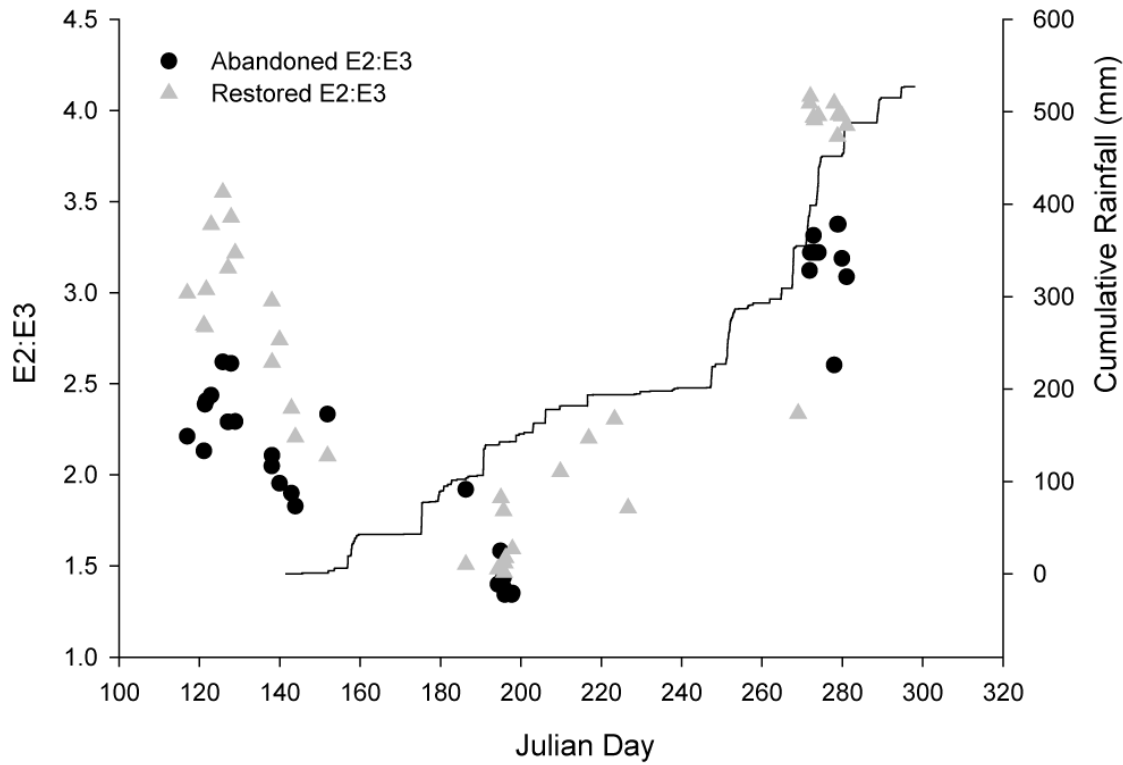


Figure 15: Changing E2:E3 seasonally at an abandoned and restored, excavated peatland shown with cumulative recorded precipitation.

Table 10: Sugars and sugar ratios from specified depths of soil at the restored site.

	Hexose mg/L	Pentose mg/L	Pentose to Hexose
50cm	5.34	122.67	45.90
75cm	6.46	106.55	36.49
100cm	5.54	105.22	39.43
125cm	4.99	39.49	15.80



Plate 2: BDB field 1: *Eriophorum vaginatum* (centre arrow) dying back after its vigorous colonization of the site early after restoration. *Polytrichum* sp., a pre-*Sphagnum* spp. colonizer, grows from the dying *Eriophorum*.

Bibliography

- Alm J, Schulman L, Walden J, Nykänen H, Martikainen PJ, Silvoia J. 1999. Carbon balance of a boreal bog during a year with an exceptionally dry summer. *Ecology* 80: 161-174
- Almendros G, Gonzalez-Vila F.J. Martin F. 1999. Fire Induced transformation of soil organic matter from an oak forest: experimental approach to the effects of fire on humic substances. *Soil. Sci.* 149 158-168
- Armstrong A, Holden J, Kay P, Francis B, Foulger M, Gledhill S, McDonald AT, Walker A. 2010. The impact of peatland drain-blocking on dissolved organic carbon loss and discolouration of water; results from a national survey. *Journal of Hydrology* 381(1-2):112-120
- Austnes K, Evans CD, Eliot-Laize C, Naden PS, Old GH. 2010. Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. *Biogeochemistry*, 99(1), 157-173.
- Baldock JA, Oades JM, Waters AG, Peng X, Vassallo AM, Wilson MA. 1992. Aspects of the chemical structure of soil organic materials as revealed by solid state ¹³C-NMR spectroscopy. *Biogeochemistry* 16:1-42.
- Baldock JA, Preston CM. 1995. Chemistry of carbon decomposition processes in forests as revealed by solid-state ¹³C-NMR. In 'Carbon forms and functions in forest soils'. Eds WW McFee & JM Kelly. pp. -89-117. Soil science society of America Inc. Madison.
- Batjes NH. 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science* 47 (2)151-163.
- Beck KG, JH Reuter, EM Perdue. 1974. Organic and inorganic chemistry of some coastal plain rivers of the southeastern United States, *Geochim. Cosmochim. Acta*, 38, 341-364

