ASSESSING DISSOLVED ORGANIC CARBON EXPORT FROM KOPUATAI BOG, NEW ZEALAND

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Abstract

Peatlands sequester carbon (C) through CO_2 uptake and, ultimately, storage as peat. Carbon is lost from peatlands though gaseous pathways (as CO_2 and CH_4) and water pathways as dissolved organic C (DOC), dissolved inorganic C (DIC), particulate organic C (POC) or dissolved CO_2 and CH_4. Many studies have shown that the loss of C through DOC export is an important component of the annual C budget, but there are very few published studies where atmospheric fluxes of CO_2 and CH_4 and waterborne fluxes of DOC are measured at the same time. Also, little is known about the spatial variations in DOC concentration within peatlands and the processes leading to the delivery of DOC into rivers.

The research described in this thesis focuses on understanding the ways in which vegetation, temperature, peat quality and hydrology interact to determine variability in DOC concentrations and export, both seasonally and spatially, at Kopuatai bog. DOC concentrations were measured at 14 sites across the bog for a year. At each site peat pore water was sampled from three different depths and represented three different vegetation types dominated by *Empodisma robustum* (jointed wire rush), *Leptospermum scoparium* (manuka) and *Sporadanthus ferrugineus*. There were no strong seasonal trends in DOC concentration, possibly due to the small seasonal range in temperatures. DOC concentrations varied spatially, with highest concentrations found under *L. scoparium* vegetation, likely due to differing chemical properties of plant materials leading to higher decomposition rates. DOC concentration did not vary significantly with depth.

DOC export was estimated using a water balance based approach where evaporation (E), precipitation (P) and change in storage were measured to determine water discharge (Q) from the eddy covariance (EC) footprint. Discharge was then multiplied by average DOC concentrations within the EC footprint to derive DOC export. This method had not been directly applied in the literature. It was estimated that 11.7 ± 0.82 g C m^{-2} of DOC was exported from the EC footprint from the year 1 February 2012 to 1 February 2013, which is at the lower end of the range when compared to literature values. DOC export had

strong seasonal variation with highest export during the winter due to high rainfall and lowest in summer due to low rainfall. A simple method to estimate DOC export was proposed using the strong correlations between DOC export and monthly *P* and *P–E*.

When annual DOC export was compared to annual net ecosystem exchange (NEE) at Kopuatai, DOC export was equivalent to only 6% of CO_2 sequestered in a year. This is in contrast to the literature where, on average, DOC export is often equal to around 25% of NEE. Preliminary analyses shows that NEE values are significantly higher at Kopuatai than NEE published for Northern Hemisphere peatlands and this is likely an effect of the dominance by vascular plants and the year-round growing conditions at Kopuatai.

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List of Abbreviations

The following list describes the various abbreviations used throughout the thesis.

AWL	Absolute water level
C	Carbon
C_{DOC}	DOC concentration
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
E	Evaporation
EC	Eddy covariance
ER	Ecosystem respiration
F_{DOC}	DOC flux/export
GPP	Gross primary production
H	Sensible heat
K	Hydraulic conductivity
LE	Latent heat
N	Nitrogen
NECB	Net ecosystem carbon balance
NEE	Net ecosystem exchange of CO_2
P	Phosphorus
P	Precipitation
POC	Particulate organic carbon
POM	Particulate organic matter
PSO	Peat surface oscillation
Q	Discharge
RWL	Relative water level
SD	Standard deviation
SE	Standard error
TOC	Total organic carbon
WT	Water table
Y	Specific yield
ΔAWL	Change in absolute water level
δC_{DOC}	Uncertainty of DOC concentration
δE	Uncertainty of evaporation
δF_{DOC}	Uncertainty of DOC export
δP	Uncertainty of precipitation
δQ	Uncertainty of discharge
ΔS	Change in storage
$\delta \Delta S$	Uncertainty of change in storage

Chapter One
Introduction

1.1 Peatlands and carbon

Peatland ecosystems are an important component of the global carbon (C) cycle, as they store large amounts of C. Although they cover only 3% of the land area, the amount of C stored in Northern Hemisphere peatlands is equivalent to one third of the world soil C pool (Gorham, 1991; Blodau, 2002; Holden, 2005). The ability of peatlands to sequester C over long time periods means that they play a major role in regulating atmospheric CO_2 concentrations. Recent modelling by Frolking and Roulet (2007) of northern peatlands over the Holocene suggests that the C stored in peatlands represents a present day cooling in global temperatures of up to –0.5 Wm^{-2}, when considering the impact of both CO_2 and CH_4.

Peatlands sequester C through CO_2 uptake and storage as peat and the long-term viability of peatlands is based on the ability to continue to store more C from the atmosphere than is lost via a number of different export pathways. Pathways for C exports from peatlands include gaseous pathways as CO_2 and CH_4 and water pathways as dissolved organic C (DOC), dissolved inorganic C (DIC), particulate organic C (POC) and dissolved CO_2 and CH_4 (Waddington & Roulet, 1997). Unfortunately, disturbance in the form of climate change, drainage, peat mining, fires and modification of peatlands can convert these areas into sources of carbon, meaning that more C is exported than stored (Holden, 2005). Changing climate or management of a peatland can alter hydrological processes by lowering water tables, and pathways for water movement below and across the peat surface will change as a result. As water storage and movement are important for C storage and export, these small-scale processes can have global impacts through enhanced terrestrial C release (Holden, 2005; Davidson & Janssens, 2006).

Research on C cycling through ecosystems is essential for local C budgets as well as global atmospheric greenhouse gas levels. While researchers have identified the range of export pathways and the different forms of C involved, there is a continuous need to improve measurement techniques and reduce levels of uncertainty in the overall C budget of peatlands (Billett *et al.*, 2010). There have been very few published examples of net ecosystem C balances (NECB) for peatland ecosystems, done over a number of years, where both atmospheric fluxes of CO_2 and CH_4 and waterborne fluxes of DOC are measured at the same time (Roulet *et al.*, 2007; Limpens *et al.*, 2008). However, many studies have shown that the loss of C through DOC export is an important component of the annual C budget (Waddington & Roulet, 1997; Fraser *et al.*, 2001b; Moore & Clarkson, 2007). The export of DOC and net ecosystem exchange (NEE) of CO_2 can be of similar size in a given year; therefore by not measuring DOC export it would not be known if the C budget was significantly different to zero (Roulet *et al.*, 2007).

Little is known about the spatial variations in DOC concentration within peatlands and the processes leading to the delivery of DOC into rivers. This is especially important as DOC can be mineralised into CO_2 resulting in greenhouse gas emissions (Thurman, 1985). There is an absence of research on DOC concentrations and chemistry in New Zealand wetlands with previous research focused on Northern Hemisphere wetlands. The research described in this thesis will focus on understanding the ways in which vegetation, temperature, peat quality and hydrology impact on DOC concentrations at Kopuatai bog, with the primary goal to determine the importance of the DOC export from Kopuatai bog in relation to NEE. This will form part of a C budget for a pristine wetland that can then be compared to degraded wetlands and will also lead to a greater understanding of peatland development and C accumulation.

1.2 New Zealand Peatlands

Raised peat bogs in northern New Zealand differ from raised bogs in the Northern Hemisphere in that they have developed under warmer and less uniform climatic conditions (Campbell, 1983). In northern New Zealand bogs, the vegetation is dominated by indigenous jointed rushes, called restiads, belonging to the Southern Hemisphere vascular plant family Restionaceae (Clarkson *et al.*, 2004a). The two main species are *Empodisma robustum* (jointed wire rush), the primary peat former, and *Sporadanthus ferrugineus* (Clarkson *et al.*, 2004a; Wagstaff &

Clarkson, 2012). This dominance of vascular plants sets New Zealand bogs apart from most other raised bogs in the world where peat formation is dominated by mosses. The dominance of vascular plants allows a much greater influence of plant physiological controls on water loss via transpiration (Campbell & Jackson, 2004). This allows bogs to form in areas of high seasonal water deficit where bogs typically would not exist (Clarkson, 2002). The effect of vascular plants on the C budget is not yet known, and is the subject of on-going research to which this thesis will contribute.

Since 1850 approximately 90% of the wetland extent in New Zealand has been lost. Most of this loss has been due to drainage and development for agriculture and urban development (Sorrell *et al.,* 2004). *Empodisma-Sporadanthus* bogs have been severely reduced in extent and the remaining restiad bogs are now confined to the Waikato between latitudes 37°S and 38°S (Clarkson *et al.,* 2004a). *S. ferrugineus* is now nationally vulnerable and confined to three Waikato peat bogs including Torohape and Kopuatai in the Hauraki Depression and at Moanatuatua in the Hamilton Basin. A few plants have also been recorded at Opuatia in the Huntly Basin (de Lange *et al.*, 1999).

1.3 Kopuatai Bog

Restiad bogs used to cover large areas of the Waikato and Hauraki Plains in the northern North Island and this is evident by looking at the occurrence of peat soil (Shearer, 1997). It is estimated that in the 1840s there was 110,000 ha of wetland that covered the lower Waikato area and Hauraki Plains (Clarkson, 2002). Over the past century approximately 75% of the peatlands across the Waikato and Hauraki Plains have been drained and converted for agricultural purposes. At present, the remaining area of wetlands is approximately 32,000 ha[1].

At approximately 10,200 ha[2] in area, Kopuatai is the largest raised bog left in New Zealand and the remaining central portion of the bog is essentially

[1] *What wetlands have we got?* Waikato Regional Council website: http://www.waikatoregion.govt.nz/Environment/Natural-resources/Water/Freshwater-wetlands/What-wetlands-have-we-got/, 10/01/13.

[2] *Kopuatai Peat Dome.* Department of Conservation website: http://www.doc.govt.nz/conservation/land-and-freshwater/wetlands/wetlands-by-region/waikato/kopuatai-peat-dome/, 10/10/12.

unmodified (Irving *et al.*, 1984; Campbell & Williamson, 1997). It is also the last large lowland restiad bog in New Zealand which still retains its native vegetation (Irving *et al.*, 1984). Kopuatai peat bog along with the Whangamarino wetland complex make up more than half of the wetland area left in the Waikato region (Clarkson, 2002).

Kopuatai was listed as a wetland of international importance under the Ramsar Convention on 4 December 1989 (Cromarty & Scott, 1995). The site is of considerable conservation value because it supports a diverse range of plants unique to New Zealand. Apart from *S. ferrugineus*, other threatened plant species include the clubmoss *Lycopodium serpentinum*, the fern *Cyclosorus interruptus*, a floating bladderwort *Utricularia australis* and the orchid *Calochilus robertsonii* (Kelleher, 2004).

Kopuatai is also home to a number of important fish species such as the endemic black mudfish (*Neochanna diversus*). Other fish there include the longfin (*Anguilla dieffenbachia*) and shortfin (*Anguilla australis*) eels. These are likely to be the only fish to be found in the peat bog whereas the rivers and mineralised fringe contain various native and exotic fish species (Kelleher, 2004).

Fifty four species of birds have been recorded at Kopuatai and of these 27 are protected, 17 unprotected and 10 are game birds. The threatened native and endemic species include the Australian bittern (*Botaurua poiciloptilus*), the North Island fernbird (*Bowdleria punctata vealeae*), banded rail (*Rallus philippensis assimillis*), marsh crake (*Porzana pusilla affinis*) and spotless crake (*Porzana tabuensis plumbea*) (Kelleher, 2004).

1.4 Thesis Objectives

The purpose of this research is to estimate DOC export from Kopuatai bog and to determine the spatial and seasonal variability of DOC concentrations within the bog and its key drivers. This study will contribute to research that is focused on producing a NECB for Kopuatai bog.

The main objectives of this study are to:

- Determine the spatial and seasonal variations in DOC concentration and drivers of DOC export within Kopuatai.
- Measure the DOC export from a representative part of Kopuatai bog over a one year period through estimating runoff from the bog surface using measured water balance components: precipitation and evaporation.
- Propose a practical way to monitor DOC exports from Kopuatai over the long term (e.g. which hydrological and DOC measurements are most useful for estimating the subsurface DOC export out of the bog).

This project is part of a larger wetland restoration project funded by Landcare Research with the purpose of informing wetland restoration efforts and determining wetland sensitivity to environmental change.

1.5 Thesis Outline

Chapter two is a review of relevant wetland research and literature which will serve as a background to this thesis. It focuses on hydrological processes within peatlands and C exchange. The review then describes C budgets and reports literature values of DOC concentration and export from peatlands.

Chapter three describes the research location, and the developmental history and present-day vegetation at Kopuatai. It also reviews the literature that is based on research at Kopuatai bog and relevant to the objectives of this thesis.

The results of this research are presented in three chapters. Chapter four compares peat physical and chemical characteristics across sites along with the vegetation composition at each site. Chapter five consists of a study of variations in DOC concentrations across different sites and vegetation across a one-year period. This chapter seeks to understand the spatial and seasonal drivers of variability in DOC concentration throughout the bog. In chapter six, the hydrological monitoring network across the site is described and the methods that were undertaken to determine DOC export from Kopuatai bog are explained.

Results presented include a water balance of the bog and annual DOC export totals, along with a discussion.

The final chapter, seven, integrates the main findings of this research and compares annual DOC export to the net ecosystem exchange of CO_2. The method used to obtain DOC export in this study is compared to methods from the literature.

Chapter Two
Literature review

2.1 Introduction

This chapter commences with a brief introduction to wetlands before reviewing the relevant literature on peatlands, focusing on the physical properties of peat and the hydrological processes that occur within peatlands. The next section describes how peatlands represent a long term net sink of atmospheric CO_2 and play an important role in the global C cycle. Peatland C cycling is discussed followed by the factors that influence decomposition of peat. The role of dissolved organic matter in the C budget of a peatland is discussed and methods for measuring dissolved organic carbon export are reviewed.

2.2 Wetland types

In New Zealand, the Resource Management Act (1991) defines wetlands as "permanently or intermittently wet areas, shallow water, and land water margins that support a natural ecosystem of plants and animals that are adapted to wet conditions". Wetlands in New Zealand can be subdivided based on broad hydrological and landform setting, salinity and temperature into nine hydrosystems. Of these, the four most important are estuarine, riverine, lacustrine and palustrine (Johnson & Gerbeaux, 2004).

Palustrine (or freshwater) wetlands form the focus of this study. Palustrine wetlands can be subdivided according to nutrient status which is linked to that of water supply. Along the nutrient spectrum, the three main types of wetland recognised are swamp, fen and bog ranging from high to very low nutrient availability (Gore, 1983; Campbell & Jackson, 2004). Wetlands change naturally over both short and long time scales. In the absence of major disturbance wetlands develop from swamps through to fens and bogs over several thousands of years in response to hydrological and nutrient changes (Clarkson, 2002). For example, a pond may fill up with sediment and develop into a swamp and be supplied by water from groundwater, runoff and rain. From this it may develop into a fen and finally a domed bog where water is supplied solely by rain. The development of peat will cause parts of the wetland to become progressively hydrologically isolated. Plant succession will occur as water and nutrient supplies and substrate change (Johnson & Gerbeaux, 2004) .

Bogs are nutrient poor (oligotrophic) and usually markedly acidic. Bog peat is poorly aerated and the water table is usually close to or at the peat surface and varies over a small range (Johnson & Gerbeaux, 2004). Raised bogs obtain water and nutrients solely from precipitation and are therefore termed ombrotrophic, although areas at the margins may be affected by runoff or groundwater (Gore, 1983). The margins of raised bogs that are groundwater fed are referred to as minerotrophic with a nutrient status of eutrophic to mesotrophic (Shearer, 1997).

The lack of nutrients in bogs constrains which vegetation grows where and how productive it is. Bogs are typically dominated by a small number of plant species capable of competing in these infertile ecosystems (Sorrell & Gerbeaux, 2004).

2.2.1 Wetlands in New Zealand

New Zealand ombrotrophic bogs are unique in their dominance by members of the vascular plant family the Restionaceae (Agnew *et al.*, 1993). Observations by Agnew *et al.* (1993) led them to believe that *Empodisma robustum*[3] is the key species in bog formation in New Zealand and Hodges and Rapson (2010) proposed it to be an "ecosystem engineer". *E. robustum* replaces the functional role of *Sphagnum* in boreal systems, in being the dominant peat former due to interactions between its morphology, the substrate and rainfall (Kuder *et al.*, 1998).

[3] *E. robustum* was previously classified as the species *E. minus* until July 2012 when it was reclassified by Wagstaff and Clarkson (2012) .

2.3 Peat physical characteristics

2.3.1 Formation of peat

Peat is a highly variable material and is formed from dead and partially decomposed plant material. The term 'peat' is used when the substrate has an organic matter content of 50% or more (Johnson & Gerbeaux, 2004). Peat accumulation occurs when the rate of production of organic matter by plants exceeds the rate of decomposition by bacteria and fungi (Clymo, 1983). Decomposition is reduced by the maintenance of a high water table leading to low oxygen levels and anaerobic conditions that decrease microbial activity. Low levels of nutrients and high acidity also contribute to the low rates of decomposition (Clymo, 1983; Blodau, 2002). However, the accumulation of peat can be very slow (Clymo, 1983), averaging 0.5 mm yr^{-1} (Gorham, 1991).

Successive generations of wetland plants grow upon this substrate and peat deposits many metres in thickness can accumulate (Campbell & Jackson, 2004). Organic material is added mostly to the top 10 cm of the surface, although vascular plants produce rhizomes and roots, and these can add material to as much as 2 m below the surface in exceptional cases. Decay may occur throughout the whole peat profile, with the highest rates of decay at the surface and much lower in the waterlogged part of the profile (Clymo, 1983).

The rate of decay of peat material is affected by temperature, water supply, oxygen supply, composition of the plant material, and nature of the microorganisms and invertebrates in the peat. These factors are not always independent, they can change with time and their effects may also interact (Clymo, 1983).

2.3.2 Bulk density

Peat properties are complicated by their vertical and lateral heterogeneity and therefore the influence of any one property is often variable. Bulk density for fresh *Sphagnum* peat near the surface is about 0.02 g cm^{-3} (Clymo, 1983). Properties of peat change with depth because at depth the peat has undergone greater amounts of decomposition and compaction. This results in decreasing pore size and permeability declines. As a result, below the surface, bulk density increases to about 0.1 g cm^{-3} (Clymo, 1983; Campbell & Jackson, 2004). Highly humified peats have a greater bulk density of about 0.12 to 0.15 g cm^{-3} but all peats typically have low bulk densities compared to mineral soils (0.5–1.8 g cm^{-3}) (Clymo, 1983).

2.3.3 Vertical structure in raised bogs

The domed form in a raised bog occurs when there is little confinement to the lateral expansion of the peatland and when there is differentiation between the more hydraulically conductive upper peat layer (acrotelm) and the lower peat layer with reduced hydraulic conductivity (catotelm) (Waddington & Roulet, 2000). This model of a two layered system has been developed to describe how peatlands function. The acrotelm has high hydraulic conductivity and a fluctuating water table. Within the acrotelm, the zone through which the water table fluctuates can be oxygenated at times allowing aerobic decomposition to occur. The catotelm is relatively inert and constitutes the permanently saturated main body of peat. As this zone is usually permanently lacking in oxygen, decomposition occurs only slowly. This model implies that most runoff production and nutrient transfer occurs in the acrotelm (Ingram, 1978). Due to the raised centre, drainage occurs as a lateral flow in the acrotelm from the centre to the margins of the bog (Waddington & Roulet, 2000).

2.4 Peatland hydrology

Hydrological processes are the most important factors controlling the establishment and maintenance of wetlands, by determining nutrient flows, water chemistry, plant assemblages, primary productivity and the build-up of organic matter (Campbell & Jackson, 2004).

2.4.1 Water movement in peat

Peat is the medium in which water is stored and transported through a peatland (Campbell & Jackson, 2004). Relatively undecomposed peats have high hydraulic conductivities, K, (about 10^{-3} to 10^{-5} m s^{-1}), and water flow through them follows Darcy's Law quite closely. In contrast, highly decomposed peat has a much lower K of around 10^{-7} m s^{-1} and water flow deviates from Darcy's Law (Clymo, 1983) Gas bubbles below the water table can also give rise to non-Darcian behaviour in peats (Carrera *et al.*, 2011).

During periods of heavy rain, water can flow vertically and then horizontally through layers of high conductance in the acrotelm of a bog but at times where the water table is very low, movement of water may be slow (Clymo, 1983).

2.4.2 The wetland water balance

Wetlands have water inputs from precipitation, groundwater and surface water inflows. Water outputs from wetlands occur as evaporation, groundwater and surface water outflows. Change in water storage occurs when water is stored in the peat or soil and can result in water table changes. Water is also stored in tissues of plants (Campbell & Jackson, 2004). These inputs and outputs lead to the water balance equation:

$$Input - output = change\ in\ storage \quad (2.1)$$

When terms are added this becomes:

$$(P + Q_{in} + G_{in}) - (E + Q_{out} + G_{out}) = \Delta S \quad (2.2)$$

Where P = precipitation, Q_{in} = surface water inflows, G_{in} = groundwater inflows, E = evaporation, Q_{out} = surface water outflows, G_{out} = groundwater outflows and ΔS = change in storage (Campbell & Jackson, 2004).

For the central parts of bogs, precipitation represents the only significant source of water so Q_{in} and G_{in} may be neglected (Figure 2.1). Evaporation includes water transpired by living plant tissues, evaporation of precipitation intercepted by the plant canopy, evaporation from open water and moist peat (Ingram, 1983; Campbell & Jackson, 2004). For bogs, water discharge occurs primarily as lateral seepage (Waddington & Roulet, 1997; Campbell & Jackson, 2004). Variation in water storage is usually indicated by changes in the water table position. This results in a simpler water balance equation:

$$P - (E + Q_{out}) = \Delta S \qquad 2.3$$

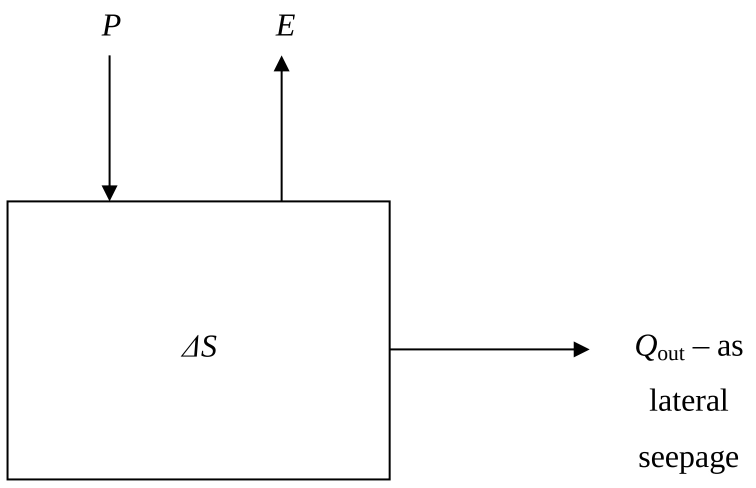

Figure 2.1: Water balance for a bog using terms from equation 2.3. *P* is precipitation, *E* is evaporation, Q_{out} is discharge out of the bog and ΔS is the change in storage. Figure redrawn from Campbell and Jackson (2004).

2.4.2.1 Specific yield

The specific yield (*Y*) is also known as aquifer yield and is commonly defined as the discharge of ground water which takes place when the water table is lowered through a unit distance (Ingram, 1983). As such it describes the magnitude of water table fluctuations in response to water storage changes in the saturated zone. *Y* diminishes rapidly with increasing humification, which is in turn closely correlated with increasing bulk density. As a result, dry periods when the water table gets particularly deep may result in smaller *Y* due to increasing decomposition resulting in smaller and less pore spaces for water to be stored (Ingram, 1983). According to Verry and Boelter (1978) fibric peat typically has a specific yield of greater than 45% and hemic peat has a *Y* of between 10% and 45% whereas sapric peat has a low *Y* of less than 10%. When *Y* is multiplied by the change in water table, ΔS of a bog can be calculated.

2.4.3 The peatland water table

The water table position is an important control on biogeochemical and ecological processes in peatlands. It affects decomposition processes along with greenhouse gas production and consumption. The water table position also controls rates of lateral seepage and evaporation and can also affect plant species composition (Fritz *et al.*, 2008).