- Bergman I, Lundberg I, Nilsson M. 1999. Microbial carbon mineralization in an acid surface peat: effects of environmental factors in laboratory incubations. *Soil biology & Biogeochemistry* 31:1867-1877.
- Billett MF, Palmer SM, Hope D, Deacon C, Storeton-West R, Hargreaves K J, Flechard C, Fowler D. 2004. Linking land-atmosphere-stream carbon fluxes. *Global Biogeochem. Cy.*, 18(1), 1–12.
- Blodau C, Basiliko N, Moore T. 2004. Carbon turnover in peatland mesocosms exposed to different water table levels. *Biogeochemistry* 67:331-351.
- Blodau C, Moore TM. 2003. Micro-scale CO₂ and CH₄ dynamics in a peat soil during a water fluctuation and sulfate pulse, *Soil Biology & Biochemistry* 35: 535–547.
- Boelter DH, Verry ES. 1977. *Peatland and water in the Northern Lake States. – General Technical Report NC-31*. U.S. Dept of Agriculture, Forest Service, North Central Expt. Station, St. Paul, MN.
- Bortoluzzi ED, Epron A, Siegenthaler D, Gilbert, Buttler A. 2006. Carbon balance of a European mountain bog at contrasting stages of regeneration. *New Phytologist* 172:708–718.
- Bourbonniere RA. 1989. Distribution patterns of dissolved organic matter fractions in natural waters from eastern Canada. *Organic Geochemistry*, 14: 97-107
- Bourbonniere RA. 2009. Review of water chemistr research in natural and disturbed peatlands. *Canadian water resources journal* 34(4):393-414.
- Brooks K. 1992. Surface hydrology. – In: Wright H E, Coffin BA, Aaseng NE. (eds), *The patterned peatlands of Minnesota*. Univ. of Minnesota Press, pp. 153–162.
- Brown VA, McDonnell JJ, Burns DA, Kendall A. 1999. The role of event water, a rapid shallow flow component, ad catchment size in summer streamflow. – *J. Hydrol.* 217: 171 –190.

- Burford JR, Bremner JM. 1975. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. *Soil biology and biochemistry*, 7(6), 389-394.
- Chantigny MC. 2008a. Soil Carbohydrates; Pentose. In (Eds.) Ellert BH. & Rock L. 2010. *Soil Sampling and Methods of Analysis*.
- Chantigny MC. 2008b. Soil Carbohydrates; Hexose. In (Eds.) Ellert BH. & Rock L. 2010. *Soil Sampling and Methods of Analysis*.
- Charman DJ. 2002. Peatland hydrology and ecology. In DJ Charman ed. *Peatlands and environmental change*. Antony Rowe Ltd. Wiltshire, England.
- Chen Y, Senesi N, Schnitzer M. 1976. Information provided on humic substances by E4:E6 Ratios. *Soil Sci Soc Am* 41-1 352-358
- Christ MJ, David MB. 1996. Temperature and moisture effects on the production of dissolved organic carbon in a spodosol. *Soil Biology and Biochemistry*, 28(9), 1191-1199.
- Clark JM, Lane SN, Chapman PJ, Adamson JK. 2007. Export of dissolved organic carbon from an upland peatland during storm events: implications for flux estimates. *Journal of Hydrology* 347(4-Mar) 438-447
- Clymo RS, Hayward PM. 1982. The Ecology of *Sphagnum*. In AJE Smith ed. *Bryophyte Ecology*. Chapman and Hall, London, UK
- Clymo RS. 1984. The limits to peat bog growth. *Philosophical Transactions of the Royal Society of London. B, Biological Sciences*, 303(1117):605-654
- Cronan CS, Aiken GR. 1985. Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. *Geochim. Cosmochim. Acta* 49:1697-1705.

- Dalva M, Moore TR. 1991. Sources and sinks of dissolved organic carbon in a forested swamp catchment. *Biogeochemistry* 15:1–19.
- Davies GM, Hamilton A, Smith A, Legg CJ. 2008. Using visual obstruction to estimate heathland fuel load and structure, *Int. J. Wildland Fire* 17 (2008), pp. 380–389.
- DeLuca TH, Keeney DR. 1993. Soluble anthrone reactive carbon in soils: effect of carbon and nitrogen amendments. *Soil Science Society Of America Journal*. 57:1296-1300.
- Dosskey MG, Bertsch PM. 1994. Forest sources and pathways of organic matter transport to a blackwater stream: A hydrologic approach. *Biogeochemistry* 24:1–19.
- Driscoll CT, Baker JP, Bisogni JJ, Schofield CL. 1980. Effects of aluminum speciation on fish in dilute acidified waters, *Nature*, 284, 161-164,
- Driscoll CT, Fuller RD, Simone DM. 1988. Longitudinal variations in trace metal concentrations in a northern forested ecosystem, *J. Environ. Qual.*, 17, 101-107, 1988
- Dunnivant FM, Jardine PM, Taylor DL, McCarthy JF. 1992. Transport of naturally occurring dissolved organic carbon in laboratory columns containing aquifer material. *Soil Science Society of America Journal*, 56(2), 437-444.
- Easthouse KB, Mulder J, Christophersen N, Seip HM. 1992. Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, Southern Norway. *Water resources research*, 28(6), 1585-1596.
- Effler SW, Schafran GC, Driscoll CT. 1985. Partitioning light attenuation in an acidic lake, *Can. J. Fish. Aquat. Sci.*, 42, 1707-1711.
- Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS. 2006. Alternative explanations for rising dissolved organic carbon exports from organic soils. *Global change biology*. 12:2044-2053.
- Feldmeyer-Christe, Schnyder EN, Bisang I. 2001. Distribution and habitats of peat mosses, *Sphagnum*, in Switzerland. *Lindbergia* 26:8–22.

- Fenner N, Ostle NJ, McNamara N, Sparks T, Harmens H, Reynolds B, Freeman C. 2007. Elevated CO₂ effects on peatland plant community carbon dynamics and DOC production. *Ecosystems* 10(4) 635-647
- Fenner N, Ostle N, Freeman C, Sleep D, Reynolds B. 2004. Peatland carbon efflux partitioning reveals that Sphagnum photosynthate contributes to the DOC pool. *Plant and Soil* 259(1)345-354
- Fiebig DM, Lock MA, Neal C. 1990. Soil water in the riparian zone as a source of carbon for a headwater stream. – *J. Hydrol.* 166: 217 –237
- Fisk MC, Ruether KF, Yavitt JB. 2003. Microbial activity and functional composition among northern peatland ecosystems, *Soil Biology and Biochemistry*, 35, 591-602.
- Franke R. 1982. Smooth Interpolation of Scattered Data by Local Thin Plate Splines. *Comp. & Maths. with Appls.* Vol. 8. No. 4. pp. 237–281. Great Britain.
- Freeman C, Fenner N, Ostle NJ, Kang H, Dowrick DJ, Reynolds B, Lock MA, Sleep D, Hughes S, Hudson J. 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels, *Nature*, 340, 195-198.
- Freeman C, Lock MA, Reynolds B. 1992. Fluxes of CO₂, CH₄ and N₂O from a Welsh peatland following simulation of water table draw-down: potential feedback to climatic change. *Biogeochemistry* 19:51–60.
- Freeman C, Ostle N, Kang H. 2001. An enzymic ‘latch’ on a global carbon store. *Nature*, 409(6817), 149.
- Frolking S, Bubier JL, Moore TR, Ball T, Bellisario LM, Bhardwaj A, Carroll P, Crill PM, Lafleur PM, McCaughey JH, Roulet NT, Suyker AE, Verma SB, Waddington JM, Whiting GJ. 1998. Relationship between ecosystem productivity and photosynthetically active radiation from northern peatlands, *Global Biogeochemical Cycles*, 12, 115-126.

- Frolking S, Roulet NT, Moore TR, Lafleur PM, Bubier JL, Crill PM. 2002. Modelling seasonal to annual carbon balance of Mer Bleue Bog, Ontario, Canada. *Glob. Biogeochem. Cycles* 16(3). 10.1029/2001GB001457
- Gallet C, Lebreton P. 1995. Evolution of phenolic patterns in plants and associated litter and humus of a mountain forest ecosystem. *Soil Biol. Biochem.* 27:157–165.
- Geisler R, Hogberg MN, Strobel BW, Richter A, Nordgren A, Hogberg A. 2007. Production of dissolved organic carbon and low-molecular weight organic acids in soil solution driven by recent tree photosynthate. *Biogeochemistry* 84(1): 1-12
- Gerdol R, Bonora A, Gualandri R, Pancaldi S. 1996. CO₂ exchange, photosynthetic pigment composition, and cell ultrastructure of *Sphagnum* mosses during dehydration and subsequent rehydration. *Canadian Journal of Botany*, 74, 726–734.
- Glatzel S, Kalbitz K, Dalva M, Moore T. 2003. Dissolved organic matter properties and their relationship to carbon dioxide efflux from restored peat bogs. *Geoderma*. 113:397-411.
- Glover GM, Webb AH. 1979. Weak and strong acids in the surface waters of the Tovdal region in Southern Norway, *Water Res* 13:781-789
- Gödde M, David MB, Christ MJ, Kaupenjohann M, Vance GF. 1996. Carbon mobilization from the forest floor under red spruce in the northeastern USA *Soil Biol. Biochem* , 28: 1181–1189
- Goldammer T, Blodau C. 2008. Dessication and product accumulation constrain heterotrophic respiration in peats of an obrotrophic temperate bog. *Soil Biology and Biochemistry* 40(8):2007-2015
- Gorham E, Rochefort L. 2003. Peatland restoration: a brief assessment with special reference to *Sphagnum* bogs. *Wetlands Ecology and Management* 11:109–119.

- Gorham E, Underwood JK, Martin FB, Ogden JG. 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. *Ecol Appl* 1:182–195.
- Gorham E, Bayley SE, Schindler DW. 1984. Ecological effects of acid deposition upon peatlands: a neglected field in acid rain research. *Canadian Journal of Fisheries and Aquatic Sciences* 41: 1256-1268.
- Griffis TJ, Rouse WR, Waddington JM. 2000. Interannual variability of net ecosystem CO₂ exchange at a subarctic fen. *Global Biogeochem Cycles* 14:1109–1121.
- Groeneveld EVG, Masse A, Rochefort L. 2007. *Polytrichum strictum* as a Nurse-Plant in Peatland Restoration. *Restoration Ecology* 15(4) 709-719,
- Guildford SJ, Healey FP, Hecky RE. 1987. Depression of primary production by humic matter and suspended sediment in limnocorral experiments at Southern Indian Lake, northern Manitoba, Can. J. Fish. Aquat. Sci., 44:1408-1417.
- Gupta UC. 1967. In *Soil biochemistry Vol. 1* (ed. McLaren AD, Peterson GH) Carbohydrates p.91–118. New York : Dekker.
- Hewlett JD, Hibbert AR. 1967. Factors affecting the response of small watersheds to precipitation in humid areas. In: *Forest hydrology. Proc. Intern. Symp. on Forest Hydrol.*, Penn State, August, 1965 (pp 275–290). Pergamon Press, NY
- Hinton MJ, Schiff SL, English MC. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry*, 36(1), 67-88.
- Höll BS, Fiedler S, Jungkunst HF, Kalbitz K, Freibauer A, Drösler M, Stahr K. 2009. Characteristics of dissolved organic matter following 20 years of peatland restoration. *Science of the Total Environment*, 408(1), 78-83.