2.4.3.1 Peat surface oscillation

The water table position can be defined in two ways, the water table position above an absolute elevation datum (absolute water level, AWL) and the water table depth below the surface (relative water level, RWL) (Figure 2.2). Although the difference between changes in AWL and RWL is assumed to be negligible in mineral aquifers, this is not the case with organic soils. When the water table drops in peat the substrate compresses because the peat matrix is no longer supported by pore water pressure. This increases effective stress in the dewatered and submerged peat layers. AWL fluctuations cause changes in the peat surface elevation, which in turn reduces water table fluctuations with respect to the surface, because the surface closely follows the movements of the water table (Fritz *et al.*, 2008). The changes in surface elevation reduce the range of RWL fluctuations (or thickness of the unsaturated zone), relative to the AWL fluctuations. The reversible change in surface elevation is called peatland surface oscillation (PSO) and is an important control on biogeochemical and ecological processes in peatlands (Fritz *et al.*, 2008).

Floating peatlands display the smallest RWL fluctuations because surface elevation follows AWL closely (Fritz *et al.*, 2008). PSO is spatially variable within a peatland. Surface elevation changes are generally greater at the centre of a bog than the margin due to larger peat thickness in the centre. Increasing bulk density also coincides with decreases in surface elevation changes. Fritz *et al.* (2008) found that vegetation types (e.g. the percentage cover of *E. robustum*), peat thickness and bulk density together explained 73% of the spatial variability in PSO at Opuatia wetland.

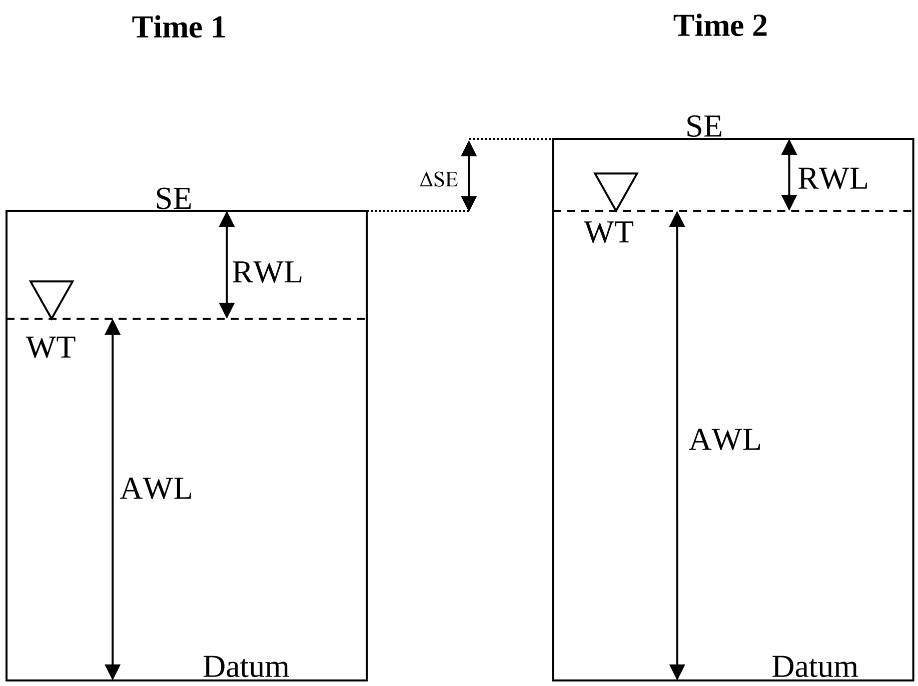

Figure 2.2: Definition diagram for peat surface oscillation. Peat thickness increases by a change in surface elevation (ΔSE) after a rain event from time 1 to time 2 with a corresponding increase in absolute water level (AWL) and an unequal decrease in relative (RWL). Figure redrawn from Fritz *et al.* (2008).

2.4.3.2 Decomposition

Mechanisms such as the effect of low oxygen availability on microbes, low pH, low nutrient supply and low temperatures are often cited to account for the slow decomposition rates in peatlands (Freeman *et al.*, 2001a). Peat accumulation tends to decrease when water tables are well below the surface (Blodau, 2002). This occurs because the oxygen availability in the upper peat layers increases and this leads to increased aerobic decomposition of organic matter and higher carbon dioxide (CO_2) emissions (Aerts & Ludwig, 1997).

Freeman *et al.* (2001a) found that the activity of the enzyme phenol oxidase is severely constrained in anaerobic environments as it requires bimolecular oxygen. Also, the activity of all major biodegradative hydrolase enzymes is depressed in peatlands even though they normally retain high activity in other anaerobic environments. The low rate of biodegradation in peatlands is due to oxygen constraints on phenol oxidase, which allow phenolic material to accumulate and inhibits the hydrolase enzymes that are responsible for degrading organic material. Lower water tables, that are associated with increased aeration, cause a drop in phenolic concentration increasing hydrolase enzyme activity and therefore resulting in increased decomposition of peat (Freeman *et al.*, 2001a). The loss of phenolic compounds means that the decomposition can continue even after the water table has risen again. This is because the enzymes are switched on by the water table draw down but not switched off as the water table rises again. As a result increased peat decomposition can occur. Hydrolases are not inhibited again after the water table recovers until phenolic compounds re-accumulate and this results in additional peat decomposition and DOC production (Freeman *et al.*, 2001a).

2.4.3.3 Greenhouse gas production and consumption

Boreal and subarctic peatlands only cover less than 3% of the Earth's land surface but store between 270 and 370 Tg C (1 Tg=10^{12} g) as peat. These deposits are the result of peatlands acting as sinks for atmospheric CO_2 via photosynthesis (Limpens *et al.*, 2008). Recent modelling suggests that the atmospheric C stored in peat has resulted in a present day cooling of up to $-0.5 Wm^{-2}$ (Frolking & Roulet, 2007). Carbon not held in the biomass or stored in peat may be returned to the atmosphere as CO_2. Anaerobic conditions within peatlands are also highly favourable for the production of methane (CH_4) and nitrous oxide (N_2O) (Clymo, 1983).

Carbon dioxide

The emission of CO_2 from the peat surface to the atmosphere is the result of plant respiration and mineralisation of organic C within the peat body. Mineralisation rates depend on the availability of oxygen associated with the depth of the water table and soil temperature. Other factors also include microbial activity, soil temperature, vegetation type and chemical characteristics of the peat (Moore *et al.*, 1998; Blodau, 2002). Carbon dioxide emission rates increase with increasing water table fluctuations (Blodau, 2002). The ratio of the production of CO_2, from peat decomposition under aerobic versus anaerobic conditions, fall into the range of 2.5:1 to 6:1 (Moore *et al.*, 1998).

Methane

The CH_4 flux from peatlands to the atmosphere is dependent on the balance between the capacity of methanogenic bacteria to produce CH_4 and methanotrophic bacteria to consume it. Methane production depends indirectly on the position of redox boundaries associated with the water table (Blodau, 2002). The development of anaerobic conditions is essential for CH_4 production by methanogenesis as methanogens are obligate anaerobes (Moore *et al.*, 1998; Blodau, 2002). Methanotrophic bacteria in the aerobic peat re-oxidise methane to CO_2 and are dependent on both oxygen and CH_4 as substrates, so the re-oxidation of methane is mostly located within 25 cm of the water table (Blodau, 2002).

In wetlands, methanogens can oxidise up to 90% of the methane produced in the anaerobic zone before it reaches the atmosphere. The depth of the water table controls the volume of anaerobic peat and therefore the rate of methane production. The water table depth also controls the thickness of the aerobic zone and therefore the percentage of methane that is oxidised before it reaches the atmosphere (Schimel & Holland, 2004).

Nitrous Oxide

Nitrous oxide is a side product of nitrification and denitrification. Oxygen availability is the major control on both these processes and in peatlands this relies on the location of the water table. Aerts and Ludwig (1997) found that in a eutrophic peatland soil (e.g. where fertiliser has been added) the lowering of the water table resulted in increased N_2O emission.

Nitrogen rich peat soils with low C:N ratio have much larger emissions of N_2O than peat soils with a high C:N ratio that are nitrogen poor (Kasimir-Klemedtsson *et al.*, 1997). Martikainen *et al.* (1995) studied the N_2O emissions from pristine and drained fens and bogs. While there were no N_2O emissions from pristine fens and bogs the emissions highly increased in the drained fen suggesting that the magnitude of N_2O emissions is generally dependent of the supply of N substrate. This also suggests that only nutrient rich sites will become potential sources of N_2O with the lowering of the water table.

2.4.4 Anthropogenic impacts on hydrology of wetlands

Human modification of wetlands includes drainage, flooding, eutrophication through nutrient addition, burning, sedimentation and the introduction of weeds and pests (Sorrell *et al.*, 2004). Peat is vulnerable to large volume changes when drained due to shrinkage and oxidation and the surface layers may dry out resulting in less permeable and hydrophobic surface peat. Colonization by trees and shrubs usually follows drainage unless the drained area is used for agriculture. In extreme cases of peatland drainage, erosion of the peat mass may set in (Tallis, 1983).

Because of their relatively shallow water tables, wetlands are highly sensitive to changes in nutrient inputs due to land management practices. While larger and deeper water bodies such as lakes may have some resilience to disturbance, wetlands can change rapidly in response to hydrological and nutrient changes (Tallis, 1983). Disturbance factors such as drainage, nutrient inputs and sedimentation accelerate the drying and infilling processes that remove wetlands from the landscape and changes the vegetation and animals associated with the ecosystem (Tallis, 1983; Sorrell & Gerbeaux, 2004). Modifying the natural hydrological regime of a wetland can lead to changes in vegetation and peat composition over time. For example, Blyth *et al.* (2012) found that the implementation of a flood control scheme at Whangamarino wetland, New Zealand, led to increasing inundation and water table fluctuations, along with greater nutrient inputs, which have altered the vegetation composition of the wetland.

2.5 Carbon balance of peatlands

Measurements of C fluxes at the ecosystem scale are needed to determine the rates and controls on C sequestration. Unmodified peatlands have slow decomposition rates due to their saturated and anoxic conditions and this leads to substantial C storage (Fraser *et al.*, 2001b). Carbon dioxide is taken up by plants during photosynthesis (gross primary production, GPP) and is released by plant leaves and roots (autotrophic respiration) and as microbes in the soil consume organic material (heterotrophic respiration). The sum of the respiration losses is called ecosystem respiration (ER). The difference between GPP and ER is the net ecosystem CO_2 exchange (NEE) and this represents the amount of CO_2 taken up or released by the ecosystem (Lafleur, 2009).

The net ecosystem carbon balance (NECB) of a peatland (Figure 2.3) with no surface or subsurface water inputs (e.g. an ombrotrophic bog such as Kopuatai bog) is the difference between the uptake of C through both GPP and the input of organic and inorganic C as part of rainwater, and the losses of C through ecosystem respiration, CH_4 emission and waterborne C fluxes (Fraser *et al.*, 2001b; Worrall *et al.*, 2003b). The waterborne flux of C from a peatland can occur in a number of forms such as dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic carbon (DIC) and dissolved gaseous CH_4 and CO_2. POC includes the colloidal and suspended forms of C. DIC refers to carbon from carbonate sources such as HCO_3^- and CO_3^{2-}. In addition, dissolved gaseous CO_2 is a form of DIC and some studies include dissolved CO_2 under DIC and some studies keep the gaseous forms of C separate (Worrall *et al.*, 2003b; Dinsmore *et al.*, 2010).

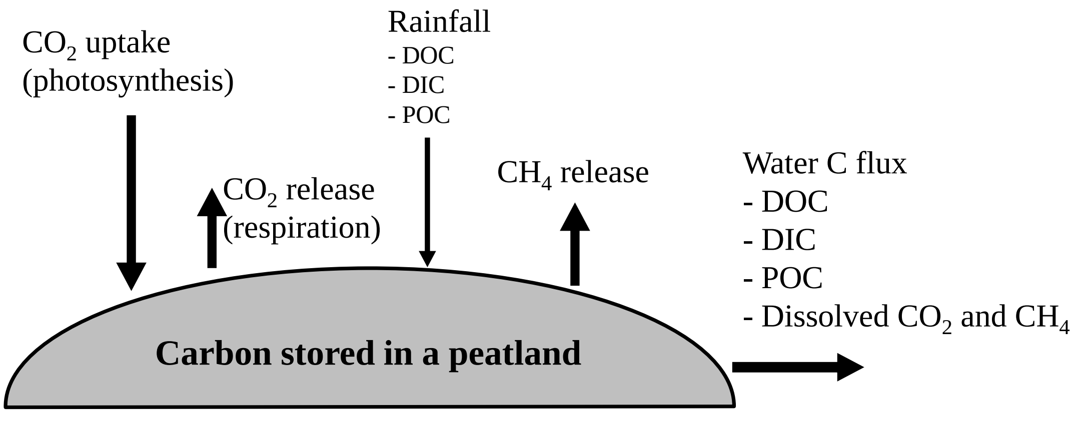

Figure 2.3: Schematic diagram of the carbon fluxes in and out of a peat bog forming a net ecosystem carbon balance (NECB). Figure adapted from Hope *et al.* (2001) and Worrall *et al.* (2003b).

2.6 Dissolved organic carbon

2.6.1 What is DOC?

Dissolved organic carbon is defined as organic compounds in water that can pass through a 0.45 µm filter and is derived from the decomposition of plant litter, root exudates, microbial biomass or soil organic matter (Roulet & Moore, 2006; Koehler *et al.*, 2009). Microbes can only take up small dissolved organic molecules with molecular weights below about 600 g mol^{-1} therefore carbon mineralisation and CH_4 production processes depend in the production of DOC (Blodau, 2002; Worrall *et al*., 2006). DOC exerts significant control over productivity, biogeochemical cycles and attenuation of visible and UV radiation in water bodies (Pastor *et al.*, 2003). The impact of DOC on the quality of water supplies is of concern in some parts of the world. DOC can impact on water quality in terms of colour, taste, safety and aesthetic values of stream water (Holden, 2005; Limpens *et al.*, 2008).

2.6.2 Global trends in DOC (and concerns)

Unmodified bogs are long-term C sinks but there is evidence of increasing C turnover in these environments that could mean peatlands switch from being a net sink of C to a net source (Worrall *et al.*, 2006). Northern Hemisphere peatlands contain 20–30% of the world's soil C stock which is equivalent of over 60% of the atmospheric C pool (Freeman *et al.*, 2001a). Peatlands release C through sub-surface pathways as DOC and there have been observations of rapidly rising DOC concentrations in rivers draining peatlands, along with other catchments, across Europe and North America, over the last two decades (Worrall *et al.*, 2003a; Freeman *et al.*, 2004b; Evans *et al.*, 2006; Clark *et al.*, 2010).

Worrall *et al.* (2004) have shown that, out of 198 catchments studied in the UK, 77% showed a significant DOC concentration increase while none showed a significant decrease. Worrall *et al.* (2003b) states that if increases in DOC concentration continue in this manner, upland peat bogs in the UK will become net sources of C within 25 years. The increase in DOC in surface waters has raised concerns about drinking water treatment and the production of carcinogenic byproducts and has also raised the further possibility that climate change may be causing degradation of soil C stores (Freeman *et al.*, 2001b; Clark *et al.*, 2010). This increased loss via fluvial pathways is indicative of either increased turnover of C within the peatlands or increasing loss of C from peatlands (Worrall *et al.*, 2006).

The reasons behind the rise in DOC concentrations has been debated (Freeman *et al.*, 2001b; Evans *et al.*, 2006; Roulet & Moore, 2006; Clark *et al.*, 2010; Evans *et al.*, 2012). Potential causal mechanisms have been put forward and include increased rates of decomposition of organic matter due to changes in moisture and temperature, and changes in hydrological pathways that have occurred in northern Europe and North America over the last 20 years. Freeman *et al.* (2001b) argues that the 65% increase in DOC concentration in freshwater draining upland catchments in the UK over the past 12 years may be driven by rising temperatures.

Anthropogenic inputs of sulphur (S) into the atmosphere increased during the industrial revolution in the 19th century resulting in acid deposition onto peatland ecosystems (Evans *et al.*, 2000). Emissions have fallen in recent years and Evans *et al.* (2006) and (2012) suggested that decreased S deposition could be a causal mechanism as S decreases the mobilization of DOC in soils. The decrease in sulphur dioxide (SO_2) causes an increase in pH and this results in higher levels of microbial activity resulting in increased decomposition and DOC formation (Evans *et al.*, 2006). Decreasing S deposition may be returning surface waters in the Northern Hemisphere to a ‘natural’, high DOC condition (Evans *et al.*, 2012). In some locations sea salt deposition is thought to be responsible for declining DOC concentrations (Clark *et al.*, 2010).

Roulet and Moore (2006) suggested that increasing deposition of nitrates is causing enhanced productivity and increased litter production and this can influence the rate of carbon mineralization in litter and soil. Freeman *et al.* (2004b) suggested that increasing DOC concentrations are possibly caused by stimulation of plant productivity due to elevated atmospheric CO_2. Their research has shown that DOC increases were induced by increased GPP and DOC exudation from roots of plants. Other reasons for increased DOC concentrations in water draining peatlands has also been explained by changes in discharge, land use and management (Fenner *et al.*, 2009).

2.6.3 DOC chemistry

DOC dynamics in peatlands are poorly understood because DOC contains several different groups of organic compounds, ranging from short-chain acids to large molecules such as fulvic and humic acids. These are derived from different sources and differ in bioavailability and ecological function (Thurman, 1985; Blodau, 2002). The lifetime of an organic molecule that makes up DOC may be very short. DOC with low molecular weight compounds (labile DOC) are readily degradable and turn over rapidly and are mineralised to CO_2. For example, simple sugars may have lifetimes of only a few minutes to a few hours. The biodegradability of DOC has been shown to decrease with an increasing presence of aromatic structures. Refractory humic substances may have lifetimes of months or longer (Thurman, 1985; Worrall *et al.*, 2006).

Humic substances contribute 50–90% of DOC concentrations in coloured waters within wetlands. Other substances which make up DOC are hydrophilic acids, carbohydrates, carboxylic acids, amino acids and hydrocarbons. Humic substances can be divided into fulvic and humic acid. Humic acid is the fraction that precipitates at pH of 2.0 or less and fulvic acid is that fraction that remains in solution at pH 2.0 or less. Water from wetlands is usually highest in fulvic acid (Thurman, 1985). Humic substances in bogs are the most aromatic of aquatic humic substances and comprise the more complex part of DOC, taking a much longer time to degrade (from weeks to months) compared with hours for the labile simple organic compounds (Thurman, 1985).

Humic substances impose their chemistry upon the water and commonly buffer pH and transport trace metals, such as iron or aluminium. Humic substances are also important in water quality. For instance, humic substances cause the formation of potentially carcinogenic trihalomethanes in water upon chlorination, complex trace metals and organic compounds, and produce protons for chemical weathering in natural environments (Thurman, 1985; Limpens *et al.*, 2008). There are at least five geochemical processes that affect DOC in water: sorption, precipitation, volatilisation or evaporation, oxidation or reduction (both chemical and biochemical) and complexation of metal ions. Humic substances perform various roles in aquatic environments, they include surfactant character (causing foaming), binding of pesticides, trihalomethane potential, and flocculation. All these processes may have an adverse effect on water quality, taste, odour, colour and toxicity (Thurman, 1985).

2.7 DOC concentration

Swamps, marshes and bogs have average concentrations of DOC ranging from 10 to 60 mg l^{-1} (also referred to as mg C l^{-1}) and their water chemistry is dominated by organic compounds. In contrast, interstitial waters of mineral soil have a range of DOC concentrations from 2 to 30 mg l^{-1} (Thurman, 1985).

Bogs have the greatest DOC concentrations of all wetland types. DOC concentrations can range from 3 to 10 mg l^{-1} for transitional bogs or fens to greater than 30 mg l^{-1} for ombrotrophic bogs (Thurman, 1985). Average DOC concentrations are usually between 20 and 60 mg l^{-1} in northern peatlands (Blodau, 2002). The high DOC concentrations within peatlands results from the build-up of organic acids in the water from the decomposition and leaching of plant material (Thurman, 1985).

2.7.1 Drivers of DOC variability in peat pore water

Influences on DOC concentration within peat pore water include temperature, vegetation type, water table regime, disturbance, and atmospheric deposition of nitrates. These drivers affect the rate of decay of peat material and DOC production. High rainfall events can result in variations of DOC due to dilution, and atmospheric deposition of sulphides and sea salt can affect the solubility of DOC affecting concentrations. These drivers can act independently and interactively to influence the processes that result in DOC production, transport and export within and from peatlands (Armstrong *et al.*, 2012).

2.7.1.1 Temperature

There appear to be clear correlations between seasonal variations in temperature and DOC in the literature (Freeman *et al.*, 2004a; Billett *et al.*, 2006). Peat pore water concentrations of DOC are usually highest following periods of warm, dry conditions when DOC has had time to build up due to higher evaporation rates and plant tissue decomposition (Waddington & Roulet, 1997; Blodau, 2002; Limpens *et al.*, 2008). Increasing temperature has been shown to enhance biological activity and increase DOC production more than DOC consumption (Koehler *et al.*, 2009). Freeman *et al.* (2001b) studied how the enzyme phenol oxidase regulates carbon storage in peatlands. They studied the thermal responses of peatland phenol oxidase in relation to the export of DOC. Phenol oxidase activity was greater at higher temperatures which were accompanied by an equivalent increase in DOC release. Higher temperatures therefore seem to accelerate DOC production compared to DOC consumption and this may be due to increased microbial and plant mediated DOC release.

2.7.1.2 Vegetation

Peatland vegetation will affect the amount of C available for mobilisation as DOC and not just the photosynthetic and respiration rates of the ecosystem (Limpens *et al.*, 2008). For example, a survey across blanket peats in the UK showed that DOC concentrations were significantly higher where woody *Calluna spp.* dominated compared to *Eriophorum*-dominated or *Sphagnum-Eriophorum* sites (Limpens *et al.*, 2008). Armstrong *et al.* (2012) conducted a study on the relationship between dominant vegetation type and DOC concentration at Bingley Moor, a blanket peat in northern England. They found that *Calluna* dominance was associated with the highest DOC concentration, *Molinia* and *Sphagnum* dominance with lower concentrations, and sedge dominance with intermediate concentrations. Artz *et al.* (2007) also studied the concentrations of DOC along with dissolved organic nitrogen (DON) and dissolved inorganic N in soil water below vegetation dominated by *Calluna*, *Molinia* or *Sphagnum.* They found that vegetation was an important control on C and N release in the studied montane system.

Neff and Hooper (2002) measured the release of CO_2, DOC and DON from tundra soils collected from beneath a variety of vegetation types. Vegetation type strongly influenced carbon fluxes with the highest CO_2 and DOC release occurring in the soils of tundra shrub communities followed by tussock soils, then spruce and wet sedge soils. They found that most variation in CO_2, DOC and DON was related to vegetation type over climatic conditions.

The difference in DOC concentration between vegetation types has been put down to three potential factors that can influence soil organic matter. Firstly, there may be direct biochemical properties of vegetation that influence and vary the decomposability of peat components. Secondly, associated with different vegetation types are differing properties of microclimate, aspect and drainage which also influence C cycling. Thirdly, microbial decomposer communities may vary across vegetation types (Neff & Hooper, 2002). All of these factors influence the subsequent decomposability of soil organic matter.

2.7.1.3 Water table regime

Water table height will influence the oxygen availability in the upper peat layer. Lower water tables can cause increased aerobic decomposition of organic matter and higher DOC production (Aerts & Ludwig, 1997; Rowson *et al.*, 2010). In contrast to this, Clark *et al.* (2009) found there was a rise in the rate of net DOC production in peatland ecosystems under high water tables and anaerobic conditions compared to conditions of water table draw-down and aerobic conditions between −10 and – 40 cm depth. This was because the increases in DOC production were only seen after water tables recovered to the surface. Secondary changes in soil water chemistry driven by sulphur redox reactions decreased DOC solubility, and therefore DOC concentrations, during periods of water table draw-down. Microbial consumption of DOC was also apparent as an additional cause of declining DOC concentrations during dry periods (Clark *et al.*, 2009).

2.7.1.4 Disturbance

Disturbance of peatlands for harvesting or restoration activities can cause higher DOC concentrations due to increased rates of decomposition which increases DOC production (Moore & Clarkson, 2007; Limpens *et al.*, 2008). Moore & Clarkson (2007) found high DOC concentrations at Torehape peat bog (in New Zealand) associated with mining of the peat. The lowering of the average water table depth due to drainage results in a deeper the aerobic zone within the peat and this can lead to an increased flux of dissolved CO_2, increased soil respiration and increased losses of DOC (Rowson *et al.*, 2010).