- Hudson JJ, Dillon PJ, Somers KM. 2003. Long-term patterns in dissolved organic carbon in boreal lakes: the role of incident radiation, precipitation, air temperature, southern oscillation and acid deposition. *Hydrol. Earth Syst. Sci.* 7, 390–398.
- Jackson TA, Hecky RE. 1980. Depression of primary productivity by humic matter in lake and reservoir waters of the boreal forest zone. *Can. J. Fish. Aquat. Sci.* 37:2300-2317.
- Jardine PM, Weber NL, McCarthy JF. 1989. Mechanism of dissolved organic carbon adsorption on soil. *Soil science society of America.* 53:1378-1385.
- Joosten H, Augustin J. 2006. Peatland restoration and climate: on possible fluxes of gases and money, In *Peat in solution of energy, agriculture and ecology problems, Proceedings of the International Conference, Minsk, Bambalov, N. (ed.), Tonpik, Minsk, pp. 412-417.*
- Kaiser K, Zech W. 1997. Competitive sorption of dissolved organic matter fractions to soils and related mineral phases. *Soil Science Society of America Journal*, 61(1), 64-69.
- Kalbitz K, Geyer S, Geyer W. 2000. A comparative characterization of dissolved organic matter by means of original aqueous samples and isolated humic substances. *Chemosphere*, 40(12), 1305-1312.
- Kennedy J, Billett MF, Duthie D, Fraser AR, Harrison AF. 1996. Organic matter retention in an upland humic podzol; The effects of pH and solute type. *Eur. J. Soil Sci.* 47:615-625.
- Kerekes J, Beauchamp S, Tordon R, Tremblay C, Pollock T, Organic vs. anthropogenic acidity in tributaries of the Kejimikujik watersheds in western Nova Scotia, *Water Air Soil Pollut.*, 31,207-214, 1986.
- Koehler AK, Murphy K, Kiely G, Sottocornola M. 2009. Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland. *Biogeochemistry*, 95(2), 231-242.

- Kononova MM. 1966. Soil Organic Matter. 2nd Ed. Pergamon Press, London.
- Koprivnjak JF, Moore TR. 1992. Sources, sinks and fluxes of dissolved organic carbon in subarctic fen catchments. *Arct. Alp. Res.* 24:204–210.
- Lafleur PM, Moore TR, Roulet NT, Frohking S. 2005. Ecosystem respiration in a cool temperate bog depends on peat temperature but not water table, *Ecosystems*, 8, 619-629
- Lafleur PM, Roulet NT, Admiral SW. 2001. Annual cycle of CO₂ exchange at a bog peatland. *J. Geophys. Res.* 106(D3):3071-3081.
- Lavoie C, Grosvernier P, Girard M, Marcoux K. 2003. Spontaneous revegetation of mined peatlands: An useful restoration tool?, *Wetlands Ecol. Manage.*, 11, 97– 107
- Lucchese M, Waddington JM, Poulin M, Pouliot R, Rochefort L, Strack M. 2010. Organic matter accumulation in a restored peatland: evaluating restoration success. *Ecological Engineering*, 36(4), 482-488.
- Lundquist EJ, Jackson L, Scow KM. 1999. Wet–dry cycles affect dissolved organic carbon in two California agricultural soils. *Soil Biology and Biochemistry*, 31(7), 1031-1038.
- Malmer N. 1986. Vegetational gradients in relation to environmental conditions in northwestern European mires, *Canadian Journal of Botany*, 64, 375-383.
- Marin LE, Kratz TK, Bowser CJ. 1990. Spatial and temporal patterns in the hydrogeochemistry of a poor fen in northern Wisconsin. *Biogeochemistry* 11:63–76.
- McCree KJ. 1981. Photosynthetically active radiation. *Encyclopedia of Plant Physiology* 12(A). Springer-Verlag, Berlin.
- Mcdowell WH, Wood T. 1984. Podzolization: soil processes control dissolved organic carbon concentrations in stream water. *Soil Science*, 137(1), 23-32.

- McDowell WH, Fisher SG. 1976. Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. – *Ecology* 57: 561 –569.
- McKnight D, Thurman EM, Wershaw R, Hemond H, Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts, *Ecology*, 66, 1339-1352, 1985.
- McNeil P, Waddington JM. 2003. Moisture controls on *Sphagnum* growth and CO₂ exchange on a cutover bog. *Journal of Applied Ecology* 40(2):354-367.
- Michalzik B, Matzner E. 1999. Fluxes and dynamics of dissolved organic nitrogen and carbon in a spruce (*Picea abies* Karst.) forest ecosystem. *Eur. J. Soil Sci*, 50, 579-590.
- Mitas L, Mitasova H. 1988. General Variational Approach to the Interpolation Problem. *Comput. Math. Applic.* Vol. 16. No. 12. pp. 983–992. Great Britain.
- Moore PD. 2002. The future of cool temperate bogs. *Environ Conserv* 29:3–20.
- Moore T, Basiliko N. 2006. Decomposition, In *Boreal Peatland Ecosystems*, Wieder, R.K., Vitt, D.H. (eds.), *Ecological Studies* Vol. 188, Springer-Verlag, Berlin, pp. 126-143.
- Moore TR, Dalva M. 1993. The influence of temperature and water table position on carbon dioxide and methane emissions from laboratory columns of peatland soils, *Journal of Soil Science*, 44, 651-661.
- Moore TR, Dalva M. 2001. Some controls on the release of dissolved organic carbon by plant tissues and soils. *Soil Sci.* 166:38–47.
- Moore TR, Jackson RJ. 1989. Concentrations, fluxes and characteristics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. II. Larry River. *Water Resour. Res.* 25:1331–1339.
- Moore TR, Trofymow JA, Siltanen M, Prescott C. 2005. Patterns of decomposition and carbon, nitrogen and phosphorus dynamics of litter in upland forest and peatland sites, central Canada. *Can J For Res* 35:133–142

- Moore TR. 1987. Patterns of dissolved organic matter in subarctic fens. *Earth surface processes and landforms* 12(4):387-397.
- Moore TR. 1988. Dissolved Iron and Organic Matter in Northern Peatlands. *Soil Science* 145(1) 70-76.
- Moore TR. 1989. Concentrations, fluxes and characteristics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand. I. Maimai. *Water Resour. Res.* 25:1321-1330.
- Murray, KJ, Tenhunen JD, Nowak RS. 1993. Photoinhibition as a control on photosynthesis and production of *Sphagnum* mosses. *Oecologia* 96 200-207.
- Neufeld KR, Teretsky MR, Kane ES. 2010. Controls of vegetation, hydrology, and climate on DOC production in Alaskan peatlands. American geophysical union, fall meeting 2010, abstract #B23E-0427.
- Nichols DS, Brown JM. 1980. Evaporation from a sphagnum moss surface. *Journal of Hydrology* 48:289-302.
- Neff JC, Finlay JC, Zimov SA, Davydov SP, Carrasco JJ, Schuur EAG, Davydova AI. 2006. Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. *Geophys Res Lett* 33:L23401, doi:10.1029/2006GL028222
- Oliver BG, Thurman EM, Malcolm RL. The contribution of humic substances to the acidity of colored natural waters, *Geochim. Cosmochim. Acta*, 47, 2031-2036, 1983.
- Olson JS, Watts JS, Allison LJ. 1983. Carbon in live vegetation of major world ecosystems. ORNL-5862. Environmental sciences division, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Ovenden L. 1990. Peat accumulation in northern wetlands. *Quaternary research* 33(3):377-386

- Pastor J, Solin J, Bridgham SD, *et al.* 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. *Oikos*, 100, 380–386.
- Peterson RC. 1990. Effects of ecosystem changes (*e.g.* acid status) on formation and biotransformation of organic acids. In: Organic Acids in Aquatic Ecosystems. Report of the Dahlem Workshop on Organic Acids in Aquatic Ecosystems, Berlin 1989, May 7–12(eds Perdue EM, Gjessing ET), pp. 151–166. Wiley, Berlin.
- Petrone RM, Waddington JM, Price JS. 2001. Ecosystem scale evapotranspiration and net CO₂ exchange from a restored peatland. *Hydrological Processes* 15: 2839–2845.
- Prentice IC. 2001. The carbon cycle and atmospheric carbon. In: Houghton JT, Ding Y, Griggs DJ, Noguer M, Van Der Linden PJ, Dai X, Maskell K, Johnson CA. eds. *Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge: Cambridge University Press, 881p..
- Prescott CE, Maynard DG, Laiho R. 2000. Humus in northern forests: friend or foe? *Forest ecology and management* 133(1-2):23-36.
- Qualls RG, Haines BL. 1991. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil Sci. Soc. Am. J.* 55:1112–1123.
- Quinty F, Rochefort L. Peatland restoration guide. Université Laval, 1997.
- Riutta T, Laine J, Aurela M, Rinne J, Vesala T, Laurila T, Tuittila ES. 2007. Spatial variation in plant community functions regulates carbon gas dynamics in a boreal fen ecosystem. *Tellus B*, 59(5), 838-852.
- Rochefort L. 2000. New frontiers in bryology and lichenology–*Sphagnum* –a keystone genus in habitat restoration. *Bryologist* 103:503–508.
- Roulet NT, Lafleur PM, Richard PJH, Moore TR, Humphreys ER, Bubier J. 2007. Contemporary carbon balance and late Holocene carbon accumulation in a northern peatland, *Global Change Biology*, 12, 1–15

- Rydin H, McDonald, AJS. 1985. Tolerance of *Sphagnum* to water level. *Journal of Bryology*, 13,571–578.
- Saarnio S, Morro M, Shurpali NJ, Tuittila ES, Makila M, Alm J. 2007. Annual CO₂ and CH₄ fluxes of pristine boreal mires as a background for the lifecycle analyses of peat energy. *Boreal Environmental Research* 12: 101-113.
- Schipperges B, Rydin H. 1998. Response of photosynthesis of *Sphagnum* species from contrasting microhabitats to tissue water content and repeated desiccation. *New Phytologist* 140:677–684.
- Schulze ED, Prokuschkin A, Ameth A, Knorre N, Vaganov EA. 2002. Net ecosystem productivity and peat accumulation in a Siberian Aapa mire. *Tellus* 54B: 531-536.
- Shantz MA, Price JS. 2006. Characterization of surface storage and runoff patterns following peatland restoration, Quebec, Canada. *Hydrological processes* 20 3799-3814
- Sholkovitz ER, Copland D. 1982. The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion, *Geochim. Cosmochim. Acta*, 46, 393-410,
- Stevenson FJ. 1982. *Humus chemistry*. John Wiley and Sons, New York
- Stewart AJ, Wetzel RG. 1982. Influence of dissolved humic materials on carbon assimilation and alkaline phosphatase activity in natural algal-bacterial assemblages, *Freshwater Biol.*, 12:369- 380.
- Strack M, Tóth K, Bourbonniere R, Waddington JM. 2011. Dissolved organic carbon production and runoff quality following peatland extraction and restoration. *Ecological Engineering*, 37(12), 1998-2008.
- Strack M, Srivastava P. 2010. Seasonal dynamics of vegetation communities of a previously harvested minerotrophic peatland: using visual obstruction methods to estimate biomass and leaf area index, *Proceedings of the 44th Annual CMOS Congress/36th Annual Scientific Meeting of CGU May 31 to June 4, 2010*