2.7.1.5 High rainfall events

DOC concentrations are generally highest during low flow periods due to low amounts of rainfall. Under wet conditions DOC concentration is typically lower at the surface than at depth due to dilution by precipitation. However, the total export of dissolved C is likely to be higher during storm flows due to higher discharge (Waddington & Roulet, 1997; Limpens *et al.*, 2008).

Heavy rainfall events can result in changes in DOC concentration of streams draining bogs. Koehler *et al.* (2009) found that DOC concentration changed in a stream draining a blanket bog in South West Ireland following storm events. There were two different patterns: in colder periods the changes in DOC concentration were independent of stream flow and in the warmer period DOC concentration rose with increases in stream flow on some occasions and decreased with increasing stream flow on other occasions.

Worrall *et al.* (2002) concluded that the time between rain events is critical for the amount of C released in any storm event. This is because it takes time for oxidation processes to generate a reservoir of available C. According to Worrall *et al.* (2002) storm events at the Trout Beck catchment in the UK are characterised by two types of water: initial runoff characterised by old water that has high DOC; and new water depleted in DOC due to exhaustion of reserves.

2.7.1.6 Atmospheric deposition of nitrates, sulphides and sea salt

The addition of nitrate lowers the ratio of soil C:N and encourages the decomposition of organic matter by microbes, followed by the release of CO_2. Deposition of nitrates can enhance ecosystem productivity resulting in increased GPP and therefore more organic matter that can contribute to the DOC pool. Elevated DOC concentrations in the Hudson River in the United States have been attributed to increased DOC production from forest soils as a result of higher nitrogen deposition along with decreased degradability of DOC once it is in the river system (Roulet & Moore, 2006).

Evans *et al.* (2006) suggested that DOC solubility is increasing in the UK due to lower soil water acidity and ionic strength which has occurred as a result of declining sulphur and sea-salt deposition since the 1980s. This is ultimately due to changes in atmospheric deposition chemistry. Statistical analysis of 11 Acid Waters Monitoring Network (AWMN) lakes suggests that rising temperature, declining sulphur deposition and changing sea-salt loading can account for the majority of the observed trend of increasing DOC concentrations in rivers in the Northern Hemisphere.

2.8 DOC export

The amount of DOC that leaves a peatland each year is called the annual DOC export (also referred to as DOC transport or DOC flux). An increase in DOC export can result from an increase in runoff with no change in DOC concentration. Alternatively, an increase in DOC export can occur with no change in hydrology, but with increased production or retention of DOC in the landscape (Roulet & Moore, 2006). DOC export is the major pathway for C transfer from terrestrial to aquatic ecosystems and is a significant indirect source of CO_2 emission to the atmosphere (Thurman, 1985; Evans *et al.*, 2012). Table 2.1 summarises literature where DOC export from peatlands was measured along with other aspects of the peatland C budgets. DOC exports range from 4 to 27 mg C yr^{-1}.

2.8.1 DOC export pathways

The spatial and temporal variability of DOC concentrations within peatlands is large (Waddington & Roulet, 1997) and water movement exerts a strong control on C export. The amount of C exported from peatlands is highly dependent on interactions between the flows of water through and across them (Holden, 2005). The dominant pathways for water movement in ombrotrophic Northern Hemisphere peatlands is in the upper peat layers resulting in near surface flow along with saturation-excess overland flow. The flow in deeper peat layers is limited by very low hydraulic conductivity. The position of the water table, the slope of the peatland and the hydraulic properties of the peat control the lateral water movement through peatlands. Since the hydraulic conductivity of peat decreases with depth, the water table position effectively controls the amount of peatland volume contributing to DOC export (Waddington & Roulet, 1997).

DOC accumulates in pore water and is flushed out by the movement of water (Limpens *et al.*, 2008). DOC export from peatlands has been found in some cases to correlate with runoff and rainfall (Blodau, 2002). Clark *et al.* (2007) reported a correlation between annual precipitation and annual DOC export, to highlight the influence high flows have on DOC exports. Koehler *et al.* (2009) also found that about 45% of DOC export occurred during storm events which corresponded to approximately 10% of the high flows.

Groundwater patterns in peatlands are subject to change throughout the year. Fraser *et al.* (2001a) found that at Mer Bleue Bog groundwater flow patterns alternated between recharge (where head gradients produced flow from the surface to deeper peat) and discharge (where head gradients produced flow from depth to the surface). These changes were caused by seasonal cycles of precipitation and evaporation and the resulting differential head response in the catotelm peat to changes in water table elevation (Fraser *et al.*, 2001a). When evaporation exceeded precipitation during summer the groundwater flow pattern changed from one of recharge to discharge for a three week period in 1998 (Fraser *et al.*, 2001a). Flow reversals also affect pore water chemistry in peatlands, but the significance of this in terms of biogeochemical processes is unknown. DOC

Table 2.1: A comparison of DOC concentrations, annual DOC export, annual NEE and annual CH_4 emissions from different wetlands around the world. Net ecosystem carbon balance (NECB) indicates whether the wetland is a net sink (negative) or a source (positive) for carbon.

Reference	Site and wetland type	Years	DOC concentration (mg C l^{-1})	Annual DOC export (g C m^{-2} yr^{-1})	Annual NEE (g C m^{-2} yr^{-1})	Annual CH_4 emission (g C m^{-2} yr^{-1})	NECB (g C m^{-2} yr^{-1})
Fraser *et al.* (2001b)	Mer Bleue bog, Canada	1998-1999	20 – 60	8.3 ± 3.7			
Worrall *et al.* (2003b)	Trout Beck blanket peat catchment, UK	1999		9.4 – 15	– 55		– 15.4 ± 11.9
Billett *et al.* (2004)	Auchencorth Moss peatland, SE Scotland	1996-1998	38.6[1]	28.3[1]	– 27.8	4.1	+8.3
Worrall *et al.* (2006)	Trout Beck blanket peat catchment, UK	1992-2002	5 – 18	4 – 7.4			
Roulet *et al.* (2007)	Mer Bleue bog, Canada	1998-2004	47.5	14.9 ± 3.1	– 0.2 ± 40.5	3.7 ± 0.5	– 21.5 ± 39.0
Nilsson *et al.* (2008)	Degero Stormyr mire, Sweden	2004-2005	27.8[1]	13.0 ± 1.5[1]	– 51.5 ± 4.9	11.5 ± 4.9	– 27.1 ± 7.0
Jager *et al.* (2009)	Salmisuo mire complex, eastern Finland (dry year)	2006	10 – 56	4.2			

Jager *et al.* (2009)	Salmisuo mire complex, eastern Finland (wet year)	2007	10 – 48	11.3			
Worrall *et al.* (2009)	Trout Beck blanket peat catchment, UK	1993-2005		39	– 178		– 20 to – 91
Dinsmore *et al.* (2010)	Auchencorth Moss peatland, SE Scotland	2007-2008	32.2 ± 2.28	25.4	– 115	0.3	– 72.4
Koehler *et al.* (2011)	Glencar blanket bog, SW Ireland	2003-2008	6.3	14.0 ± 1.6	– 47.8 ± 30.0	4.1 ± 0.5	– 29.7 ± 30.6

[1] values are for total organic carbon (TOC) not DOC.

may be transported to depth in peatlands that experience flow reversals and play a role in anaerobic respiration deeper in the profile (Fraser *et al.*, 2001a).

2.9 Cycling of aquatic carbon within peatland ecosystems

DOC is the main component of the waterborne C flux out of peatlands. DOC is added to peat pore water following decomposition of organic matter. Biological processes can affect the fate of DOC as *in situ* microbial consumption of available DOC can occur throughout a peatland (Fraser *et al*., 2001a). DOC is used as an energy source for heterotrophic bacteria which results in a decrease in DOC concentration and its conversion to CO_2 through respiration (Koehler *et al.*, 2009). DOC can be immobilised as biota convert DOC into POC while the breakdown of POC by biota can also add DOC to the peat pore water (Worrall *et al*., 2006; Dawson *et al*., 2004).

Within streams or canals bordering peatlands a significant amount of DOC removal may happen close to its source due to in-stream processes (Worrall *et al*., 2006). An increase in pH through dilution of peat water can cause coagulation and flocculation of DOC. Other chemical processes such as photodegradation and adsorption can remove DOC from stream water, although adsorption of DOC requires contact with an adsorptive surface (Worrall *et al*., 2006).

2.9.1 POC

The turnover of DOC is rapid and occurs in a small period of time when compared to the turnover of POC (Thurman, 1985). DOC is chemically more reactive because it is a measure of individual organic compounds in the dissolved state, whereas POC consists of discrete plant and animal organic matter and organic coatings on silt and clay. DOC is degraded principally by microorganisms whereas decomposition by animals and microorganisms occurs simultaneously on POC. POC may reside in channel or floodplain sediments for tens to thousands of years depending on how large the river is. POC may decompose within the catchment and as a result the C is kept within the ecosystem (Thurman, 1985).

POC is organic carbon greater than 0.45 μm in size (Thurman, 1985). Most sampling programmes have ignored POC removal from peatlands. POC export from natural, undamaged, non-eroding peat bogs tend to be very low (Lindsay, 2009), however, POC export can be large in disturbed landscapes affected by erosion. Measured POC exports vary from 3.4 g C m^{-2} yr^{-1} in a small un-eroded peatland catchment to over 90 g C m^{-2} yr^{-1} in severely eroded peatland systems (Billett *et al.*, 2010).

2.9.2 Dissolved CH_4 and CO_2

Peatland streams can be supersaturated with dissolved gaseous CO_2 and CH_4 and results in the evasion of dissolved gases from the water surface to the atmosphere (degassing) (Billett *et al.*, 2010). Within peat pore water the spatial and temporal variability of dissolved CH_4 and CO_2 is large (Waddington & Roulet, 1997) and the flux of dissolved CO_2 and CH_4 leaving peatlands in streams can also vary both spatially and temporally, making it difficult to quantify accurately at a landscape scale (Billett *et al.*, 2010). However, according to Hope *et al.* (2001) dissolved CH_4 is negligible when measured in canal outlets draining peatlands but the concentration of dissolved CO_2 may be significant.

2.9.3 DIC

In wetlands, dissolved organic matter generally exceeds dissolved inorganic matter (Thurman, 1985). In low pH waters, DIC tends to contribute a smaller proportion of the total carbon export and only occurs as dissolved free CO_2 and HCO_3^- ions (lacking in CO_3^{2-}) (Dawson *et al.*, 2002).

2.10 DOC in New Zealand peatlands

There have been relatively few studies of DOC concentrations and chemistry in wetlands in New Zealand. DOC dynamics were studied by Moore and Jackson (1989) in three small wetland catchments in north Westland, New Zealand. One was covered in manuka scrub and the other two had previously been cleared. Over a four month sampling period, DOC concentrations averaged 46.0 and 45.7

mg l^{-1} in the surface soil water and subsoil water respectively in the scrub forest catchment.

Moore and Clarkson (2007) measured the concentration of DOC in samples of water collected from groundwater, pore water, drainage ditches, and streams draining peatlands in New Zealand in 2006 (Table 2.2). The smallest concentrations of DOC were found in three small peatlands in Tongariro National Park. This was due to high iron concentrations resulting in a decrease in DOC concentration due to sorption onto iron oxide surfaces. The high concentrations of iron in these peatlands were brought in by groundwater or weathering of iron rich volcanic rocks beneath the peatland (Moore & Clarkson, 2007).

Ombrotrophic peatlands appear to have some of the highest DOC concentrations (50 to 100 mg l^{-1}) in New Zealand and this is possibly due to an absence of DOC immobilisation by iron or base cations associated with groundwater flow (Moore & Clarkson, 2007). Mean DOC concentration ± standard deviation (SD) in 12 samples taken at Kopuatai bog was 53.0 ± 37.7 mg l^{-1}. Moore and Clarkson (2007) estimated the export of DOC from New Zealand peatlands to be between 10 and 50 g m^{-2} yr^{-1}, likely comprising a substantial portion of the overall carbon budget of peatlands.

Table 2.2: DOC concentration (mg l^{-1}) (mean ± standard deviation) in peat pore water and streams or ditches by location. Data from Moore and Clarkson (2007).

Site	Location	*n*	DOC (mg l^{-1})
Waikato	Kopuatai bog	12	53.0 ± 37.7
	Torehape peat mine	49	109 ± 198
	Torehape reserve (bog)	4	70.3 ± 9.2
	Opuatia (fen)	41	32.1 ± 25.4
	Whangamarino wetland	14	91.4 ± 35.5
Central North Island	Water samples from bogs at Tongariro National Park, Te Ponanga, Ketetahi and National Park	28	15.0 ± 5.8
Southland	Water samples from bogs at Awarua, Borland, Dunearn (partially drained) and Pukerau	39	49.8 ± 18.6

2.11 Approaches to measuring DOC export

Several methods have been used to estimate DOC export. These include a catchment based method using discharge weighted equations, a groundwater method worked out by measuring hydraulic conductivities in the peatland, and a water balance based method.

2.11.1 Catchment method

A catchment-based method for deriving DOC export utilises the equation

$$F_{\mathrm{DOC}} = t \times Q_r \times \left(\frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \right) \qquad 2.4$$

Where F_{DOC} (mg C) is the total DOC load carried over a certain time period (e.g. a year), t is the number of seconds in the time period, Q_{r} (l s^{-1}) is the mean discharge from a continuous record, Q_i is instantaneous discharge, C_i is the instantaneous DOC concentration (mg C l^{-1}) and n is the number of samples. The load is converted into an export value (the mass transported per unit catchment area per unit time) by dividing by the catchment area (Koehler *et al.*, 2009).

Discharge is measured from a stream that leaves the bog and the DOC concentration of outflow water is analysed to determine the total DOC export. Roulet *et al*. (2007), Worrall *et al*. (2006 & 2003b), Dawson *et al.* (2004) and Koehler *et al*. (2009) used equation 2.4 (also known as ‘Method 5’ from Walling and Webb (1985)) to calculate DOC export since there was no relationship or only a weak relationship found between DOC concentration and discharge (Koehler *et al*., 2009; Fraser *et al*., 2001a). This method utilises both instantaneous concentration and discharge at the time of sampling and the mean discharge determined from continual discharge measurements (Dawson *et al*., 2004).

Koehler *et al*. (2009) used the catchment based method to determine DOC export from an Atlantic blanket bog in south-west Ireland and compared the results to the DOC export calculated from a continuous sampling method (where DOC samples were taken continuously). They found that the annual DOC export estimates for 2007 were 14.1 (± 0.1), 14.1 (± 0.6) and 14.1 (± 1.8) g C m^{-2} yr^{-1} for infrequent sampling of once a day, once a week and once every month, respectively, which compared with 14.1 g C m^{-2} yr^{-1} measured with 30-min continuous sampling.

They determined that a sampling frequency of weekly or monthly was adequate to calculate the annual export of DOC in their study site. The only difference between the values was higher uncertainty estimates where there were lower numbers of samples. A majority of the published studies of DOC export from peatlands use the catchment-based method and measure DOC export at stream sites.

2.11.2 Groundwater method

Waddington and Roulet (2000) determined DOC export from Stor-Amyran peatland, in Sweden, by estimating the groundwater flux within the bog. Peat pore water was sampled at a number of depths down to 3 m along a transect across the bog. Groundwater flow nets were constructed using hydraulic head data obtained from a series of groundwater piezometers installed along the same transect and hydraulic conductivity was determined for every piezometer. The groundwater flux was calculated from weekly flow nets using Darcy's law and converted to an equivalent depth of runoff by dividing the volumetric flux by the area at each location. The waterborne fluxes of DOC were calculated by multiplying the concentrations of DOC by the calculated runoff (Waddington & Roulet, 1997).

Fraser *et al.* (2001b) took a similar approach to estimating DOC export in Mer Bleue Bog, in Canada, and also compared it to the catchment based approach. They believed it was important to determine if DOC export measured at the peatland outflow was a suitable proxy for seepage flux and vice versa, and to isolate the controls on DOC export and biogeochemistry. A relationship was determined between runoff at a weir and water table position, and using this and the hydraulic conductivities of the peat, a Dupuit-Forchheimer (D-F) approximation of groundwater lateral seepage was determined. This was coupled with DOC concentrations of peat pore water to calculate the DOC export at the peatland margins. This was then compared to discharge and DOC export measured at the basin outflow which was 4 km downstream. There was a 21% discrepancy or 1 g C m^{-2} difference between the measured and the D-F approximated DOC export. DOC export measured at the outflow was lower than that measured using piezometers due to higher DOC concentrations at the groundwater transects compared to the outflow. This was explained by processes that occur along the pond network such as photodegradation, methanogenesis and flocculation resulting in a decrease of DOC. Fraser *et al.* (2001b) concluded that measuring DOC export from the outflow was a suitable substitution in the absence of the D-F based approach (which was more accurate).

Groundwater models for peatlands rely on the assumption that the lateral water flux corresponds to that given by Darcy's Law. However, there is potential for pores of peat to become blocked by gas bubbles generated by microbial activity and this can prevent water flow (Campbell & Jackson, 2004).

2.11.3 Water balance method

Sanderman and Amundson (2008) used a water balance method to quantify the magnitude of DOC leaching and subsequent retention in soils for a coniferous forest and a coastal prairie ecosystem. The vertically infiltrating DOC fluxes were calculated by multiplying the DOC concentration for each sampling period by the water flux through a section of soil of a period of time and then summing to obtain annual values. Lohse and Matson (2005) used a similar approach to determine DOC leaching from tropical forests. Both studies calculated the water fluxes using two different methods and then compared them. The methods were:

1. A simple water balance equation:

$$Q = P - E - \Delta S \qquad 2.5$$

Where a daily water loss (Q) was solved for given inputs of precipitation (P) and changes in water storage (ΔS) and evaporation (E) losses.

2. A Darcian-based model where water flux (J_w) was proportional to the potential gradient multiplied by the hydraulic conductivity (K_h):

$$J_w = K_h \frac{\partial h}{\partial z} \qquad 2.6$$

The Darcian-based approach is similar to the groundwater flux based approach used by Waddington and Roulet (2000) and Fraser *et al.* (2001b) in Stor-Amyran peatland and Mer Bleue bog. The difference is that Sanderman and Amundson

(2008) were measuring vertical infiltration of the DOC flux and hydraulic conductivity was calculated over different depths, whereas Waddington and Roulet (2000) and Fraser *et al.* (2001b) determined the lateral movement of the DOC flux by determining the hydraulic conductivity over different distances across the peatlands.

Overall, Sanderman and Amundson (2008) found that there was good agreement between the two methods. At the site where soils were saturated and drained very rapidly the two methods agreed well. However, at other sites the water balance method seemed to move water through the soil at a too rapid rate. The Darcian results were more in line with field data and observations meaning that is was the more favourable approach. The two methods Lohse and Matson (2005) used showed variation in timing and magnitude of Q between them and therefore DOC export. Overall, the water balance method measured soil water fluxes during storm events better and provided a continuous record of soil water drainage.

Chapter Three
Site description

3.1 Introduction

This chapter will describe the physical and biological environment of Kopuatai bog and will review previous research conducted on the bog. The specific field site locations used for this research will then be described.

3.2 Development of Kopuatai bog

Kopuatai is the largest raised bog in New Zealand still in its natural state (Maggs, 1991). Kopuatai is situated in the Hauraki Lowlands and covers approximately 10,200 ha[4] (Newnham *et al.*, 1995). The bog is orientated north to south, with a length of 17 km and a width of 6 km (Figure 3.1). It is bounded on the western side by the Piako and Waitoa Rivers and on the eastern side by the Elstow Canal and with the sea about 15 km to the north. Approximately 1,500 m from its edge, the bog surface is 4 m above the surrounding ground level, illustrating the raised nature of the bog (Shearer, 1997). Kopuatai has two domes, a north and a south dome, and this research took place on the northern dome, towards the eastern side. The peat reaches thicknesses of about 8 m in the north and 12 m in the south (Newnham *et al.*, 1995).

Kopuatai bog lies within the Hauraki Depression which is a rift structure bounded on each side by faults (Newnham *et al.*, 1995). The rift structure is infilled with Tertiary and Quaternary terrestrial sediments that reach thicknesses of up to 3 km (Hochstein & Nixon, 1979). Most of the near surface fill of the rift is the Hinuera Formation, which consists of alluvium of a large braided river delta complex. After the post-glacial rise in sea level, the Hinuera Formation became overlain in places by thin marine and estuarine muds, river sediments and peats including the Kopuatai bog (Hochstein & Ballance, 1993).

[4] *Kopuatai Peat Dome.* Department of Conservation website: http://www.doc.govt.nz/conservation/land-and-freshwater/wetlands/wetlands-by-region/waikato/kopuatai-peat-dome/, 10/10/12.

Newnham *et al.* (1995) proposed a model for the bogs development. Throughout its development Kopuatai has remained close to sea level and has had rivers in close vicinity, resulting in a high stable water table. The earliest wetlands developed originally in a poorly drained palaeochannel within the Kopuatai Depression (a faulted basin) and was originally vegetated with swamp forest and subjected to regular flooding. The earliest peats are dated at c. 11,700 radiocarbon years BP. The bog became mostly oligotrophic by c. 8,500 BP and a domed surface had developed in the south-eastern and western parts of the bog

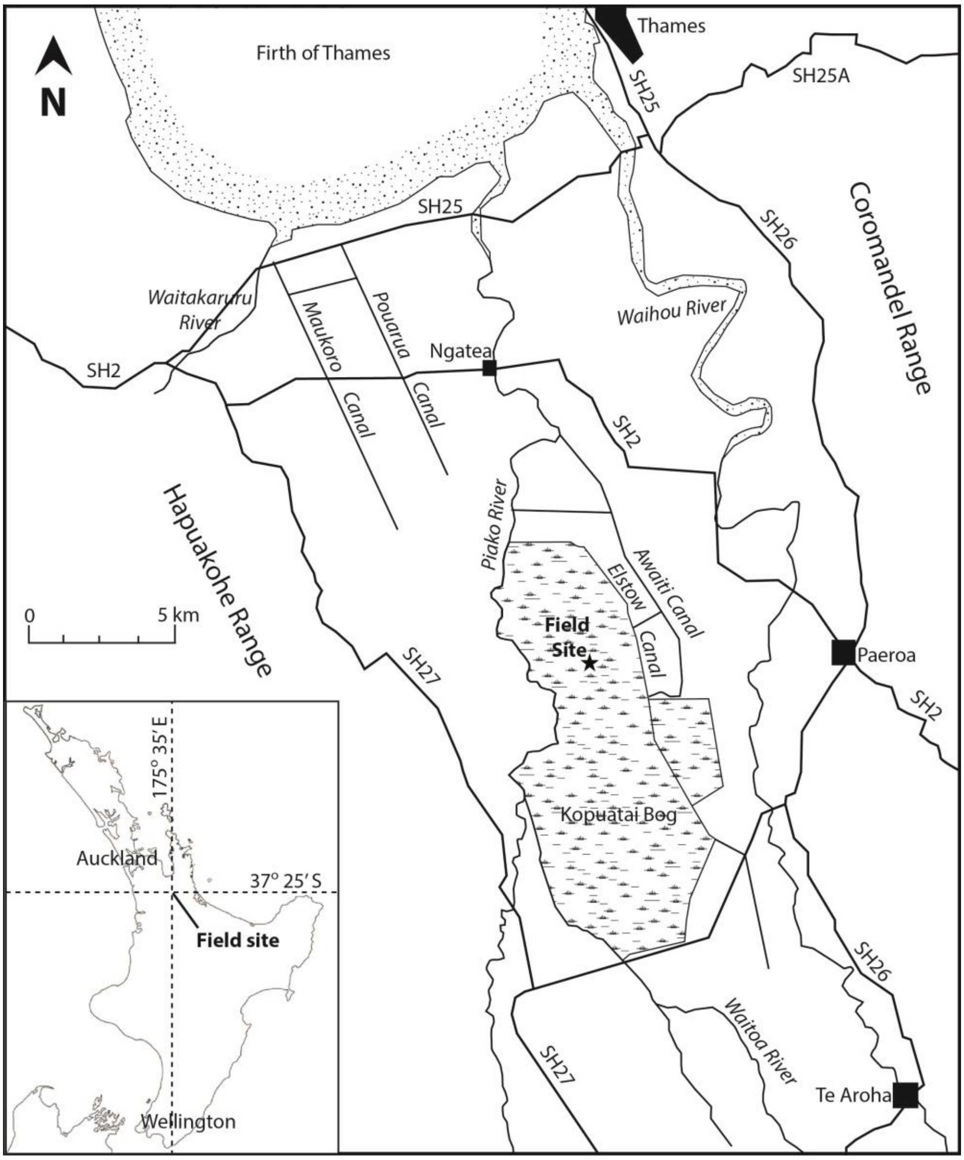

Figure 3.1: Location of Kopuatai bog and research site. Figure redrawn from Campbell and Williamson (1997).

system. The mid-Holocene sea level transgression elevated the groundwater table. Populations of sensitive oligotrophic species declined and the northern third of the depression was buried under deltaic muds. By 6,000 BP most of the bog, apart from small parts of its south western and eastern ends was covered in shallow seawater. As sea level receded oligotrophic conditions returned to most areas of the bog. By c. 700 BP full oligotrophic conditions were finally established in the northern area of the bog (Newnham *et al.*, 1995).