- Strack M, Waddington JM, Bourbonniere RA, Buckton EL, Shaw K, Whittington P, Price JS. 2008. Effect of water table drawdown on peatland dissolved organic carbon export and dynamics. *Hydrological Processes*, 22(17), 3373-3385.
- Thurman EM. 1985. *Organic geochemistry of natural waters* (Vol. 2). Springer.
- Titus JE, Wagner DJ, Stephens MD. 1983. Contrasting water relations of photosynthesis for two *Sphagnum* mosses. *Ecology*, 64, 1109–1115.
- Titus JE, Wagner DJ. 1984. Carbon balance for two *Sphagnum* mosses: water balance resolves a physiological paradox. *Ecology* 65(6).
- Tuittila ES, Komulainen VM, Vasander H, Laine J. 1999. Restored cut-away peatland as a sink for atmospheric CO₂. *Oecologia* 120: 563–574.
- Tuittila ES, Vasander H, Laine J. 2004. Sensitivity of C sequestration in reintroduced *Sphagnum* to water-level variation in a cutaway peatland. *Restoration Ecology* 12:483–493.
- Turetsky MR, Crow SE, Evans RJ, Vitt DH, Wieder RK. 2008. Trade-offs in resource allocation among moss species control decomposition in boreal peatlands. *Journal of ecology* 96(6):1297-1305.
- Urban NR, Bayley SE, Eisenreich SJ. 1989. Export of dissolved organic carbon and acidity from peatlands, *Water Resour. Res.*, 25(7), 1619–1628,
- Waddington JM, Griffis T J, Rouse WR. 1998. Northern Canadian wetlands: net ecosystem CO₂ exchange and climatic change. *Climatic Change*, 40(2), 267-275.
- Waddington JM, Price JS. 2000. Effect of peatland drainage, harvesting, and restoration on atmospheric water and carbon exchange. *Physical geography* 21(5): 433
- Waddington JM, Roulet NT. 1997. Groundwater flow and dissolved carbon movement in a boreal peatland, *Journal of Hydrology*, 191, 122-138

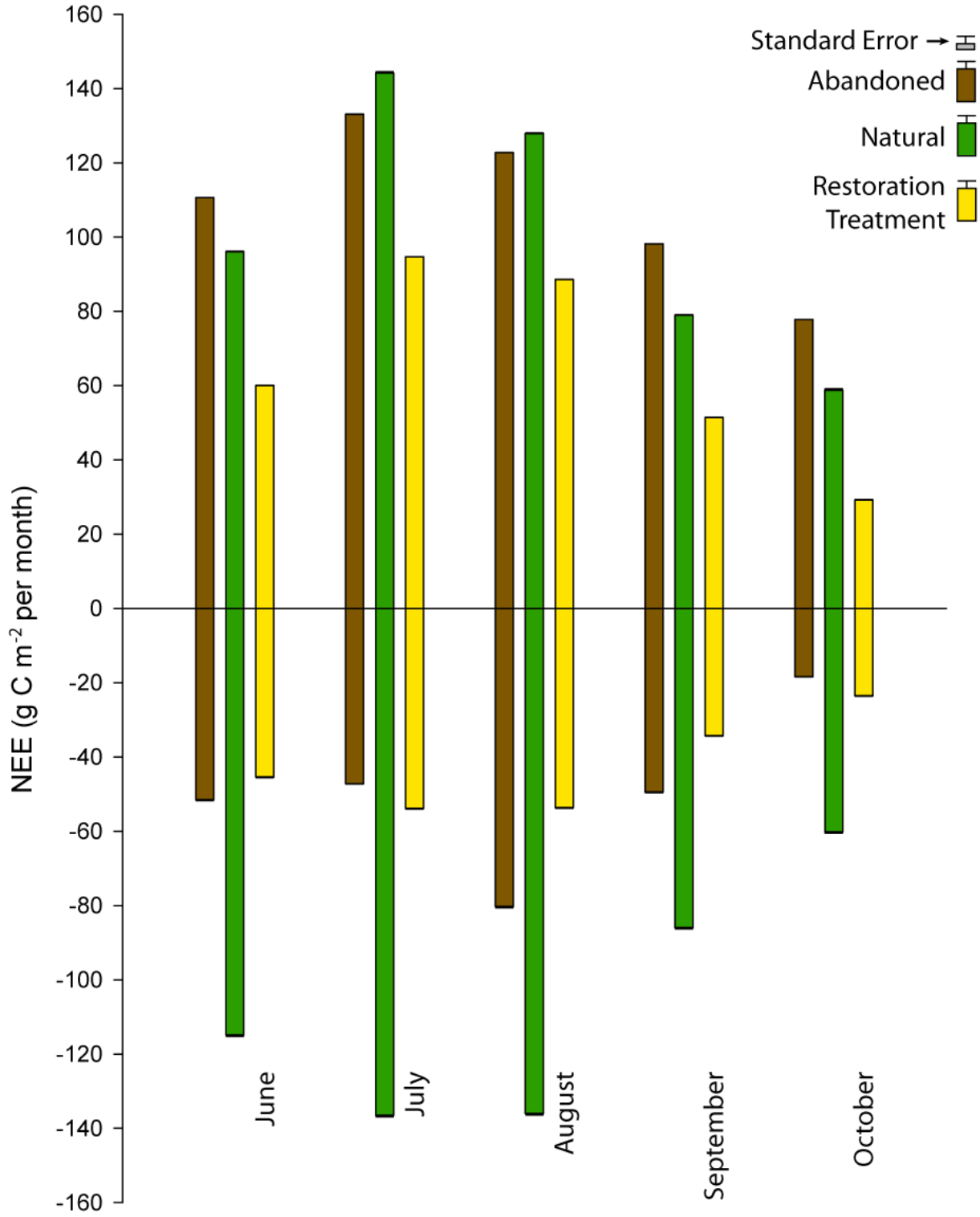
- Waddington JM, Strack M, Greenwood MJ. 2010. Toward restoring the net carbon sink function of degraded peatlands: Short-term response in CO₂ exchange to ecosystem-scale restoration. *Journal of Geophysical Research*, 115(G1), G01008.
- Waddington JM, Warner KD, Kennedy GW. 2002. Cutover peatlands: A persistent source of atmospheric CO₂. *Global biogeochemical cycles* 16 (1):2-7
- Waddington JM, Warner KD. 2001. Atmospheric CO₂ sequestration in restored mined peatlands. *Ecoscience* 8:359–368.
- Wallage Z, Holden J, McDonald AT. 2006. Drain blocking: an effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. *Science of the total environment* 367(2-3):811-821.
- Wilson L, Wilson J, Holden J, Johnstone I, Armstrong A, Morris M. Ditch blocking, water chemistry and organic carbon flux: Evidence that blanket bog restoration reduces erosion and fluvial carbon loss. *Science of the total environment* 409(11):2010-2018.
- Worrall F, Gibson HS, Burt TP. 2007. Modelling the impact of drainage and drain-blocking on dissolved organic carbon release from peatlands, *Journal of Hydrology* 338(1-2) 15-27.
- Wright HE, Coffin BA, Aaseng NE. (eds) 1992. *The patterned peatlands of Minnesota*. – Univ. of Minnesota Press.
- Verhoff FH, Melfi DA, Yaksich SM. 1980. River nutrient and chemical transport estimation. *Journal of the Environmental Engineering Division*, 106(3), 591-608.
- Yli-Patäys M, Laine J, Vasander H, Tuittila ES. Carbon gas exchange of a revegetated cut-away peatland five decades after abandonment. *Boreal environment research* 12(2): 177-190.