The northern area of Kopuatai, in which this study was undertaken, developed around 6000 BP after marine transgression covered the majority of Kopuatai bog (Newnham *et al.*, 1995).

3.3 Vegetation

Kopuatai is a restiad bog meaning that the vegetation is dominated by members of the Southern Hemisphere vascular plant family, Restionaceae. In northern New Zealand, the main species are *Empodisma robustum* and *Sporadanthus ferrugineus* (Figure 3.2). *E. robustum* is the primary peat former in these bogs (Clarkson *et al.*, 2004a; Wagstaff & Clarkson, 2012). Vegetation zones on Kopuatai bog correspond partly with the degree of wetness (water table elevation), nutrient availability and history of fire occurrence.

Figure 3.2: Isolated stand of *S. ferrugineus*, with *E. robustum*, *Baumea spp*. and *Gleichenia dicarpa* in the foreground, at Kopuatai bog.

Plant succession in New Zealand bogs is controlled by water and nutrient supply as the system changes from minerotrophic to an ombrotrophic restiad bog. Succession can be summarised in three phases (Clarkson *et al.*, 2004a). Phase 1 is the early successional pre-restiad state where the wetland is dominated by sedges such as *Baumea rubiginosa* and *Baumea teretofolia*, ferns such as *Gleichenia dicarpa* and shrubs such as *Leptospermum scoparium* (manuka) (Figure 3.3). Phase 2 is the establishment and dominance of *E. robustum* along with minor amounts of the shrub, *Epacris pauciflora*. Phase 3 begins with the establishment of the late-successional restiad species, *S. ferrugineus*, and this eventually becomes the dominant vegetation (Clarkson *et al.*, 2004a).

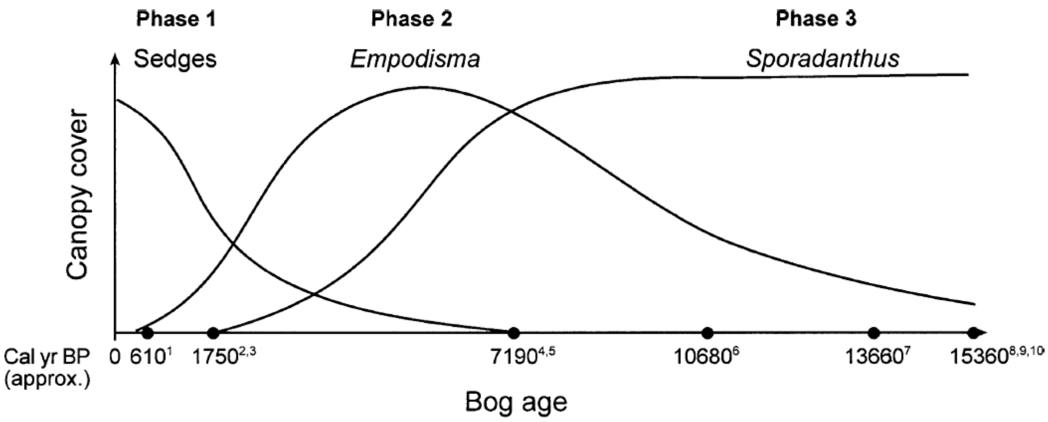

Figure 3.3: Diagram showing species dominance over time during the development of restiad bogs from Clarkson *et al.* (2004a). The ages of peat wetlands in the Waikato are shown. 1 = Duck Creek wetland, 2 = Whangamarino wetland, 3 = Opuatia wetland, 4 = Torehape, 5 = Kopuatai (northern part), 6 = Lake Maratoto, 7 = Kopuatai (southern part), 8 = Te Mimiha, 9 = Moanatuatua North, 10 = Moanatuatua.

3.3.1 Vegetation Zones

The vegetation of Kopuatai bog was surveyed by Irving *et al.* (1984) and also by the Department of Conservation in 2008. The detailed Department of Conservation map can be found in Appendix B. For the purposes of this study a generalised vegetation map (Figure 3.4) was constructed based on the Department of Conservation map and the older vegetation map by Irving *et al.* (1984). There are five vegetation zones described by Irving *et al.* (1984).

Sporadanthus ferrugineus rushland

S. ferrugineus is distributed down the eastern part of the dome with a small patch in the south west. It forms dense stands up to 2.5 m in height broken by areas of *Schoenus/Empodisma* communities (Irving *et al.*, 1984).

Empodisma robustum rushland

This zone also consists of *Schoenus brevifolia* amongst the *E. robustum* and is located across the eastern to middle areas of the dome and is also found in and around *S. ferrugineus* communities (Irving *et al.*, 1984). It constitutes a low (<0.5 m) canopy. In areas where the lower canopy is more open, there is a bryophyte dominated ground cover. The types of species growing here include mosses (*Sphagnum cristatum*, *Campylopus acuminatus* var. *kirkii*), liverworts (*Goebelobryum unguiculatum*, *Riccardia crassa*), lycopods (*Lycopodiella lateralis*) and carnivorous herbs such as the bladderwort (*Utricularia delicatula*) and sundews (*Drosera binata* and *D. spathulata*) (Clarkson, 2002; Clarkson *et al.*, 2004a).

Baumea teretifolia/Empodisma robustum zone

This type of community is typical of the very wet areas of the south-eastern part of the dome. The drier parts are covered by a dense growth of *E. robustum* with occasional bog sedges such as *B. teretifolia* and *S. brevifolia*. Plants reach a height of 1 m. Around the pools, *B. teretifolia* becomes dominant (Irving *et al.*, 1984).

Baumea teretifolia/Gleichenia dicarpa sedgeland

The sedge *B. teretifolia* and tangle fern *G. dicarpa* form a community type reaching an average height of about 1 m. This type is mostly found bounding the *L. scoparium* (manuka) on the western side and northern end of the dome. Where this vegetation changes from a *L. scoparium* community to a *Baumea/Gleichenia* community, woody species such as *Dracophyllum lessonianum* and *E. pauciflora* (bog *epacris*) also occur in the upper canopy and are therefore more common at the margins of the bog (Irving *et al.*, 1984; Clarkson *et al.*, 2004a).

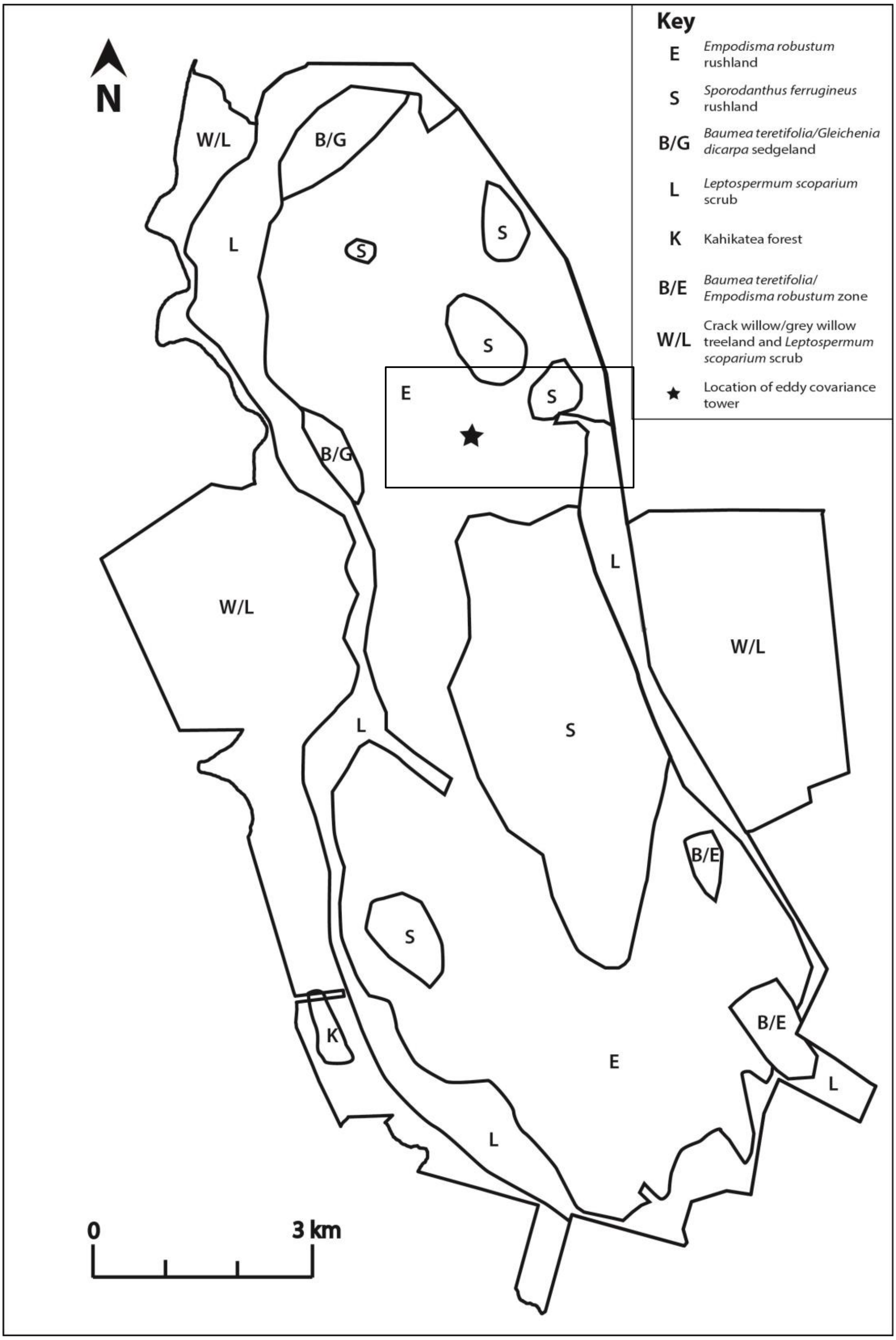

Figure 3.4: Simplified vegetation map of Kopuatai bog. Figure based on Irving *et al.* (1984) and Department of Conservation (2009). The box in the vicinity of the eddy covariance tower indicates the study area for this research.

Leptospermum scoparium scrub

The *L. scoparium* zone forms the more mesotrophic fringe of the bog and probably results from surrounding land development. The width of the *L. scoparium* band varies from a thin strip of 10 m to large several hundred metres. Some trees can reach up to 3 m in height. Species such as *G. dicarpa*, bracken, *Dianella nigra* and *B. teretifolia* grow under less dense *L. scoparium* (Irving *et al.*, 1984).

Surrounding the bog is a zone of crack willow and grey willow treeland and manuka scrub along with an area of kahikatea forest at the south-western edge of the bog.

3.3.2 Hydrological significance of *Empodisma robustum*

Empodisma robustum is from the monocotyledonous angiosperm family Restionaceae, which is mainly found in the drier regions of southern Africa and Australia (Ingram, 1983). The genus *Empodisma* (Restionaceae) was until recently comprised of two species with a distribution in western and south-eastern Australia, Tasmania and New Zealand. These species were *Empodisma gracillimum* found on coastal plains in Australia and *E. minus* found in lowland to alpine zones from Queensland to South Australia, Tasmania and New Zealand (Wagstaff & Clarkson, 2012). Wagstaff and Clarkson (2012) have since proposed that the northern New Zealand species (at less than 38ºS) should be recognised as the new species *Empodisma robustum*.

E. robustum is often associated with *S. ferrugineus* and the two species are co-dominants in the bog community in which bryophytes are unimportant. The root systems of *E. robustum* have primary roots that are stout and grow horizontally out from the vertical rhizomes. They bear very numerous, fine, secondary roots, many of which grow upwards. The secondary roots are covered with root hairs. The white masses of roots resemble *Sphagnum* in appearance. These root masses are sponge-like, with a water content up to fifteen times their dry weight (Campbell, 1964).

In *E. robustum* bogs, *Sphagnum* mosses are often abundant around the edges but absent or uncommon in the centre where the surface is instead covered by the white hairy rootlets of the restiad. *E. robustum* has a lower water holding capacity but a similar base exchange capacity by unit surface area basis as *Sphagnum* (Agnew *et al.*, 1993). It has a great peat forming capacity which maintains it as a dominant in spite of the presence of *Sphagnum* (Agnew *et al.*, 1993). *E. robustum* roots are living, loose and spongy to a depth of 7–10 cm and fibrous to depths of 50 cm (Agnew *et al.*, 1993).

E. robustum plays a key role in the development of restiad bogs as it is the main peat forming vegetation and the senescent roots of *E. robustum* form the main mass of peat (Kuder *et al.*, 1998). Hodges and Rapson (2010) proposed that *E. robustum* is the "ecological engineer" of the fen-bog transition zone i.e. an organism that influences the availability of resources to other species by causing physical changes in biotic and abiotic materials. The hummock and hollow pattern in the vegetation is caused by *E. robustum* creating patches of higher peat accumulation. *E. robustum* stems channel rainwater to the surface where the rootlets can then take up the nutrients (Agnew *et al.*, 1993). Clarkson *et al.* (2009) demonstrated that *E. robustum* was efficient at scavenging nitrogen using this method. It is tolerant of a wide environmental range and is therefore able to initiate restiad bog development early in minerotrophic wetlands. An *E. robustum* phase is necessary for the establishment of *S. ferrugineus* which occurs in the late phase of bogs where it becomes the physiognomic dominant (Clarkson *et al.*, 2004a).

Kuder *et al.* (1998) reported on the chemical properties of *E. robustum* and *S. ferrugineus*. They found that, unlike *Sphagnum*, restiads possess lignin in their tissues. In addition, the presence of non-lignin polyphenols (including tannins and phenolic acids) in restiads may be an important factor in peat formation due to allelopathic[5] decay retardation. The allelopathic properties of the restiad tissues may facilitate exclusion of other species and lead to development of uniform communities, water logging and initiation of peat formation. Decay resistance is also increased by the presence of these compounds due to the inhibition of

[5] Allelopathic is the inhibition of growth in one species of plants by chemicals produced by another species.

microbial activity and the inherent inertness of lignin and tannin. This may be significant to the restiads ability to form peat particularly given that climatic conditions are not ideal for peat formation (Kuder *et al.*, 1998).

Conservative transpiration rates may also partially explain the potential of *E. robustum* to form peat in an environment with moderate rainfall, high summer temperatures and high potential evaporation (Campbell & Williamson, 1997).

3.4 Hydrology

3.4.1 Hydraulic conductivity

The variation in peat saturated hydraulic conductivity was measured *in situ* at Kopuatai using the piezometer method by King (1999). Hydraulic conductivity (K) ranged between 4.47×10^{-3} and 2.45×10^{-7} m s^{-1}. The effect of depth on hydraulic conductivity was significant, with hydraulic conductivity decreasing from 0.80-0.85 m down to 3.20-3.25 m. Peat hydraulic conductivity exhibits a high degree of spatial variability and this is apparent at the small (e.g. 1 m) to the large (e.g. 1000 m) spatial scales. King (1999) found that the von Post humification scale (the state of decomposition of peat) can be used to predict the hydraulic conductivity of peat at Kopuatai as there is a strong relationship between log K and degree of decomposition as determined by the von Post method (Figure 3.5).

Modelling by King (1999) showed that the majority of groundwater discharge (c. 85%) occurred through the top 1.0 m thickness of peat. There was also a lack of any significant difference between mean log K values for the top three depth intervals of 0.20-0.25, 0.4-0.45, and 0.80-0.85 m, implying that the acrotelm may be as deep as 0.85 m. It was concluded that the diplotelmic hypothesis was valid for Kopuatai, however the acrotelm was deeper at Kopuatai than in many Northern Hemisphere bogs dominated by *Sphagnum*. There appears to be negligible vertical movement of pore water within the peat matrix (as indicated by the lack of vertical head gradient) and the direction of groundwater flow is predominantly horizontal. Surface flow mechanisms may also be important in the discharge of water from Kopuatai bog.

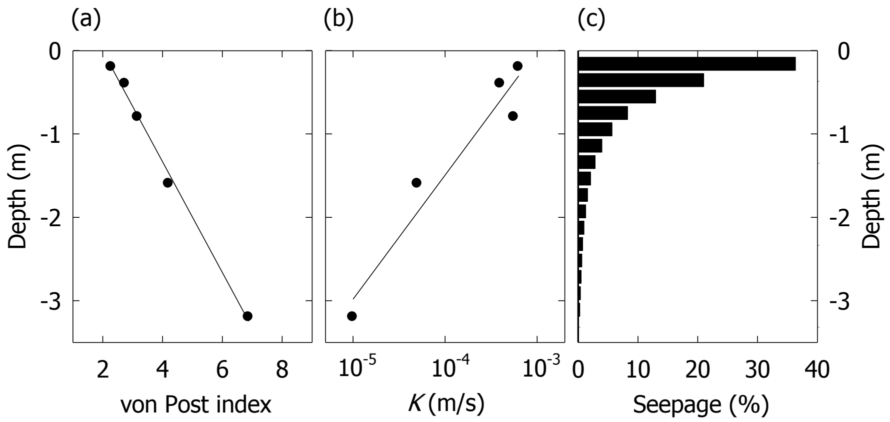

Figure 3.5: Plots showing variation in peat physical and hydraulic properties with depth for Kopuatai bog: (a) peat decomposition states given by the von Post scale (b) hydraulic conductivity measured *in situ* using a piezometer method (c) percentage of lateral flow occurring within 0.2 m increments of depth, calculated using Darcy's law. From Campbell and Jackson (2004), data source King (1999).

3.4.2 Flow direction

Surface elevation data was obtained for Kopuatai bog (Figure 3.6) and two distinct north and south domes can be recognised. The study site is located on the northern dome and indicates that surface and groundwater flows move from the EC site towards the western side of the bog (Figure 3.7).

3.5 Anthropogenic influences

Kopuatai bog is surrounded by productive agricultural land and, presently, the most serious threat to Kopuatai is the continuing drainage of the surrounding area. Canals draining the bog can be closed to prevent the lowering of water levels during summer months and water level is maintained at high levels to prevent decomposition of the peat. There is potential for fertilizer drift from surrounding farmland and the addition of nutrients to the bog. The mineralized wetland margin creates a buffer zone that helps to stop the aerial drift of fertilizer onto the bog. The addition of nutrients into the margins of the bog can cause nutrient enrichment that can stimulate high primary productivity and faster decomposition along with allowing invasive exotic species to dominate (Clarkson, 2002).

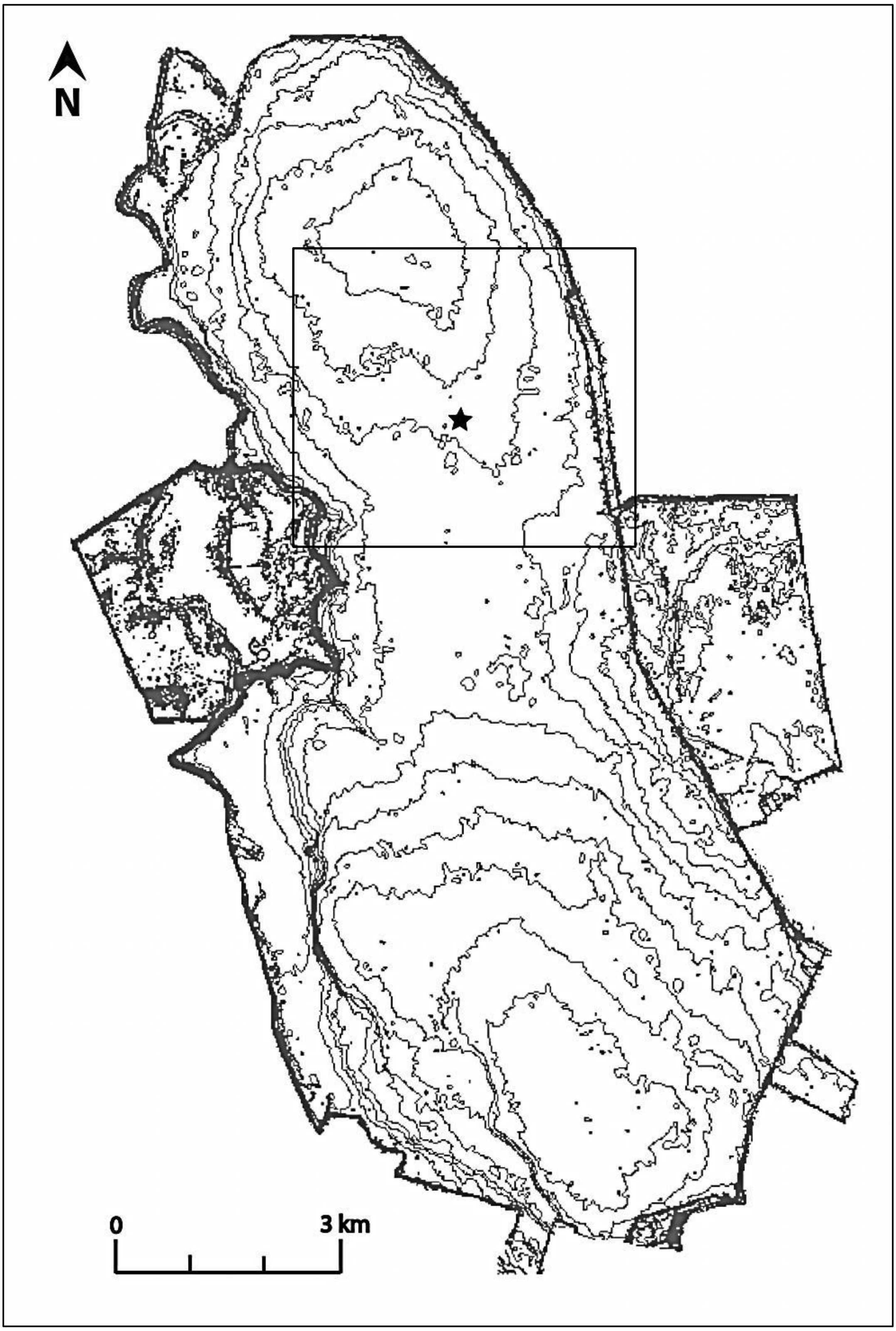

Figure 3.6: Surface elevation contours of Kopuatai bog from LIDAR data. Contours are 0.5 m intervals. The star indicates the location of the eddy covariance (EC) tower and the box identifies the location of the study site (which is enlarged in Figure 3.7).