- Zech W, Sensei N, Guggenberger G, Kaiser K, Lehmann J, Miano TM, Miltner A, Schroth G. 1997. Factors controlling humification and mineralization of soil organic matter in the tropics. *Geoderma* 79:117-161.
- Zhao FJ, Wu J, McGrath SP. 1996. Soil organic sulphur and its turnover. In: Humic substances in terrestrial ecosystems. Ed. Piccolo A. Elsevier. Amsterdam.
- Zoltai SC, Pollett FC. 1983. Wetlands in Canada: their classifications, distribution and use. In: Gore AJP. ed. 1983. *Mires: Swamp, Bog, Fen and Moor* vol. B, Elsevier, Amsterdam.
- Zsolnay A. 1996. Dissolved humus in soil waters. *Humic substances in terrestrial ecosystems*, 171-223.

Appendix A:

Site	Water Table (cm)		Temperature (°C)		Vegetation Biomass	
	Max	Min	Max	Min	Max	Min
C10A	-24.1	-58.0	23.40	5.20	44.93	12.22
C10B	-33.1	-59.5	25.80	3.90	9.47	1.10
C10C	-30.2	-71.0	23.10	3.30	34.44	14.59
C11A	-45.2	-65.5	26.70	2.00	33.42	10.95
C11B	-25.6	-59.5	28.90	3.50	6.27	0.52
C11C	-41.6	-57.0	26.30	2.20	3.87	0.13
D2.5	19.8	-30.0	25.10	7.40	12.09	4.69
D5.5	9.9	-40.1	24.50	4.40	39.14	12.67
D6.5	19.0	-63.8	23.70	4.50	19.45	0.89
M14	-11.0	-44.7	24.00	14.10	12.26	4.66
M23	12.0	-22.0	31.70	15.10	12.26	4.66
M48	21.0	-16.0	26.30	9.40	12.26	4.66
N10A	-11.4	-28.0	22.30	10.60	48.16	44.05
N10B	-11.4	-35.4	25.80	11.40	48.16	44.05
N4A	3.5	-18.4	20.40	4.50	38.14	12.40
N4B	-7.0	-19.5	22.90	9.20	7.02	3.61
N8A	-2.6	-20.3	24.20	5.70	31.11	12.49
N8B	-16.9	-20.9	19.00	1.80	16.86	9.54
NSA	-3.2	-41.0	18.10	6.40	7.25	1.98
NSB	-10.8	-59.0	22.20	5.60	7.25	1.98
R1	-7.4	-44.0	25.10	1.30	15.39	4.98
R2A	18.7	-33.3	23.90	2.50	35.47	11.24
R2B	-4.6	-46.6	25.60	3.40	34.02	4.93
R3	-3.0	-62.4	23.30	6.20	9.48	3.66
R4A	-1.8	-68.9	22.80	1.00	46.91	7.00
R4B	-1.4	-37.5	21.80	2.30	31.59	9.89
R5	-6.0	-47.0	23.90	4.60	23.37	12.21
R6A	0.9	-50.0	22.30	4.80	16.75	10.60
R6B	0.9	-55.4	27.10	6.20	42.96	12.13
R6C	-6.3	-53.0	26.10	4.00	26.07	5.88
R7B	-2.8	-49.0	24.00	2.00	24.02	15.66
R7C	-6.4	-54.0	20.30	6.10	21.94	2.21
R8A	-9.6	-71.1	20.70	4.60	33.68	12.19
R8B	5.9	-52.4	24.30	5.50	18.68	2.15

Appendix B



Appendix C

Comparing the three sites based on the environmental variables of: Biomass, Soil temperature at 5cm depth, and Water table depth below ground level.

Biomass	Min	Mean	SD	Max
Abandoned	0.1	15.3	11.8	44.8
Restored	2.2	16.9	8.7	46.9
Natural	2.0	17.5	14.9	48.2

Temperature	Min	Mean	SD	Max
Abandoned	2.7	14.6	7.2	28.1
Restored	1.6	13.8	6.5	36.4
Natural	0.4	14.1	5.6	23.8

Water Table	Min	Mean	SD	Max
Abandoned	-71.0	-46.9	9.6	-24.1
Restored	-75.2	-26.7	18.1	18.7
Natural	-59.0	-16.7	12.0	3.5

Appendix D

<i>R</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>air</i>	<i>soil</i>	<i>PAR</i>	<i>JD</i>	<i>Veg</i>
WT	-0.294	-0.463	0.0734	-0.531	-0.475	-0.18	0.447	-0.15
	2.71E-14	6.27E-35	0.0651	6.08E-48	4.79E-37	4.44E-06	8.47E-33	0.000138
	642	633	633	642	636	642	642	642
NEE		0.494	0.67	0.21	0.245	-0.489	-0.0745	0.194
		7.78E-44	1.75E-91	1.59E-08	4.75E-11	7.09E-44	0.0473	1.99E-07
		692	692	709	699	709	709	709
Rtot			-0.314	0.544	0.503	0.0871	-0.3	0.311
			2.6E-17	1.15E-54	3.79E-45	0.0218	7.57E-16	5.48E-17
			692	692	683	693	693	693
GEP				-0.233	-0.159	-0.61	0.172	-0.0588
				5.22E-10	3.13E-05	1.27E-71	5.68E-06	0.122
				692	682	692	692	692
air					0.745	0.383	-0.475	0.263
					1.4E-124	3.25E-26	4.14E-41	1.09E-12
					699	709	709	709
soil						0.189	-0.365	0.303
						4.84E-07	1.87E-23	2.52E-16
						700	700	700
PAR							-0.217	0.00505
							5.31E-09	0.893
							711	711
JD								0.081
								0.0308
								711

<i>N</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>air</i>	<i>soil</i>	<i>PAR</i>	<i>JD</i>	<i>Veg</i>
WT	-0.11 0.157 168	-0.347 4.01E-06 168	0.295 0.000106 168	-0.398 9.12E-08 168	-0.606 2.12E-17 160	0.0836 0.281 168	-0.227 0.00312 168	-0.182 0.0179 168
NEE		0.502 3.29E-16 232	0.305 2.19E-06 232	0.249 0.00013 232	0.253 0.000127 224	-0.483 5.85E-15 232	-0.138 0.036 232	0.266 0.000041 232
Rtot			-0.671 1.17E-31 232	0.59 3.91E-23 232	0.453 9.58E-13 224	0.0801 0.224 232	-0.214 0.00103 232	0.55 9.02E-20 232
GEP				-0.436 3.38E-12 232	-0.285 1.45E-05 224	-0.502 3.04E-16 232	0.118 0.0737 232	-0.378 2.72E-09 232
air					0.613 1.69E-24 224	0.268 0.000036 232	-0.369 6.94E-09 232	0.286 9.94E-06 232
soil						-0.095 0.156 224	0.0034 0.96 224	0.478 3.46E-14 224
PAR							-0.189 0.00244 256	-0.0317 0.613 256
JD								0.133 0.0329 256

<i>C</i>	<i>NEE</i>	<i>Rtot</i>	<i>GEP</i>	<i>air</i>	<i>soil</i>	<i>PAR</i>	<i>JD</i>	<i>Veg</i>
WT	0.112 0.0571 290	0.0257 0.67 278	0.073 0.225 278	-0.0577 0.327 290	-0.0674 0.277 262	-0.0977 0.0969 290	0.00612 0.917 290	-0.00776 0.895 290
NEE		0.486 2.4E-18 286	0.498 2.43E-19 286	0.0699 0.225 304	0.155 0.0101 276	-0.316 1.84E-08 304	0.0439 0.445 304	-0.0956 0.0963 304
Rtot			-0.516 7.5E-21 286	0.208 0.000394 286	0.309 3.95E-07 258	0.0544 0.359 286	-0.0849 0.152 286	0.15 0.0111 286
GEP				-0.142 0.0159 286	-0.171 0.00575 258	-0.358 4.44E-10 286	0.0915 0.123 286	-0.254 0.000014 286
air					0.835 5.8E-73 276	0.389 1.89E-12 304	-0.572 8.81E-28 304	0.0664 0.249 304
soil						0.163 0.00668 276	-0.608 2.44E-29 276	0.111 0.0659 276
PAR							-0.228 5.87E-05 304	-0.0613 0.286 304
JD								0.019 0.742 304

Appendix E

Collar	Total vegetation	Water	Litter	Anaphalis margaritacea	Betula papyrifera	Betula populifolia	Calamagrostis canadensis	Carex limosa	Carex oligosperma	Carex trisperma	Chamaedaphne caliculata	Drosera rotundifolia	Empetrum nigrum	Equisetum arvense	Eriophorum vaginatum	Lycopodium angustifolium	Hieracium pratense	Juncus effusus	Kalmia angustifolia	Kalmia polifolia	Larix laricina	Ledum groenlandicum	Maianthemum trifolium	Myrica anomala	Onoclea sensibilis	Picea mariana	Pohlia nutens
C10A	98			1										12			2										
C10B	45													2								1					
C10C	17																				1					15	
C11A	65																										
C11B	6													4													
C11C	6																					3					
D2.5	35						5				3																
D5.5	75						1																				
D6.5	60						5																				
M14	90	10					1		1																		
M23	25	75																									
M48	80	20						3																			
N10A	100										1	1										1	7	3		85	
N10B	100											1							3				2			80	
N4A	100										1	1			1						2	1	1	2		3	1
N4B	100										1	1			2							2	4	17			
N8A	100										2	1			3						5	3	2	1			
N8B	100										1	1	1		9				25		8	1	1	1		1	
NSA	100										1								3				12			5	
NSB	100									1									2				10				
R1	95		5								10	1										1	3				
R2B	85		5							1	1	1			10				1		1	2		1		8	1
R2A	80		20				3					1			30												1
R3	100										1	1			1							1					
R4A	99		25								1	1			15				1			5		1			

R4B	100	2		6		1		3	12		5
R5	100	2		2		2	1	1	6	1	1
R6A	99			1	1	7	4	1	7	1	
R6B	95		2	15	1	1	1	2	2	5	
R6C	97				1		5		2		1
R8A	95		6		1	1	3		1	6	1
R7B	80		2		1	1	4		1		
R7C	99				1	1	5			1	
R8B	82			3	3	2	3				1