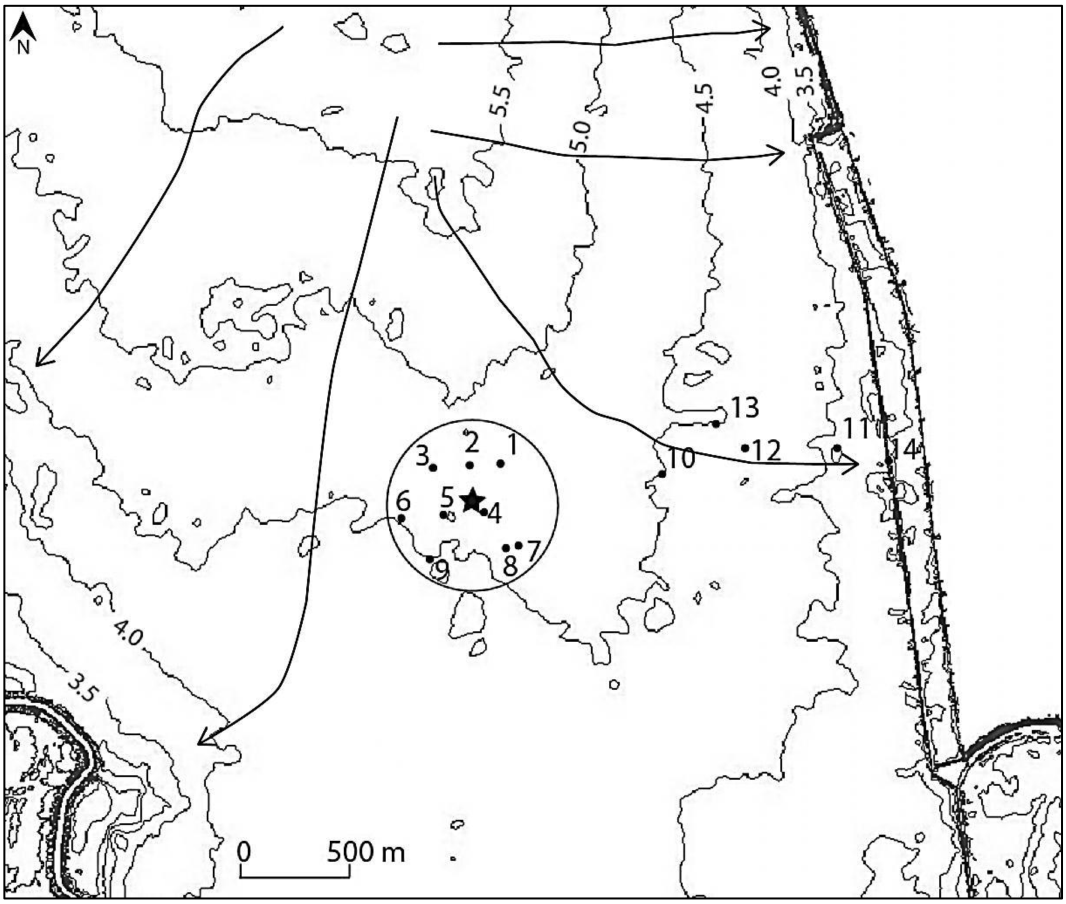

Figure 3.7: Enlargement of part of Figure 3.6 showing surface elevation contours of Kopuatai bog with flow lines and site locations.

Fires are part of the natural bog ecosystem when caused naturally by lightning strike or volcanic eruption. However, due to large scale land clearance and the introduction of steam trains, fire frequency increased dramatically in the 1900s. Fire resets the wetland development back to the early high nutrient stage although recovery is rapid when there are pre-fire vegetation communities around (Clarkson, 2002). Severe fires occurred regularly at Kopuatai bog up to the mid-1970s, including an extensive fire in approximately 1950 which swept up the southern part of the bog (Maggs, 1991).

3.6 Previous published research on Kopuatai bog

A range of scientific studies have been undertaken at Kopuatai bog. Only studies relevant to this research and that have not already been covered in previous sections are summarised below.

Campbell and Williamson (1997) measured summer time evaporation rates over *E. robustum* vegetation in Kopuatai using the Bowen ratio method. They found that evaporation rates were much lower for *E. robustum* than for other wetland vegetation types reported in the literature. The conservative evaporation regime at this site was caused by a very large canopy resistance and this was due to plant response to a nutrient poor environment along with the extremely dense canopy. The canopy restricts transpiration and acts as mulch preventing solar energy reaching the peat surface and water vapour diffusing into the atmosphere above. As a consequence *E. robustum* must be adapted to high sensible heat loading (Campbell & Williamson, 1997).

Thompson *et al.* (1999) also measured evaporation rates at Kopuatai but over areas dominated by *S. ferrugineus* and reported similar evaporation rates to other wetlands with vascular plant covers. Evaporation rates in *S. ferrugineus* were constrained by the combination of plant physiological and canopy structural factors which worked together to prevent high rates of evaporation from the peat surface. The highly conservative evaporation regimes for both *S. ferrugineus* and *E. robustum* are responsible for maintaining the wet conditions in these peat bogs and therefore the effects of drought and artificial drainage are lessened (Thompson *et al*., 1999).

Clarkson *et al.* (2004a) sampled a chronosequence of restiad bogs in the Waikato region to identify the major environmental determinants of vegetation pattern and dynamics. They presented a conceptual model of succession for restiad peatlands in New Zealand. As previously discussed in Section 3.3, the sequence of plant establishment was from sedges to *E. robustum* through to the late successional *S. ferrigineus*. Different factors such as vegetation and nutrient content were assessed in plots from a range of peatland sites of varying ages, including Kopuatai. As the age of a bog increases and succession proceeds, total and available nutrient contents decrease and peat become increasingly less decomposed.

Shearer (1997) studied the natural and anthropogenic influences on peat development in Waikato and Hauraki Plains restiad bogs and included in this study were the Kopuatai, Whangamarino and Moanatuatua wetlands. Of the three restiad bogs studied, Kopuatai had been little affected by human influences while Moanatuatua and Whangamarino were subjected to lowered local water tables due to being surrounded by farmland. The influences on the water table and nutrient content of surface water had resulted in degradation of peat at these two areas.

Schipper *et al.* (1998) determined trends in biochemical and physical properties along a 1500 m transect into Kopuatai bog. Bulk density, anaerobically-mineralisable N and microbial biomass were all greatest at the edge of the bog due to a lower water table and greater N availability from surrounding agricultural land through spray drift of fertiliser onto the bog. This impact did not extend beyond 200 m into the bog suggesting that the majority of the bog is little affected by surrounding agricultural practices.

3.7 Field site locations

Fourteen sites were established within Kopuatai bog. These sites were accessed via a track from the north-eastern side of the bog at farmland east of Carter's Canal (Figure 3.8). Sites 1 to 11 were established in the *E. robustum* rushland area, with site 1-9 in the middle of the bog (Figure 3.9). Sites 1 to 3 were located along an east-west transect approximately 200 m north of the eddy covariance (EC) tower (the northern transect). Sites 4 to 6 were located along an east-west transect parallel to the northern transect. This transect was on the main track where the EC tower was located (the middle transect). Sites 7 to 9 were located on a third transect which was parallel to the other transects and approximately 200 m to the south of the EC tower (the southern transect). These sites were all randomly placed along each transect with the exception of Site 4 which was deliberately located at the EC tower site, approximately 1810 m from Carter's Canal. Sites 1 to 9 are all located within a 300 m radius of the EC tower. This area was known as the EC footprint which was the area from which the CO_2 flux is mainly being measured by the EC tower.

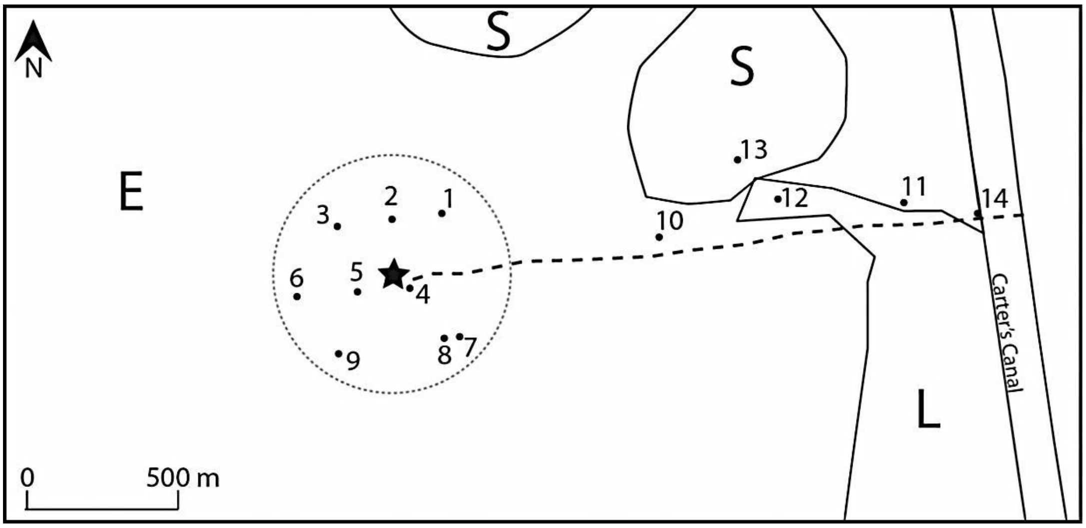

Figure 3.8: Location of sites within Kopuatai bog. The star indicates the location of the eddy covariance (EC) tower and the dotted circle represents the general extent of the EC footprint. Sites 1 to 9 are located within the footprint. E indicates *E. robustum* as the dominant vegetation, S is the area dominated by *S. ferrugineus* rushland and L is the area dominated by *L. scoparium* scrub. Dashed line is the track to the EC tower. Figure is based on Irving *et al.* (1984) and Department of Conservation (2009).

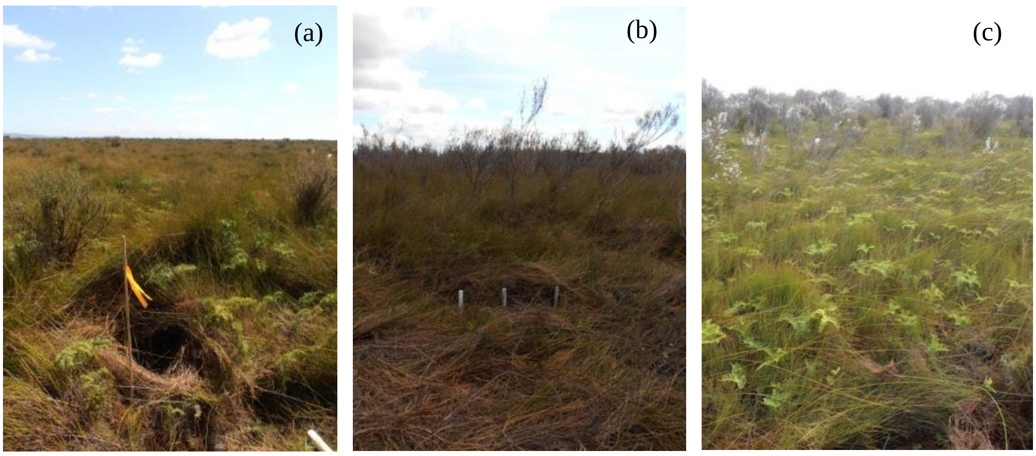

Figure 3.9: Sites 1 to 9 are dominated by *E. robustum* with some *Baumea spp.* or *S. brevifolia*. Site 2 (a) was a typical site within the EC footprint. Sites 10 (b) and 11 (c) were also dominated by *E. robustum* and are located 920 m and 210 m into the bog respectively. Sampling piezometers can be seen in figure (b).

Site 10 was located mid-way along the track to the EC tower approximately 920 m from Carter's Canal. Site 11 was near the edge of the track about 210 m from Carter's Canal (Figure 3.9). Site 12 was set up within an *L. scoparium* (manuka) stand, and site 13 was set up in a stand of *S. ferrugineus* (Figure 3.10). Site 14 was located at Carter's Canal at the edge of the bog (Figure 3.11), although there was a buffer zone between the canal and farmland of approximately 150 m.

Figure 3.10: (a) Site 12 where vegetation is dominated by *L. scoparium* with a lower canopy of *E. robustum* and *G. dicarpa*. (b) Site 13 where vegetation is dominated by *S. ferrugineus* with some *L. scoparium* shrubs and a lower canopy of *E. robustum*.

Figure 3.11: Site 14 at Carter's Canal where water samples were retrieved for analysis.

Chapter Four

Peat and vegetation characteristics

4.1 Introduction

Peat physical and chemical characteristics were studied in order to determine any differences between sites that may affect DOC concentrations. Properties measured were degree of peat humification, dry bulk density, total carbon, nitrogen and phosphorus, and pH. The vegetation composition at each of the 13 sites was also assessed.

4.2 Methods

4.2.1 Peat humification index

The state of decomposition of peat was assessed by the extent to which plant structure is visible and the colour of the peat (Clymo, 1983). Field assessments are usually made using the von Post humification index which consists of a numerical scale based on specific criteria. Criteria include the colour of the fluid expressed when a portion of peat is squeezed in the hand, and the proportion and character of the material which remains in the hand after squeezing (Clymo, 1983).

The state of decomposition was assessed three times at each site for peat samples extracted down to a depth of 20 cm and given a score of H1 to H10 using the criteria for peat described by Clymo (1983) (Appendix A). These results were then averaged for each site.

4.2.2 Dry bulk density

Peat cores for dry bulk density (DBD) determination were taken from the top 10 cm of peat from the surface, excluding the top 1–2 cm. Three were taken from each site within approximately a 1 m radius from the area where water samples were extracted. Samples were collected by coring, where a sharpened thin-walled metal cylinder (volume 147 cm^3) was gently rotated to cut into the peat at right angles to the ground surface, taking care to avoid compressing the peat. The cylinder was then cut out and the peat at either end was trimmed to a plane surface (Figure 4.1). The core was gently pushed out of the cylinder, bagged and transported to the laboratory where it was oven-dried at 105°C until a constant weight was achieved and weighed. The procedure was based on that described by Gradwell and Birrell (1979).

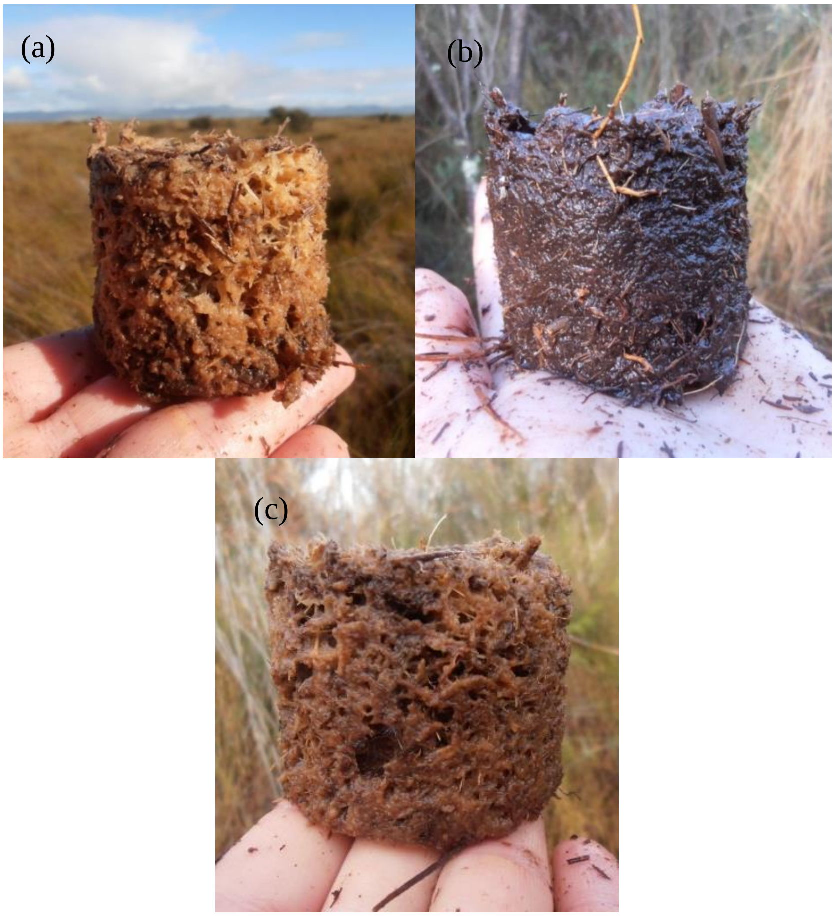

Figure 4.1: Typical peat cores from (a) *E. robustum* (b) *L. scoparium* and (c) *S. ferrugineus* sites.

4.2.3 Carbon, nitrogen, phosphorus and pH

Total carbon and total nitrogen

Portions of the three cores from each site were bulked together after drying. The cores from sites 1, 2 and 3 were bulked together, sites 4, 5 and 6 were bulked together and sites 7, 8 and 9 were bulked together. Cores from sites 10, 11, 12 and 13 were analysed individually. This produced a total of seven samples. The dried samples were then ground in a blender until a fine powder was achieved. Portions of these samples were analysed by a Truspec LECO CN machine via combustion at the University of Waikato laboratory for total carbon (TC) and total nitrogen (TN). The percentages of C and N were then adjusted using bulk density to calculate volumetric concentrations in mg cm^{-3}.

Total phosphorus

Portions of the ground samples were sent to Hills Laboratories (Hamilton) to determine total phosphorus (TP). This was phosphorus extracted by hot, concentrated acid and included unavailable inorganic and organic forms of P. This value is not well correlated to plant available P but does provide a measure the amount of P in the soil phosphorus cycle[6] and can be compared to Clarkson et al (2004) values for TP in peat from New Zealand bogs and swamps.

pH

pH was measured in the field at sites 4, 5, 6, 10, 11 and 14. This represented a transect from the middle to the eastern edge of the bog and within the canal. Peat water was collected from three piezometers (piezometer A, B and C at depths 0–0.3, 0.3–0.6, 0.6–1.0 m respectively) at each site. A pH and conductivity meter (YSI model 63) was used to measure the relative levels of each water sample once readings had stabilised. The pH meter was calibrated in the field using buffer solutions (pH 4 and 7).

4.2.4 Vegetation composition and patterns

Plots were established and vegetation composition assessed at each of the sites (excluding the canal site) to determine the dominant vegetation type.

Plot structure and composition was assessed using the methods described by Clarkson *et al.* (2004b) that includes estimating percentage species cover. At each site the vegetation was surveyed within a two metre radius of the water sampling wells in order to assess vegetation potentially affecting the water sample obtained from each area. The percentage cover of species was assessed for the canopy and

[6] *Technical notes: Soil phosphorus tests.* Hills Laboratories website: http://www.hill-laboratories.com/file/fileid/17695, 16/01/13.

ground layers along with maximum vegetation height. All sites were surveyed by the same observer.

4.2.5 Water table monitoring

Manual measurements of the water table were made at each DOC sampling site throughout the year. A pipe was inserted into the peat at each site and water table height was measured from the top of the water table (observed within the pipe) to the surface of the peat.

4.3 Results

4.3.1 Peat humification index

The degree of peat humification was generally very low across all sites. There was a range in the von Post index of 1 to 1.3 in the EC footprint (sites 1 to 9) and site 10 (Figure 4.2). Humification increased slightly at site 11 (edge of bog) to 1.7 and at site 13 (*S. ferrugineus* site) to 1.5. The most obvious difference in peat humification was at site 12 (*L. scoparium* site) where humification averaged 4.7. Peat at site 12 was weakly to moderately decomposed and yielded turbid brown waters with mushy residue.

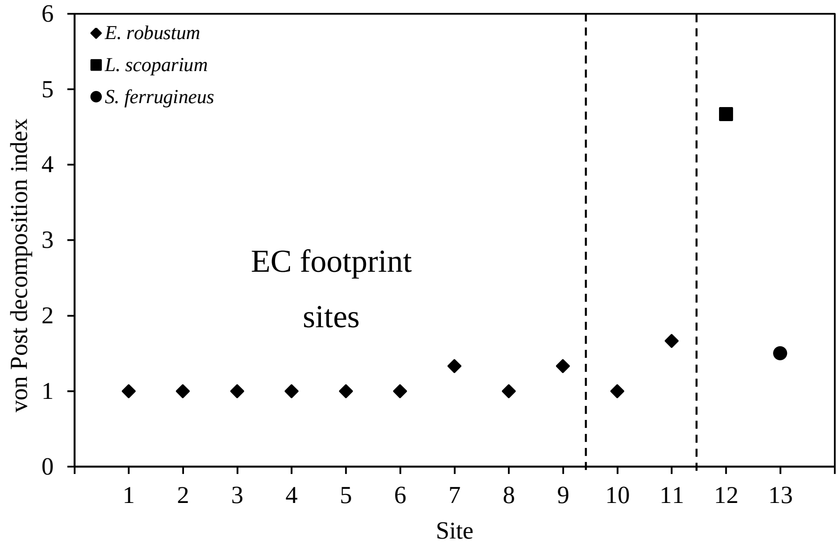

Figure 4.2: Peat decomposition in the top 20 cm at sites 1 to 13 at Kopuatai bog using the von Post decomposition index. Each point represents the mean of three cores. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

4.3.2 Dry bulk density

Lowest bulk density was found at site 13 (*S. ferrugineus* site), followed by site 2 in the EC footprint (Table 4.1, Figure 4.3). The highest bulk density was found at site 12 (*L. scoparium* site) followed by site 11 at the edge of the bog. The mean (± standard deviation) bulk density for peat at Kopuatai was 44.9 ± 9.05 kg m^{-3} (n = 39 cores) and for only *E. robustum* sites excluding site 11 it was 43.5 ± 4.69 kg m^{-3} (n = 30).

Bulk density was generally higher in the southern transect of the EC footprint. The mean of the southern transect bulk densities was significantly different (using a paired t-test) from the middle transect (p = 0.006) and was not significantly different from the northern transect (p = 0.07). Values of bulk density were similar between the northern and middle transects (p = 0.62).

Table 4.1: Bulk density values (mean ± SD) for each site. Three cores were taken at each site and bulk density values are averages of these.

Site	Location	Mean bulk density kg m^{-3}
Site 1		39.3 ± 5.44
Site 2	Northern transect	37.5 ± 7.60
Site 3		47.3 ± 7.75
Site 4		38.0 ± 1.61
Site 5	Middle transect	38.7 ± 0.97
Site 6		43.2 ± 4.30
Site 7		48.1 ± 7.19
Site 8	Southern transect	46.4± 10.61
Site 9		49.6 ± 4.30
Site 10	920 m into bog	46.7± 10.30
Site 11	210 m into bog	56.9 ± 11.47
Site 12	*L. scoparium* site	59.7 ± 6.22
Site 13	*S. ferrugineus* site	37.3 ± 7.64

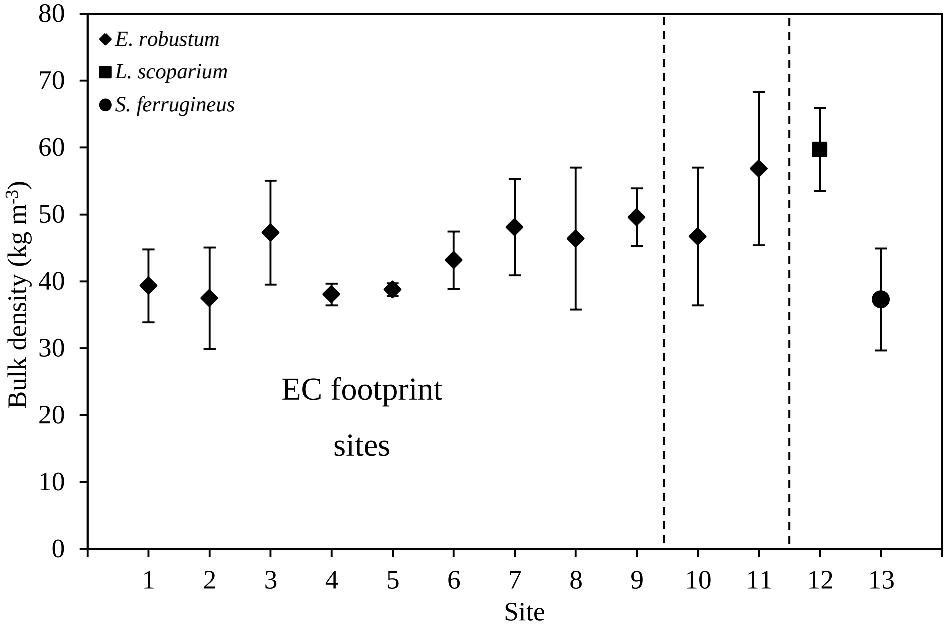

Figure 4.3: Average bulk density (± SD) of cores taken at sites 1 to 13 at Kopuatai bog (*n* = 3). Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

4.3.3 Carbon, Nitrogen, Phosphorus and pH

Total carbon and total nitrogen

Seven samples of peat were analysed for TC and TN. Gravimetric carbon (% by weight) was very similar across all sites ranging from 43.2% (site 12) to 44.7% (site 11). When adjusted by bulk density, volumetric carbon ranged from 16.6 mg cm^{-3} (site 13) to 25.8 mg cm^{-3} (site 12) (Figure 4.4).

TN was similar across all sites with a range of 0.51% (site 10) to 1.05% (site 12). Expressed on a volumetric basis, TN ranged from 0.24 mg cm^{-3} (site 10) to 0.63 mg cm^{-3} (site 12) (Figure 4.5).

Total phosphorus

TP concentrations ranged from 0.0035 mg cm^{-3} (site 10) to 0.025 mg cm^{-3} (site 12) (Figure 4.6). The detection limit for TP at Hills laboratory was 40 mg kg^{-1} and peat TP values fell between 75 to 419 mg kg^{-1}.

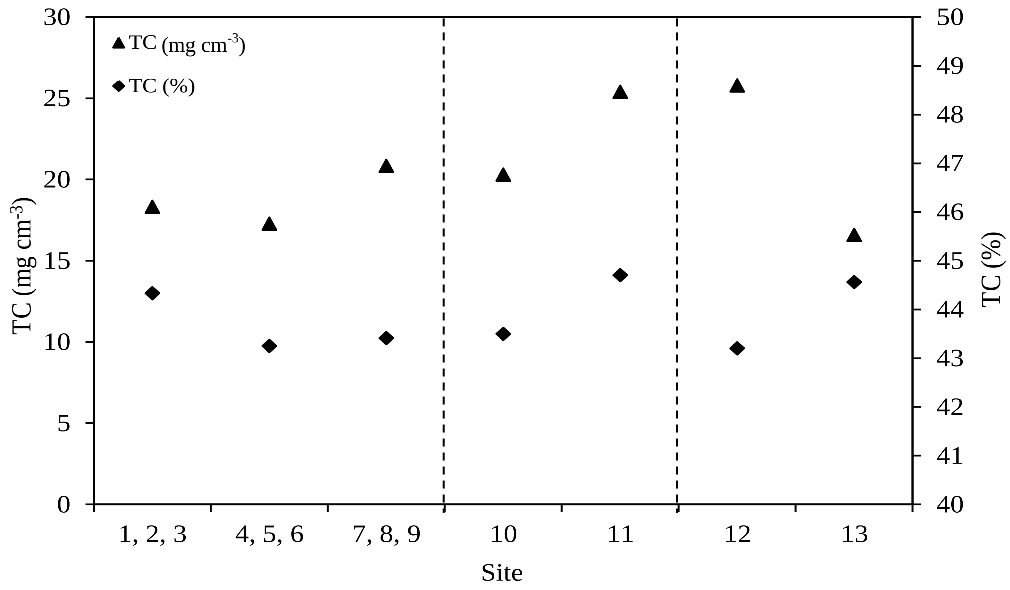

Figure 4.4: Gravimetric and volumetric values of total carbon (TC) from seven samples of peat from Kopuatai. Samples across sites 1, 2 and 3, sites 4, 5 and 6 and sites 7, 8 and 9 were bulked together to make three samples. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

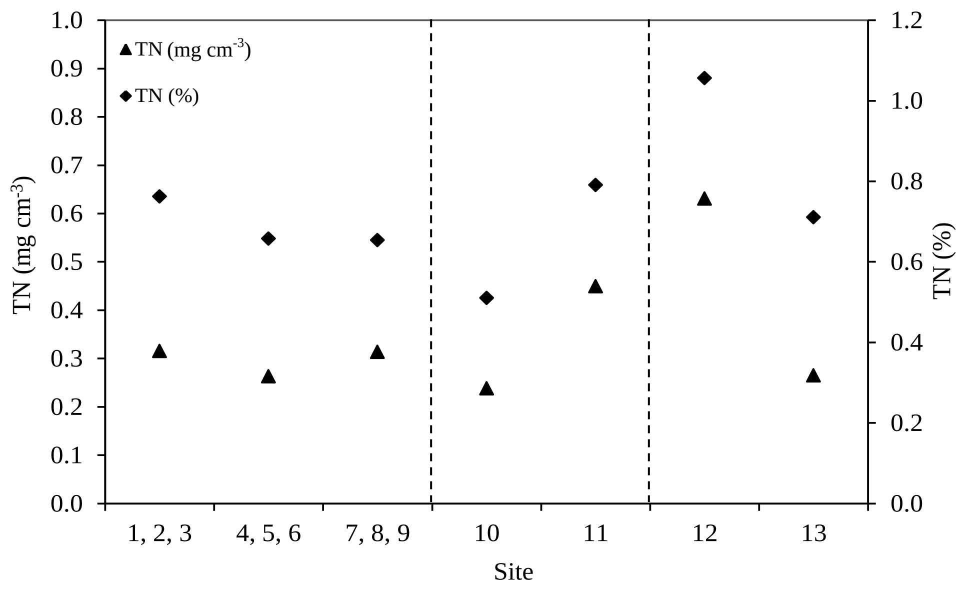

Figure 4.5: Gravimetric and volumetric values of total nitrogen (TN) from seven samples of peat from Kopuatai. Samples across sites 1, 2 and 3, sites 4, 5 and 6 and sites 7, 8 and 9 were bulked together to make three samples. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

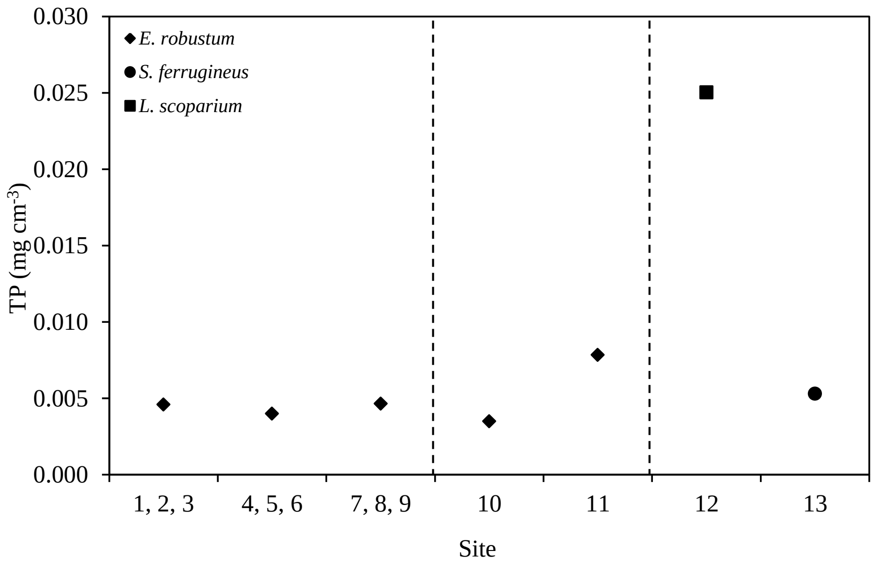

Figure 4.6: Gravimetric values of total phosphorus (TP) from seven samples of peat from Kopuatai. Samples across sites 1, 2 and 3, sites 4, 5 and 6 and sites 7, 8 and 9 were bulked together to make three samples.

C:N, C:P and N:P

The ratios C:N, C:P, and N:P are more characteristic of wetland classes and vegetation types and can indicate degree of nutrient enrichment (Clarkson *et al.*, 2004b). The lowest C:N ratio of 40.9 was measured at the site 12. The maximum was measured at the site 10 with a ratio of 85.2 (Figure 4.7).

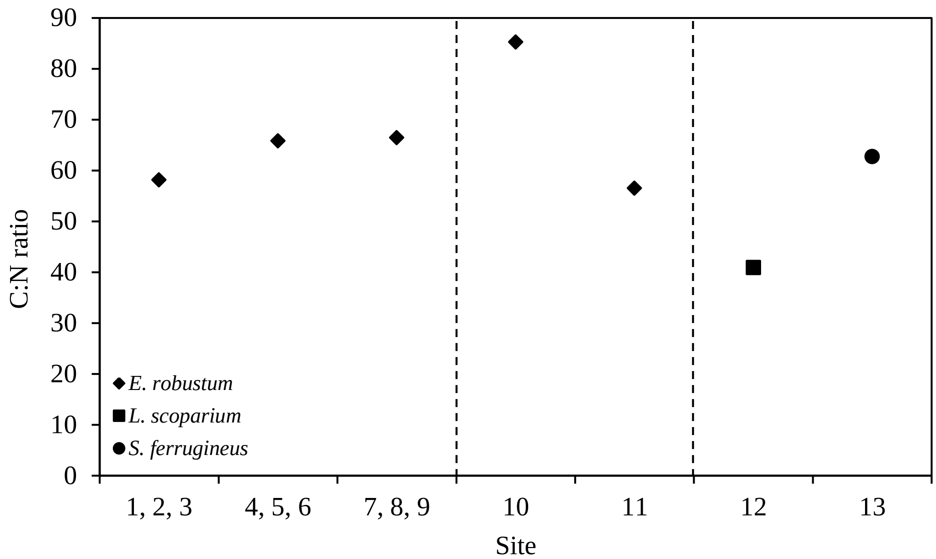

Figure 4.7: C:N ratios from seven samples of peat from Kopuatai. Samples across sites 1, 2 and 3, sites 4, 5 and 6 and sites 7, 8 and 9 were bulked together to make three samples. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

The lowest C:P ratio occurred at site 12 with a ratio of 1031 and the maximum occurred at site 10 with a ratio of 5800. The lowest N:P ratio again occurred at site 12 (25.2) and the maximum again occurred at site 10 (68.7) (Figure 4.8).

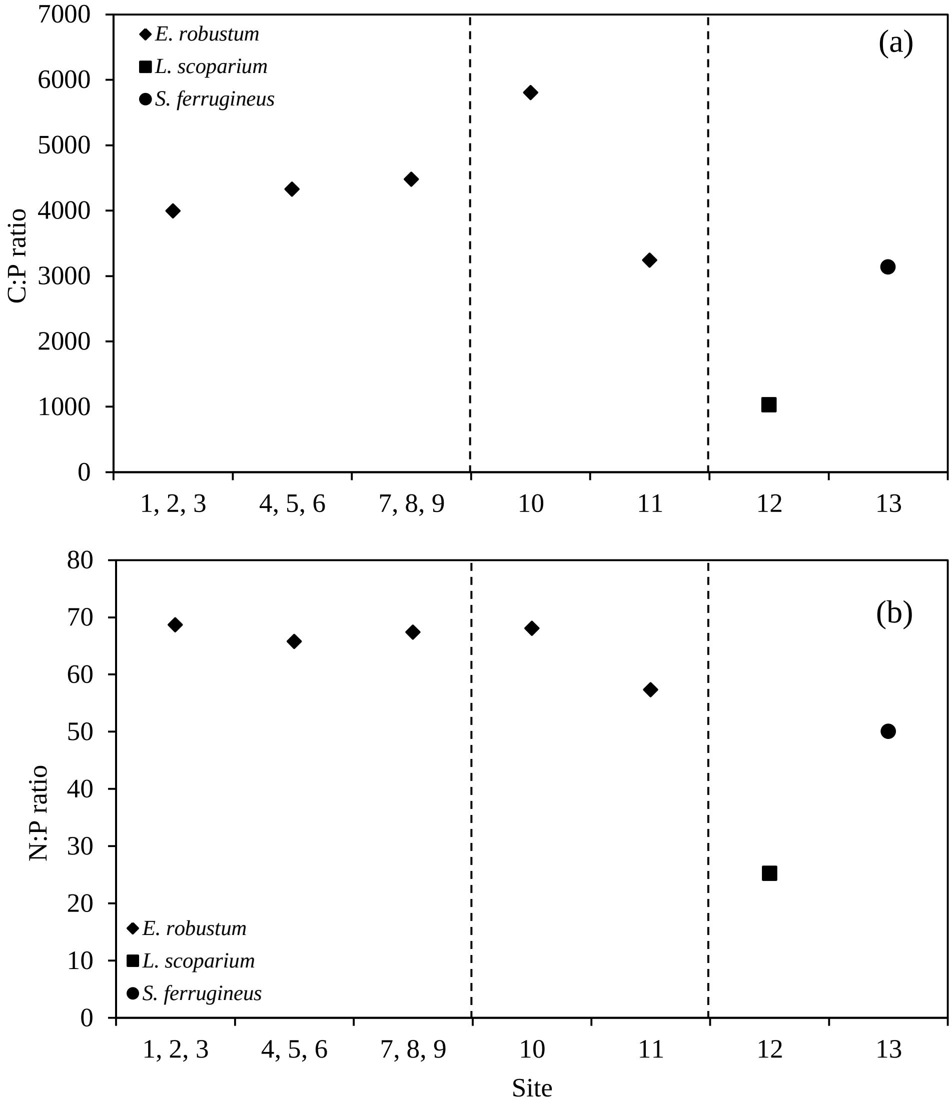

Figure 4.8: (a) C:P and (b) N:P ratios in seven samples of peat from Kopuatai. Samples across sites 1, 2 and 3, sites 4, 5 and 6 and sites 7, 8 and 9 were bulked together to make three samples. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium* and *S. ferrugineus* sites.

pH

pH was measured on 2 August 2012. There had been heavy rainfalls during the previous five days and sites were quite flooded. Only pH at depths 0–0.3 m (from piezometer A) and 0.6–1.0 m (piezometer B) are shown here as 0–0.3 and 0.3–0.6 m (piezometer C) values were very similar for all sites. Sites 4 and 12 had pH values from piezometer A and C that were similar. The highest pH was measured in the canal (site 14) (Figure 4.9).

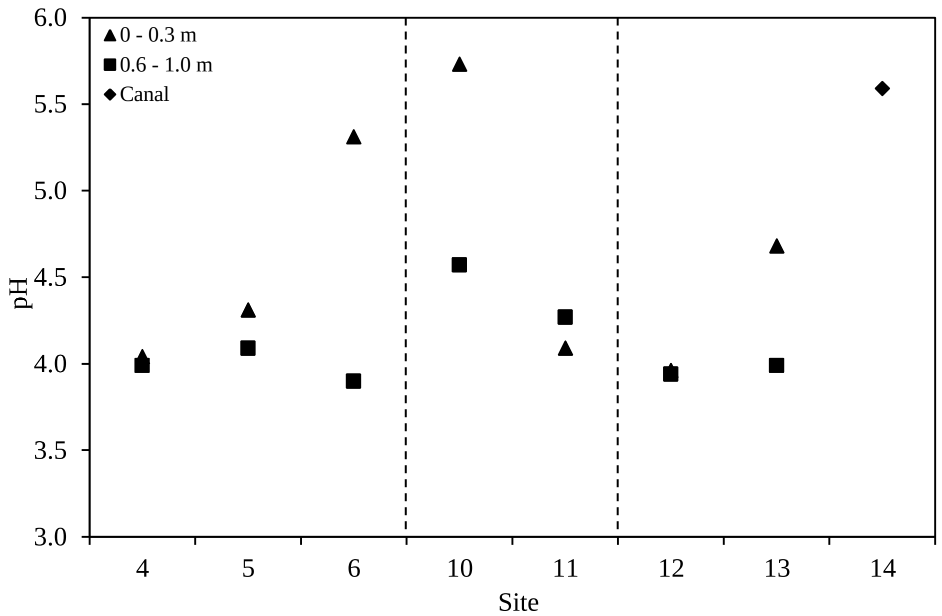

Figure 4.9: Comparison of pH values across sites and depths. Vertical dashed lines separate EC footprint sites from the two transect sites and from the *L. scoparium*, *S. ferrugineus* and canal sites.

4.3.4 Vegetation composition and patterns

The individual assessments of vegetation composition at each site can be found in Appendix C. Table 4.2 gives the average percentage of each vegetation type at sites 1 to 9 and the total percentage of each vegetation type at sites 10 to 13. *E. robustum* was present across all sites, dominating canopy cover at sites 1 to 11, and present as both canopy and groundcover at sites 12 and 13. At sites 1 to 11, *E. robustum* reached heights between 0.7 and 1 m in the open but when it was supported amongst *S. ferrugineus* or *L. scoparium* (sites 12 and 13) it reached heights of over 1.5 m. *L. scoparium* at site 12 reached a maximum height of approximately 3.5 m, and *S. ferrugineus* at site 13 reached a maximum height of approximately 2.5 m (vegetation height information along with laboratory analysis results in Appendix D).

Baumea spp. was more common in the north-eastern area of the EC footprint, where there were wetter conditions (section 4.2.5). The coverage of *S. brevifolius* increased in the southern transect where there were relatively drier conditions due to lower water tables. In this transect, the *E. robustum* canopy was occasionally more open and in some areas *Sphagnum* dominated and it could almost be considered a lawn.

3.7.1 Water table monitoring

Throughout the year water table depth below the peat surface ranged from approximately 0 to –0.15 m across the EC footprint sites (Figure 4.10). Out of the EC footprint sites, site 2, 7, 8 and 9 consistently had the lowest water tables and sites 3 and 6 consistently had the highest water tables. In August, September and October water tables were at their highest, with site 6 nearly reaching 15 cm above the surface. Lower water tables at sites 7, 8 and 9 were consistent with the drier conditions in the southern transect. Higher water tables at sites 1, 3 and 6 were consistent with wetter conditions in the northern and also western areas of the EC footprint.

Outside of the EC footprint, sites 10, 11, 12 and 13 water table depths were compared (Figure 4.11). Site 10 had the lowest water tables reaching approximately 0.2 m below the peat surface. The water table at the *L. scoparium* site (site 12) was also relatively high compared to other sites.

Table 4.2: Vegetation canopy cover percentage and ground cover of sites 1 to 13. Percentages were averaged (± SD) across sites 1 to 9 (the eddy covariance flux footprint).

	Average of sites 1 to 9		Site 10		Site 11		Site 12		Site 13	
Vegetation	% canopy cover	% ground cover	% canopy cover	% ground cover	% canopy cover	% ground cover	% canopy cover	% ground cover	% canopy cover	% ground cover
Empodisma robustum	67 ± 8.3		65		68		30	60	20	60
Sporadanthus ferrugineus									60	
Baumea spp.	17 ± 9.7		20		15					5
Schoenus brevifolius	6 ± 8.9									
Gleichenia dicarpa	9 ± 6.8		5		15			10		10
Leptospermum scoparium	<1 ± 0.9		5		1		70		15	
Epacris pauciflora	<1 ± 1.7		5		1				5	
Sphagnum spp.		9 ± 6.8								
Liverwort		6 ± 9.5		50				20		5
Lycopodium spp.		2 ± 3.5		5						

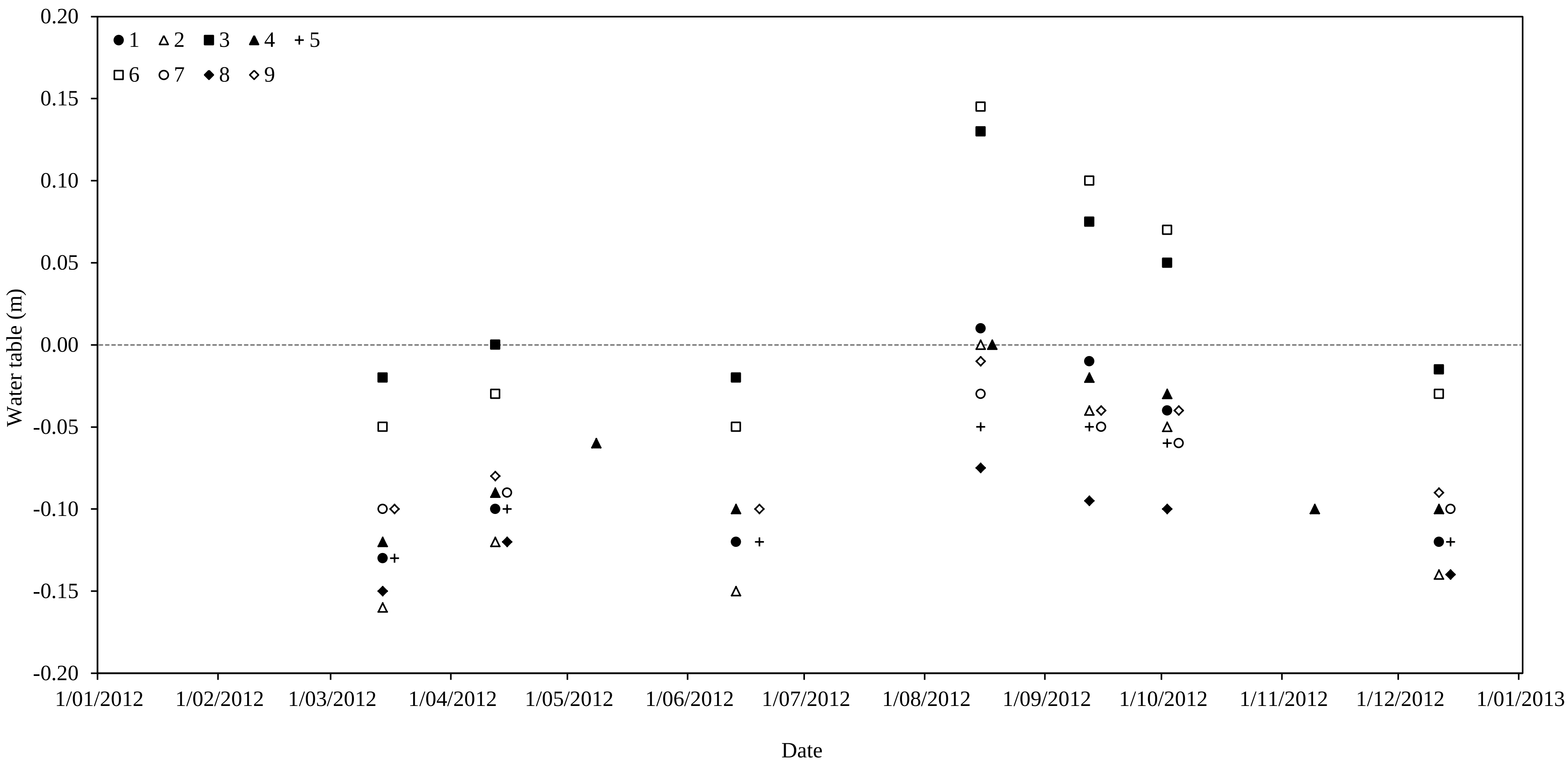

Figure 4.10: Manual water table measurements of sites 1 to 9 in the EC footprint. The horizontal dashes line represents the peat surface. Where two sites fell at the same depth on the same day, the measurement has been offset by three days.

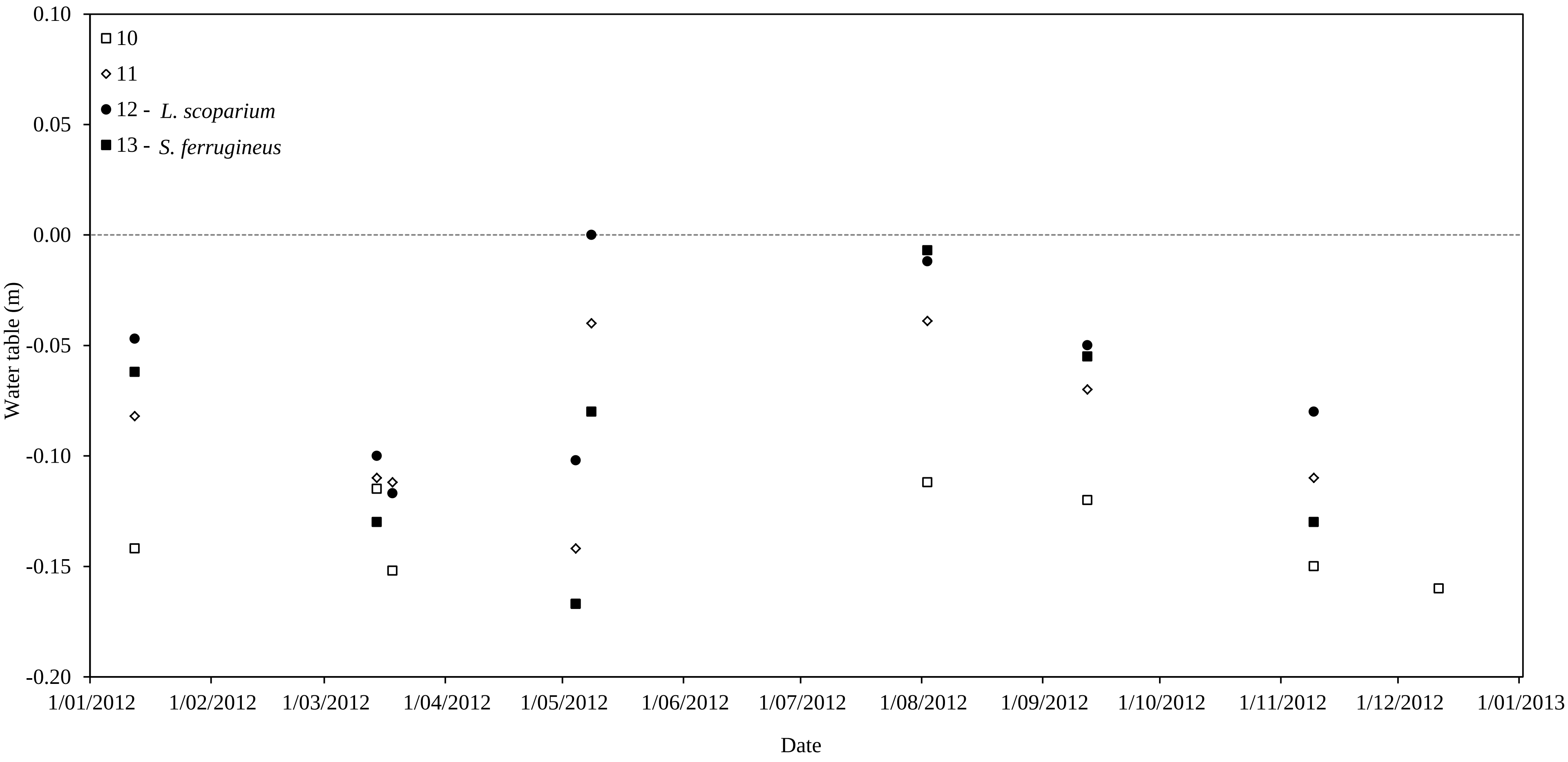

Figure 4.11: Manual water table measurements of sites 10 to 13. The horizontal dashes line represents the peat surface.

4.4 Discussion

Bulk density, humification index and pH can give an indication of the condition of a wetland at that point in time. The results presented in this chapter were from unreplicated samples, so are illustrative only. The samples for TC, TN, and TP were bulked samples so spatial variability in the EC footprint was not quantified.

Peat humification

The low von Post values of 1 to 2 at Kopuatai (Figure 4.2) are indicative of the stage of bog development under *E. robustum* and *S. ferrugineus*. As peat accumulates, the peatland surface becomes isolated from nutrient inputs from ground water. Plants respond to the lower nutrient supply by lowering the concentrations of nutrients in their tissues, withdrawing nutrients during senescence and also may produce substances to inhibit herbivores and microbial activities. These factors can slow litter decomposition and therefore produce less degraded peat (Clarkson *et al.*, 2004a). Relatively high von Post values were found at site 12 *(L. scoparium* site) of 4 to 5, indicating higher peat decomposition at this site.

Dry bulk density

DBD can be used as an indicator of peat degradation. DBD is low for all peats compared to mineral soils, but are generally lowest in fibric peat (least decomposed peat) at less than 90 kg m^{-3}. These peats generally occur in the top 30 cm of the surface within the acrotelm of bogs (Verry & Boelter, 1978). A comparison between samples taken in this study with Kopuatai DBD values reported by Clarkson *et al.* (2004a) and only including cores with a von Post of 2 or less gives an average DBD of 43.9 ± 11.1 kg m^{-3} which is almost identical to the average from sites 1 to 9 in the present study of 43.1 ± 7.0 kg m^{-3}. King (1999) measured DBD of peat at Kopuatai, which ranged from 40 and 65 kg m^{-3}, and the results were similar to values found in the present study.

With an average of 44.9 ± 9.05 kg m^{-3} across all 13 sites, peat DBD at Kopuatai was low compared to other bogs around New Zealand. Average bulk densities across peat wetlands in the Waikato (Duckcreek, Whangamarino, Opuatia, Torehape, Kopuatai and Moanatuatua) were measured by Clarkson *et al.* (2004a) to be 83.3 ± 43.77 kg m^{-3} with minimum and maximum values of 20.0 kg m^{-3} and 234.0 kg m^{-3} respectively (from 69 sites). Blyth (2011) measured bulk densities between 50 and 100 kg m^{-3} at Whangamarino wetland increasing to 280 kg m^{-3} towards the wetland edges near farmland and the Whangamarino River. Research at Opuatia wetland by Fritz *et al.* (2008) measured peat bulk density measurements averaging 90 kg m^{-3} with a range of 50 to 180 kg m^{-3}. These were assessed from cores taken from a transect through the peatland and no spatial trend was found except for sites near dryland where bulk densities exceeded 100 kg m^{-3}.

There was no obvious spatial trend in bulk densities at Kopuatai except for slightly larger values at sites 11 and 12 and where the southern transect in the EC footprint had significantly higher values than the middle transect. DBD was generally variable across sites. Higher bulk density can either mean greater amounts of mineral material within the sample or a higher degree of peat decomposition and consolidation. At site 12 (*L. scoparium*), there was a higher bulk density and, although the inorganic fraction of the peat cores was not measured, it is unlikely that there would be an addition of mineral particles this far into the bog (700 m into the bog). Therefore higher bulk density at site 12 was likely due to a higher amount of peat decomposition and consolidation and this is supported by the higher mean von Post index of 4.7. The peat was more decomposed at this site resulting in less pore spaces and more compaction.

TC, TN and TP

Enrichment by nutrients can alter vegetation composition and health of wetlands (e.g. establishment of invasive weeds) as species vary in their ability to grow at different nutrient levels. Within bogs, species diversity is low with vegetation dominated by a small number of species that are specialised to grow under low nutrient levels. As nutrients are added, species diversity increases until tall, productive species out compete others for light and the number of species declines (Clarkson *et al.*, 2004b). Clarkson *et al.* (2004b) have developed indicators of nutrient enrichment for New Zealand wetlands. Table 4.3 lists means and ranges of TC, TN and TP along with ratios of C:N, C:P and N:P, including results from this study.

Table 4.3: Means and ranges (in brackets) for peat or soil parameters of six bogs and 17 swamps sampled in New Zealand by Clarkson *et al.* (2004b) and seven bog sites sampled at Kopuatai bog during this study. TC = total carbon, TN = total nitrogen and TP = total phosphorus.

	Bogs (6)	Swamps (17)	Kopuatai (7)
TC (mg cm^{-3})	92.7 (24.1-239.8)	39.8 (5.2-100.6)	20.7 (16.6-25.8)
TN (mg cm^{-3})	0.82(0.02-1.83)	2.12 (1.15-3.24)	0.35 (0.23-0.63)
TP (mg cm^{-3})	0.08 (0.01-0.20)	0.28 (0.15-0.59)	0.008 (0.004-0.025)
C:N	48.5 (35.9-79.7)	18.0 (14.2-30.6)	62.3 (40.9-85.2)
C:P	1904 (533-4221)	163 (45-435)	3715 (1031-5800)
N:P	39.0 (20.6-81.6)	9.1 (4.0-20.6)	57.5 (25.2-68.7)

TC is usually higher in bogs than swamps (Clarkson *et al.*, 2004b). TN and TP do not differ greatly between classes of wetlands (bog, fen or swamp) but there can be large variations within individual wetlands. In the current study, the gravimetric C concentration (g g^{-1}) in peat samples was very similar for all sites. Site 12 had the lowest percentage of C per sample but once this value was adjusted to volumetric C, site 12 had the highest C density consistent with higher DBD. The values of volumetric C ranged from 16.6 to 25.8 mg cm^{-3} which was less that the range of TC listed for bogs by Clarkson *et al.* (2004b) of 24.1 to 239.8 mg cm^{-3} likely reflecting the low bulk density at each of the sites.

Restiad peat bogs in New Zealand have very low nutrient inputs and the vegetation N and P concentrations in tissues are also very low, with P usually being the growth limiting nutrient (Clarkson *et al.*, 2004b). Total N values at Kopuatai ranged from 0.24 to 0.63 mg cm^{-3} and the highest values were at site 12 (Figure 4.5). These values fell within the range of 0.02 to 1.83 mg cm^{-3} that Clarkson *et al.* (2004b) reported for bogs. Total P values ranged from 0.0035 to 0.025 mg cm^{-3} and these were effectively at the bottom of the range reported by Clarkson *et al.* (2004b). The highest value occurred at site 12 and this was the only value that fell within the TP range stated for bogs by Clarkson *et al.* (2004b) of 0.01 to 0.20 mg cm^{-3}. This may reflect the low bulk density values found at Kopuatai in this study.

Ratios of nutrients are more diagnostic of classes of wetland and vegetation types and these can be used to detect eutrophication. C:N, C:P and N:P ratios are generally higher in bogs than in swamps and reflect the accumulation of organic matter within bogs and the low nutrient input (Clarkson *et al.*, 2004b). C:N ratios at Kopuatai ranged from 40.9 to 85.2 and this range compared well with that from Clarkson *et al.* (2004b) of 35.9 to 79.7. The C:P ratios ranged from 1031 to 5800 in comparison to Clarkson *et al.* (2004b), who reported for bogs a range of 533 to 4221. The C:P ratio at Kopuatai was high reflecting the lack of phosphorus in the ecosystem. N:P ratios ranged from 25.2 to 68.7 at Kopuatai compared to other bog sites of 20.6 to 81.6 (Clarkson et al., 2004). The low levels of nutrients within Kopuatai reflect the sole water source being rainfall and low nutrient addition from other sources, such as fertiliser drift (Schipper *et al.*, 1998) and dry deposition of ammonia (Blyth, 2011).

The physical and chemical parameters at Kopuatai did not vary much spatially and were indicative of an undisturbed bog (Clarkson *et al.*, 2004a). The *L. scoparium* site (site 12) stood out as having a higher bulk density and von Post index compared to the *E. robustum* and *S. ferrugineus* sites, along with lower C:N, C:P and N:P ratios. Although these values were all within normal bog ranges (Clarkson *et al.*, 2004b), they were higher at site 12 than the other sites at Kopuatai dominated by restiads.

The higher bulk density and von Post values at the *L. scoparium* site may result from this vegetation lacking the allelopathic properties of the restiads that have been shown to retard decomposition of organic matter (Kuder *et al.*, 1998). The higher TP in peat beneath *L. scoparium* may be because *L. scoparium* does not have the ability to scavenge out P whereas low TP under *S. ferrugineus* and *E. robustum* could indicate ability to scavenge P (Clarkson *et al.*, 2005). Temperature, soil aeration and nutrient availability are important controlling factors of organic matter decomposition in peatlands, through their effects on microbial and root activities (Carrera *et al.*, 2011). There were higher nutrient levels in the peat below the *L. scoparium* stand and the difference in nutrient availability could be why the degree of decomposition was higher at this site. It is also possible that *L. scoparium* is growing in an area of converging water flows, leading to a concentration of nutrients.

pH

Bogs generally have a pH below 4.0 because nutrient uptake by plant roots is accompanied by proton (H^+) excretion from root cells, which lowers the pH. Although this occurs in all wetland types, bogs remain acidic because rainwater, as the sole water source, has little ability to buffer an increase in H^+ concentrations (Clarkson *et al.*, 2004b; Sorrell & Gerbeaux, 2004). pH values measured at Kopuatai were generally at or below 4. The average pH at a depth of 0.6–1.0 m (piezometer C) was 4.1, whereas, the average pH of peat pore water at the surface down to 0.3 m depth was 4.5. It was assumed that heavy rainfalls lead to dilution of the shallow peat pore water. The pH in the canal was 5.6 and likely reflects increased dilution by rainwater, surface flows and groundwater. Furthermore, the impact of farming practices (which are closer to the canal than the other sites) such as NH_4^+ inputs through volatilisation and deposition may have increased the pH.

Vegetation composition and water table depths

Sites 1 to 11 were all dominated by *E. robustum* (60–68% cover) with *Baumea spp.* and *G. dicarpa* also present. Site 10 had a more open canopy than the other *E. robustum* sites and there was a large percentage (50%) of the ground covered with liverworts. Site 12 was dominated by a canopy of *L. scoparium* (70%) with the ground cover dominated by *E. robustum*. Site 13 had a canopy dominated by *S. ferrugineus* (60%) with the ground cover dominated by *E. robustum*. Vegetation present in Kopuatai was indicative of phase 2 and 3 of restiad bog vegetation succession reported in Clarkson *et al.* (2004a). Phase 2 represents the establishment and dominance of *E. robustum* and phase 3 represents the establishment of the *S. ferrugineus*, which becomes the dominant vegetation such as at site 13 (Figure 3.3).

4.4.1 Summary

- Peat humification was generally low at Kopuatai with von Post values between 1 and 2, except at the site dominated by *L. scoparium* (von Post value of 4.7). DBD was highest at this latter site and the bog edge site (site 11).
- DBD in areas dominated by *E. robustum* were very low (43.5 ± 4.69 kg m^{-3}) compared to measurements from other bogs in New Zealand.
- All sites had TC, TN and TP values generally in the range of other bogs and C:N, C:P and N:P ratios were also within range. Site 12 has the highest values compared to other sites.
- *E. robustum* was present at all sites and was the dominant vegetation at sites 1 to 11. *L. scoparium* dominated the canopy at site 12 and *S. ferrugineus* dominated the canopy at site 13.

Chapter Five
Seasonal and spatial trends in DOC concentration

5.1 Introduction

In order to determine drivers of variability in DOC concentrations at Kopuatai, 14 long term sampling sites were established. Water samples were analysed for DOC concentration throughout the year and peat temperature and water table regimes were also monitored. These data were used to determine whether DOC concentration varied seasonally and if temperature, precipitation and water table height were drivers of DOC variability. DOC concentrations in peat pore water under three vegetation types were analysed in order to determine if vegetation was an important driver of spatial variability of DOC concentration.

5.2 Methods

5.2.1 Sampling procedure

Three sampling piezometers constructed from 20 mm PVC pipe were installed at each site. Holes were drilled to create a screen to sample peat pore water from specific depths. Piezometer A sampled from 0–0.3 m depth, piezometer B sampled from 0.3–0.6 m depth and piezometer C sampled from 0.6–1.0 m depth (Figure 5.1). Piezometers were inserted into the peat in February 2012 and left in place for the duration of the research.

Peat pore water from sites 1 to 13 was sampled once every two months over the year 1 February 2012 to 31 January 2013 (Figure 5.2). Sites 1 to 9 and sites 10 to 13 were sampled on alternate months from each other. On the months that sites 1 to 9 were sampled, they were bulked by depth. All three depths at site 4 were individually sampled every month (for sampling regime see Appendix C). Carter's Canal (site 14) DOC concentrations were measured every one to two months by collecting a sample from the top 0.3 m of the water column. Sites 1 to

11 were in *E. robustum* vegetation and Sites 12 and 13 were in *L. scoparium* and *S. ferrugineus* vegetation respectively.

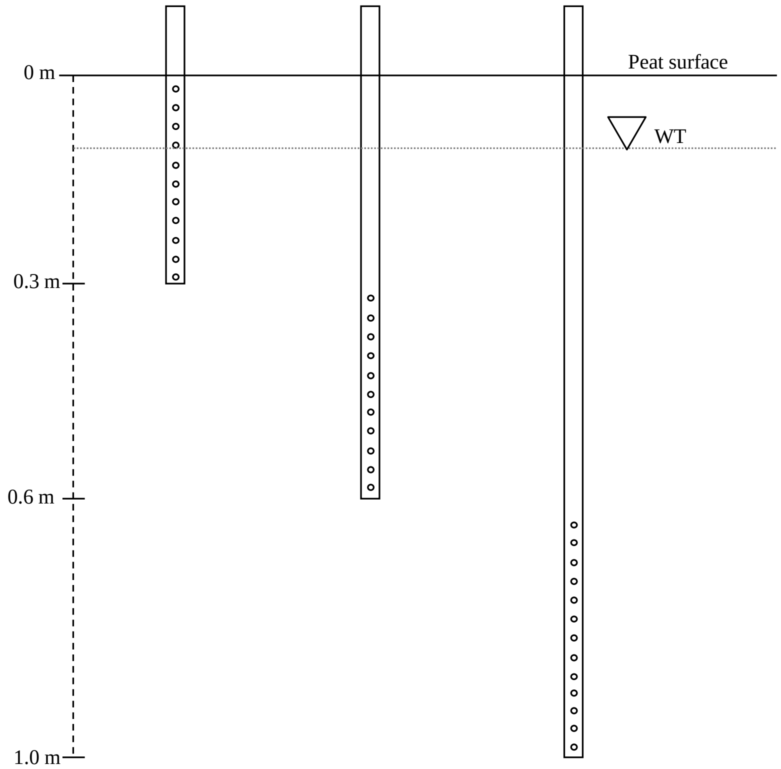

Figure 5.1: Example of how the sampling piezometers were positioned in the field. The three piezometers at each site were positioned approximately 0.3 m apart. WT is the approximate position of the water table.

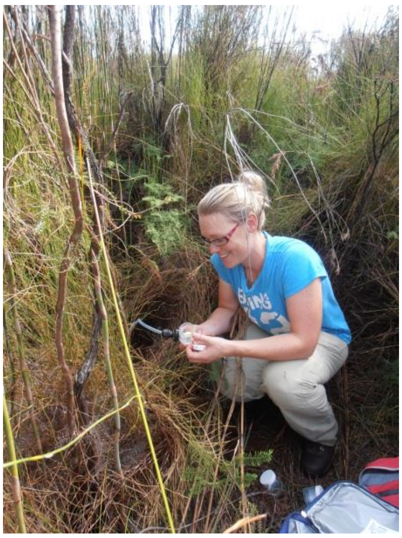

Figure 5.2: Using a pump to extract peat pore water from the sampling piezometers at site 13.

To obtain an average DOC concentration from each site from samples taken from three different depths, a weighted average was used, following King (1999). King (1999) measured hydraulic conductivity at different depths and at a number of sites across the width of Kopuatai and, using this information, calculated the relative contribution towards total groundwater discharge for 0.2 m depth intervals down to 3.25 m (Figure 3.5). He found that 85% of total lateral discharge occurred in the top 1 m. The weighted contribution of DOC samples at each depth interval was calculated by applying the contribution towards lateral flow from King (1999), for example, of the 85%, 56% was contributed by the 0–0.3 m interval, 28% from 0.3–0.6 m and 16% from 0.6–1.0 m. The weighted average DOC concentration was used as the average DOC concentration at that site at each sampling period.

5.2.1.1 Autumn and spring large scale sampling

In order to sample the DOC concentration across different vegetation types in the bog, 10 DOC samples were taken randomly from within each dominant vegetation type (*E. robustum, L. scoparium and S. ferrugineus*). As these sites were not permanent and involved the disturbance of peat in order to get the samples (i.e. pushing a small sampling well into the peat down to 0.3 m depth) these samples were called ‘disturbed’ samples and it was assumed that there may be slightly higher DOC concentrations from these sites compared to undisturbed samples (where sampling piezometers were left in the peat and not moved). Each site was sampled twice: when DOC concentrations were expected to be the highest (early autumn at the start of March 2012); and when they were expected to be the lowest (early spring at the start of September 2012). Each sampling was conducted over two consecutive days that were rain free. Five sites within both *L. scoparium* and *S. ferrugineus* vegetation were located approximately two kilometres south of the study area to get a more representative sample of differences in vegetation across the bog (Figure 5.3).

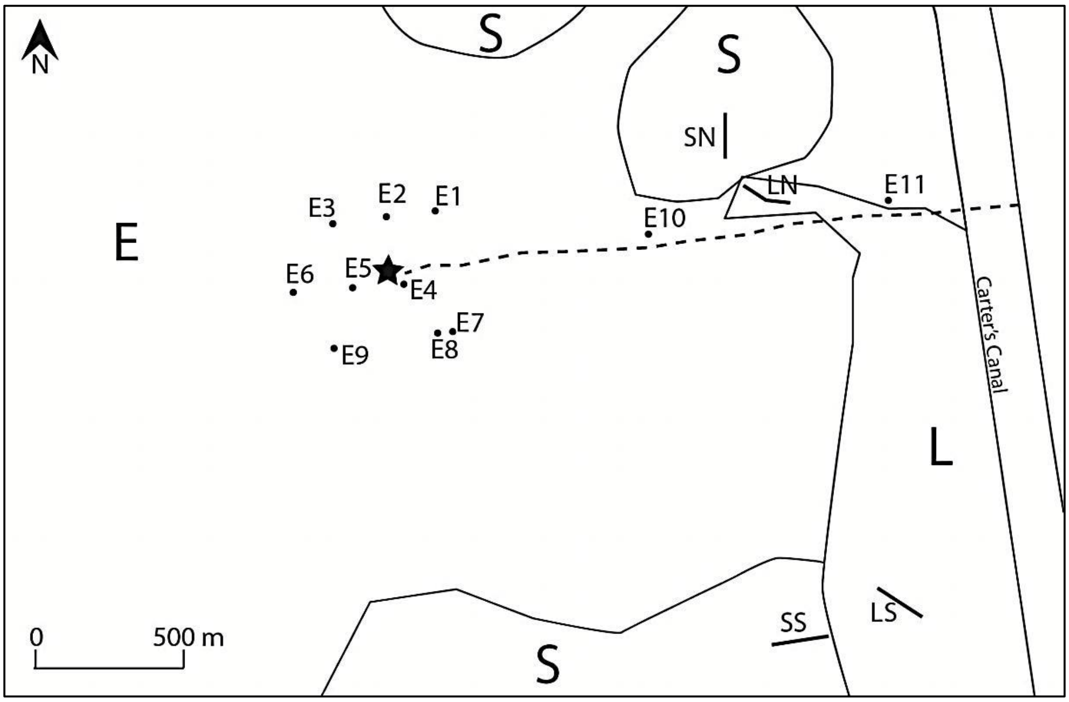

Figure 5.3: The location of sites for the large scale spatial sampling that took place twice in 2012. E, S and L are areas dominated by *E. robustum*, *S. ferrugineus* and *L. scoparium* respectively. E1 to E11 were sites in *E. robustum*. SN is the *S. ferrugineus* transect to the north where 5 sites were sampled. LN is the *L. scoparium* transect to the north where 5 sites were sampled. SS is the *S. ferrugineus* transect to the south where 5 samples were taken and LS is the *L. scoparium* transect to the south where 5 samples were taken. Transects were 100 m long and samples were taken from random locations along each transect, except for the *E. robustum* samples which were sampled next to pre-existing sites. The dashed line is the track to the EC tower which is represented by a star.

5.2.1.2 Disturbed samples vs undisturbed samples

When the autumn and spring large scale sampling was conducted in the bog, samples taken by disturbing the peat by inserting a piezometer were compared to undisturbed samples at the same location (sites 1 to 13). By comparing the difference in DOC concentration between the disturbed and undisturbed water sample results we could determine whether sampling technique had an effect on measured DOC concentration (Figure 5.4). Both methods produced similar results as the scatter plot generally clusters around the 1:1 line (apart from four outliers). A paired t-test on the undisturbed vs the disturbed samples showed that the means were not significantly different in March 2012 (22.3 ± 2.2 mg l^{-1} and

24.2 ± 5.1 mg l^{-1}, $p = 0.23$) or September 2012 (21.4 ± 6.1 mg l^{-1} and 24.9 ± 8.1 mg l^{-1}, $p = 0.26$). When data over the two sampling periods were combined, the mean and standard deviation of the undisturbed samples compared with the disturbed samples was 21.9 ± 4.5 mg l^{-1} and 24.6 ± 6.7 mg l^{-1} respectively, indicating that the disturbed samples had larger variation. The means of samples obtained using these two methods were not significantly different ($p = 0.11$).

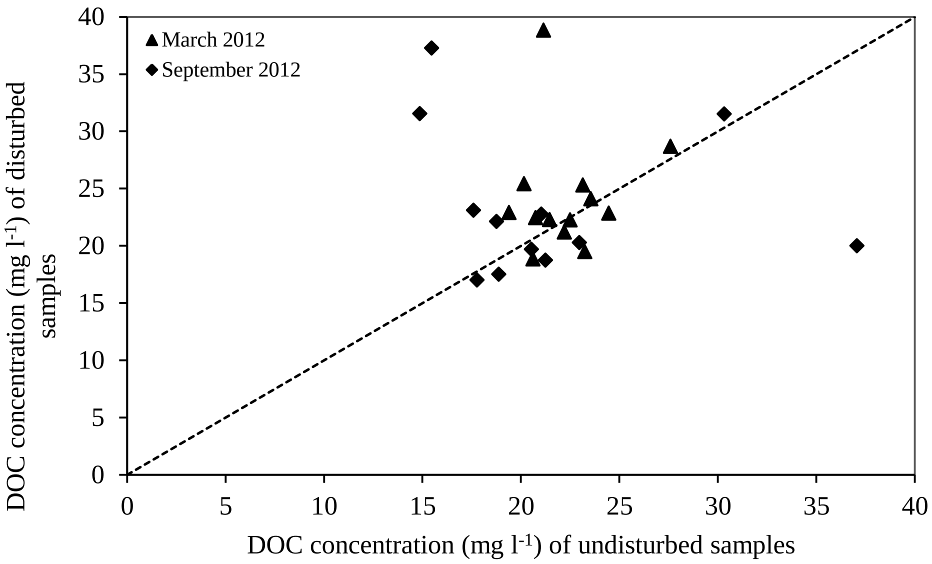

Figure 5.4: Scatter plot of disturbed vs. undisturbed DOC concentration values. The dotted line indicates the 1:1 relationship.

5.2.2 Analysis of samples for DOC

In order to obtain a water sample, a hand pump was used to withdraw stagnant water from within the piezometer. Once the piezometer filled up again a sample was taken. Samples were analysed similar to Ghani *et al.* (2010). Glass bottles were first rinsed with a small amount of the peat pore water before the sample was collected. Samples were stored at 4°C overnight then filtered through 0.45 µm cellulose nitrate membrane filters prior to analysis. As filters can potentially leach DOC they were first flushed through with 25–30 ml of distilled water.

For each sampling period a deionised water sample was used as a control. This control sample became a measure of the potential contamination of DOC, for example, from the filter or bottles. The DOC values from the controls were subtracted from the DOC concentrations of the samples if they were higher than zero.

Filtered samples were stored in a fridge or freezer for up to a week before analysis at AgResearch. The concentration of DOC was determined on a Shimadzu TOC-VCSH analyser fitted with a TNM-1 analyser. The extracts (40 µl) were injected into a detection chamber set at 680°C, where C in the sample was combusted and converted into CO_2, which was detected with an infrared gas analyser. The machine was set up to do 3–5 injections of sample until the coefficient of variation was below 2%. All raw chemistry results can be found in Appendix D.

After six months of sampling the TOC analyser broke down and sample analysis was delayed for four months over September, October, November and December 2012. The samples were kept in the freezer during this time.

5.2.2.1 Comparison of DOC analysis at two laboratories

Nine samples of peat pore water were split and one set of subsamples was sent to AgResearch and one sent to Landcare Research for analysis. Figure 5.5 shows the results from the different labs in a scatterplot and indicates that both gave similar DOC concentrations for the peat pore water samples, although those samples analysed at AgResearch had a larger range. Landcare Research samples had a mean ± SD of 23.11 ± 3.7 mg l^{-1} and AgResearch samples had a mean ± SD of 23.09 ± 5.0 mg l^{-1}. A paired t-test indicated that there was no significant difference between measurements (p = 0.98).

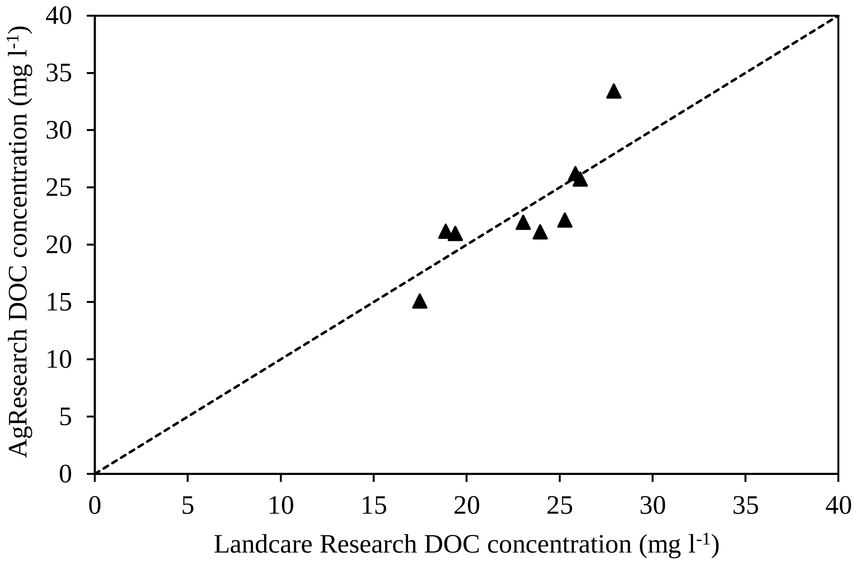

Figure 5.5: Nine samples of peat pore water were split and sent to two different laboratories (AgResearch at Ruakura and Landcare Research at Palmerston North) to determine if there were differences in DOC concentration due to lab methods. The dotted line is the 1:1 line.

5.2.3 Water table regime

The relative water level (RWL) was measured at sites 10, 11, 12 and 13 by self-logging pressure transducers (Solinst Canada Ltd., Georgetown, Ontario, Canada) to compare the water table regimes under different vegetation types. RWL was also measured at the EC tower (near site 4) and 400 m to the west and 400 m to the east of the EC tower (which will be referred to as the footprint west site and the footprint east site). These data determine the variability in the water table in the area that surrounds the EC tower, although RWL in the north and south was not measured. RWL was measured from 17 December 2011 to 17 December 2012.

RWL was measured using dipwells pushed into the peat consisting of 60 mm PVC pipe covered by a geotextile sleeve to keep out large particles (Figure 5.6). The water level probe was suspended from a metal rod at the surface of the peat and hung approximately 1.5 m below the surface, measuring the height of the water table above it (Figure 5.7). The RWL measurement was calculated by subtracting the height of the water table above the probe from the length of non-stretch cord the probe was suspended from.

Figure 5.6: Installing the RWL sites. The photograph to the right shows the wooden base board wired to the surface of the peat, and the metal bar to which non-stretch cord suspending the water level probe was attached.

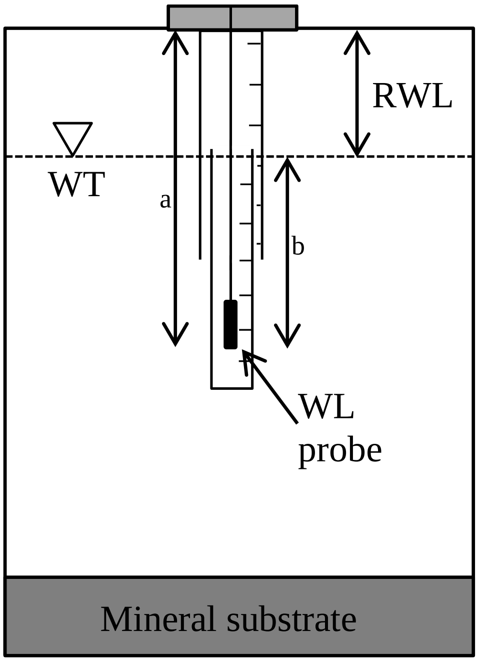

Figure 5.7: Construction of wells for measurement of relative water level (RWL) at Kopuatai. The water level probe was suspended using non-stretch cord to a wooden board positioned on the surface of the peat and measured the height of the water table (WT) above it, *b*. RWL is the water level relative to the surface of the peat. RWL = *b* – *a* where *b* was measured at 30 minute intervals by the solinst water level probe and *a* was measured at installation.

5.2.4 Temperature regime

Temperature data loggers (TidbiT v2 Water Temperature Data Logger, Onset Computer Corporation, Massachusetts, USA) were placed into the peat 5 cm below the surface at sites 2, 4, 10, 11, and 13. These data were used to compare temperature regimes across the bog under the three vegetation types. Temperature was not measured over a full year but only from 13 April 2012 to 17 December 2012.

5.2.5 Data analysis

DOC concentration statistics were analysed using the software program STATISTICA, which was also used to create the box and whisker plots for different sites and vegetation types.

5.3 Results

5.3.1 Seasonal variation of DOC concentrations

Seasonal variability was not apparent in DOC concentrations at any sites (Figure 5.8). Weighted average DOC concentrations at site 4 (*E. robustum*) had a maximum of 24.6 mg l^{-1} in May and a minimum of 17.1 mg l^{-1} in September. Maximum DOC concentrations reached 32.5 mg l^{-1} in *L. scoparium* in September and a minimum of 23.4 mg l^{-1} in July. DOC concentrations reached a maximum of 30.2 mg l^{-1} in *S. ferrugineus* in September and a minimum of 22.9 mg l^{-1} in February.

The range of DOC concentrations over the year for all depths across all *E. robustum* sites was 12.4 mg l^{-1} to 30.7 mg l^{-1}. The range within *L. scoparium* and *S. ferrugineus* combined was 19.9 mg l^{-1} to 46.4 mg l^{-1}.

5.3.1.1 Effect of temperature and rainfall on DOC concentrations

Daily mean air temperature decreased from February 2012 to June 2012 and reached its lowest at 2.5ºC in mid-June (Figure 5.8). Air temperature then warmed to its peak in mid-January 2013 at 21.9ºC. Precipitation was fairly consistent in the first half of the year until July 2012 when heavy falls occurred and these carried through into August. Lower precipitation occurred from September through to January 2013 and it was especially dry in December and January 2013.

Temperature does not appear to have influenced DOC concentration. DOC concentrations from piezometer A from six of the long term sites (sites 4, 10, 11, 12, 13 and 14), including bulked samples from sites 1 to 9, were plotted against the mean air temperature of the week preceding sample collection and no corellation was found (Figure 5.9). These DOC concentrations were also plotted against total precipitation in the week preceding sample collection and again no correlation was found (Figure 5.10). Even in August, approximately 80 mm of rain in the previous week did not decrease DOC concentrations.

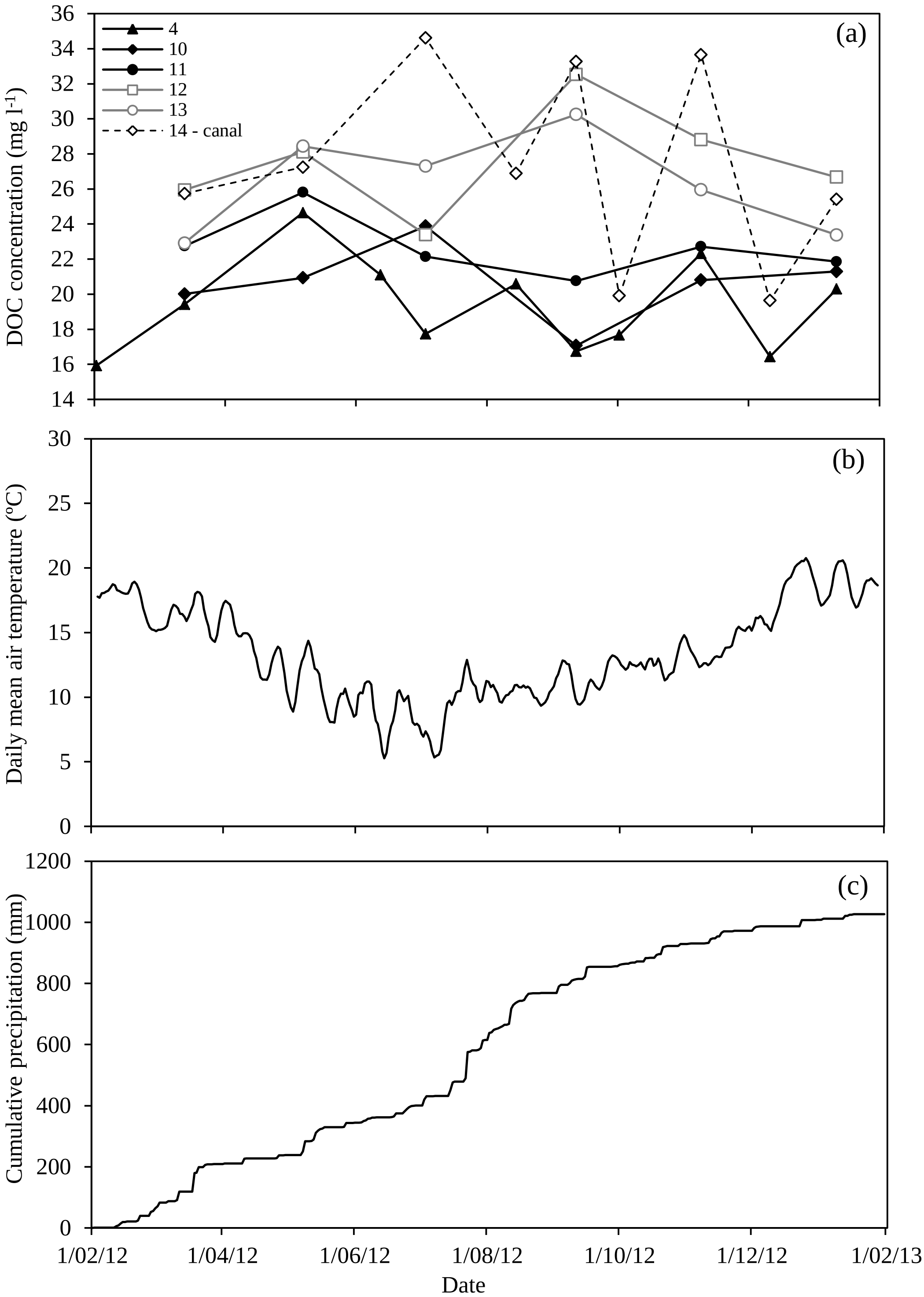

Figure 5.8: (a) DOC concentrations at site 4, 10, 11, 12, 13 and 14 from February 2012 to February 2013. (b) Daily mean air temperature and (c) cumulative precipitation for the same period.

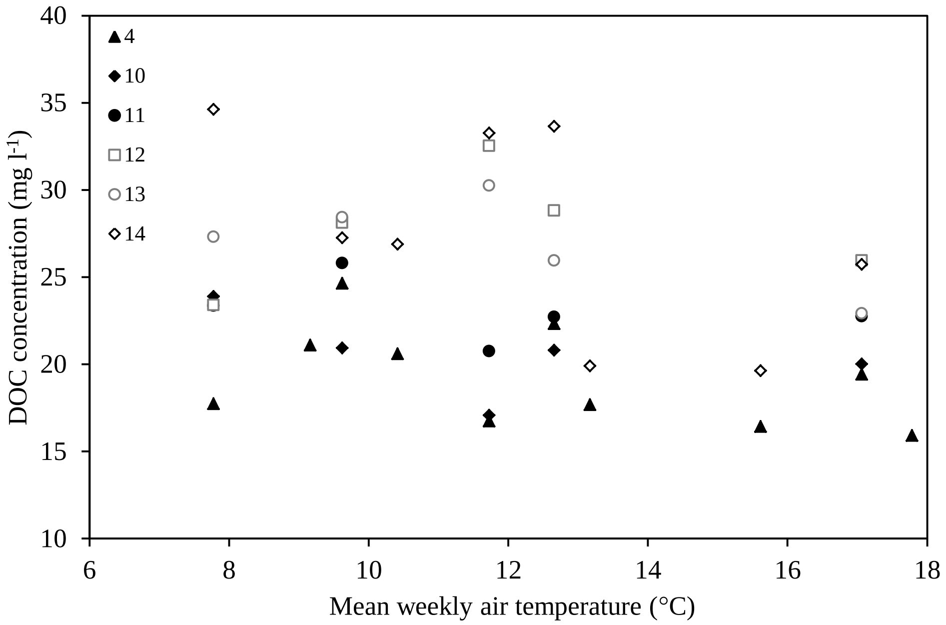

Figure 5.9: DOC concentrations from 0–0.3 m plotted against the mean weekly air temperature for the week preceding sampling.

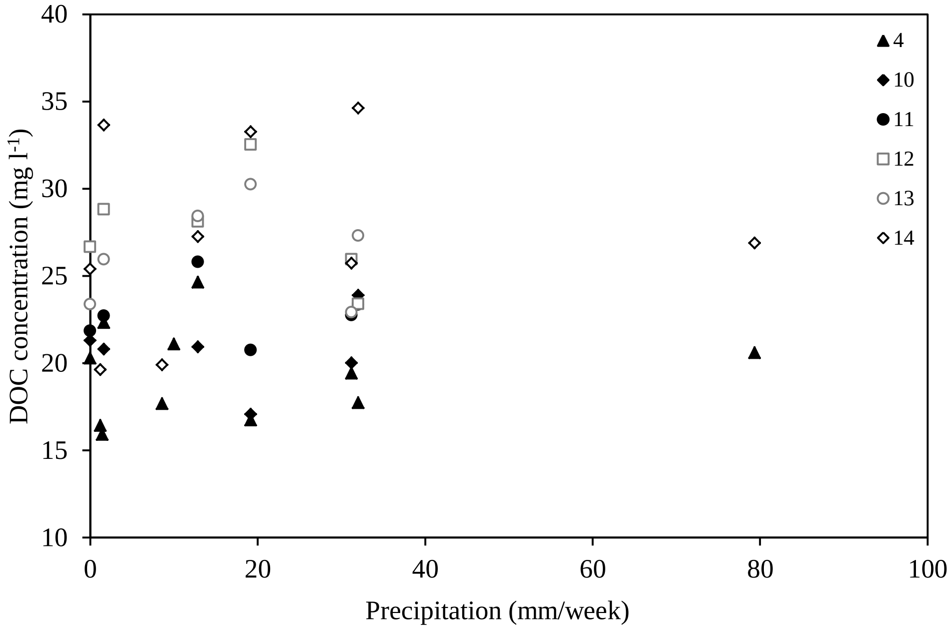

Figure 5.10: DOC concentrations from 0–0.3 m plotted against the sum of weekly precipitation from the week when sampling took place.

5.3.2 Water level regime

The water table (WT) was well below the surface at the start of 2012 (RWL most negative) reflecting smaller amounts of precipitation during the summer months (Figure 11). The months of December 2011 and January 2012 were wetter relative to other summers (21% higher precipitation than the 30 year average measured at Paeroa) and as a result the WT at the start of the year was perhaps not as low as ‘normal’ years. During March, April and May (autumn), the WT increased and heavy rainfall in July and August (winter) resulted in the highest WT. In July/August the WT at site 12, 13 and the footprint west site rose above the surface of the peat (positive RWL). At the footprint west site it remained flooded for over two months. As precipitation in spring and summer was relatively lower than in winter, the WT declined at all sites.

The lowest WT occurred at site 10, the footprint east site and at the EC tower (near site 4). These sites all occur within 1800 and 900 m from the eastern edge of the bog. The highest WT occurred at the footprint west site and this site was approximately 2200 m from the eastern edge of the bog reflecting wetter conditions west of the EC tower. The generally higher WT on the western side of the EC tower was supported by manual measurements made in this area.

The sites that had the highest WT (site 12, 13 and footprint west) also had the biggest range in WT (Table 5.1). The sites with the lowest WT range (sites 10, EC tower and footprint east) also had the smallest range in WT. Where measurements are available, the WT at all sites was within 0.25 m of the surface of the peat. Only measurements of RWL at the EC tower were available from 17 December 2012 to 31 January 2013 and as this was a very dry period, the WT dropped below –0.25 m.

Table 5.1: Highest WT depth, deepest WT depth, range and mean WT depth for seven sites within Kopuatai bog. FP = footprint sites.

Site	Highest WT depth (m)	Deepest WT depth (m)	Range (m)	Mean WT depth (m)
EC tower	-0.01	-0.25	0.15	-0.18
10	-0.11	-0.24	0.14	-0.19
11	-0.002	-0.19	0.19	-0.13
12	0.05	-0.18	0.23	-0.10
13	0.02	-0.23	0.25	-0.14
FP east	-0.01	-0.22	0.12	-0.17
FP west	0.11	-0.17	0.27	-0.06

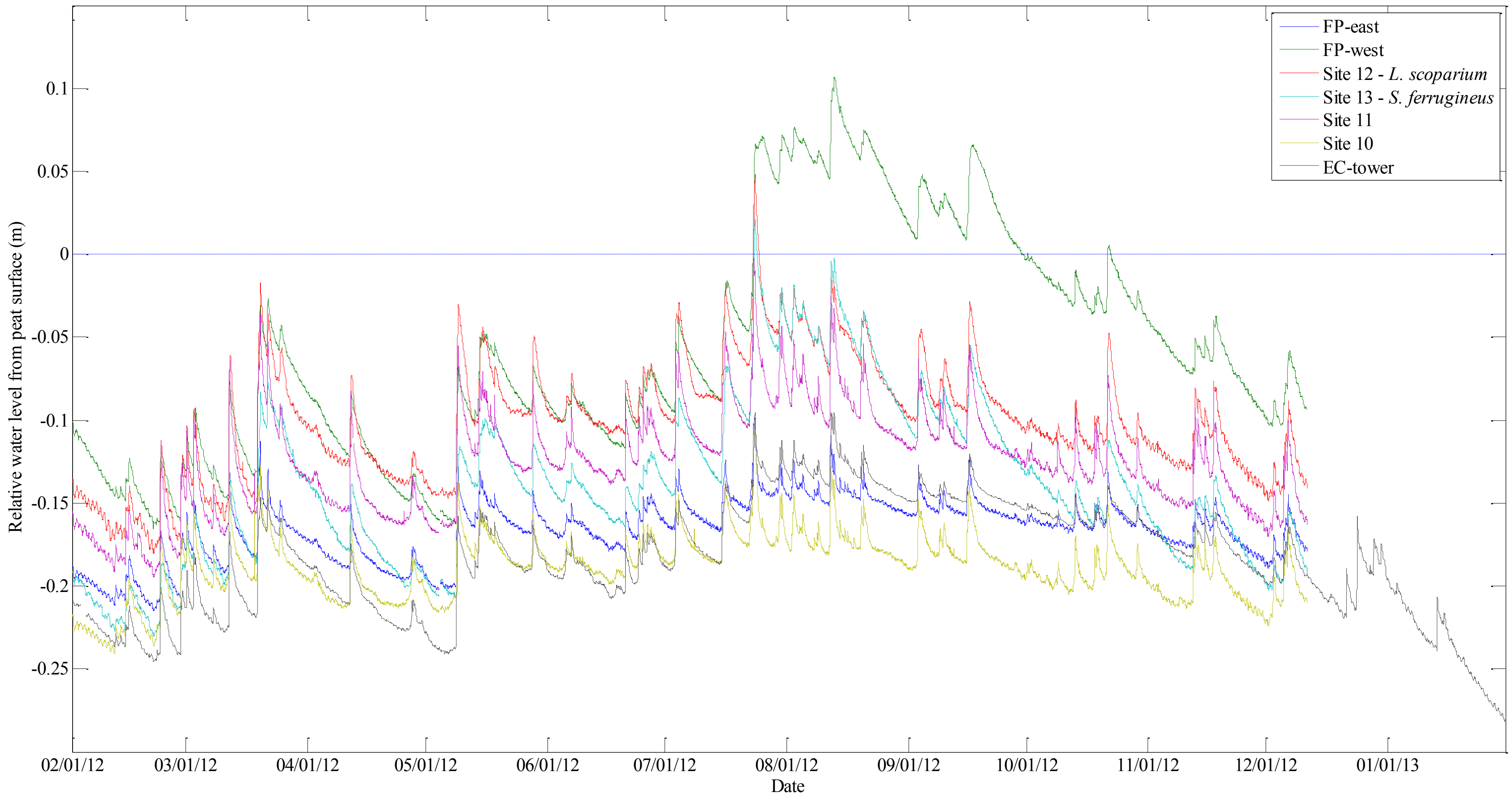

Figure 5.11: Relative water level for seven sites within Kopuatai over a year (01/12/11 to 01/12/12). FP = footprint sites. The EC-tower site is located near site 4. Horizontal dashed line is the peat surface. Only data for the year of sampling is shown.

5.3.3 Peat temperature regime

Peat temperature (Figure 5.12) followed trends in air temperature although there was a smaller range in peat temperatures. Daily mean peat temperatures decreased from April to July to a minimum of ~4.5ºC. After July peat temperatures increase at all sites reaching maximums of ~16ºC, although at site 10 peat temperature reached 18ºC (Table 5.2).

Daily mean peat temperatures at all sites converged during winter (June, July and August) and diverged in the summer (November and December). The highest peat temperature at 5 cm depth consistently occurred at Site 10. Compared to other sites, site 13 (*S. ferrugineus* site) was relatively cooler during the summer but was similar to other sites during winter.

Mean peat temperature does not appear to be a driver in the variability of DOC concentrations at Kopuatai. There appears to be no obvious correlation between mean peat temperature for the preceding week before sampling and DOC concentration from piezometer A at five sites within the bog (Figure 5.13).

Table 5.2: Minimum daily, maximum daily and mean temperatures at 5 cm peat depth at five sites at Kopuatai bog.

Site	Minimum daily mean temperature (°C)	Maximum daily mean temperature (°C)	Mean temperature (°C)
4	4.9	15.8	10.2
10	5.6	18.0	11.9
11	4.6	16.2	10.1
12	5.2	15.9	10.6
13	4.7	15.7	10.0

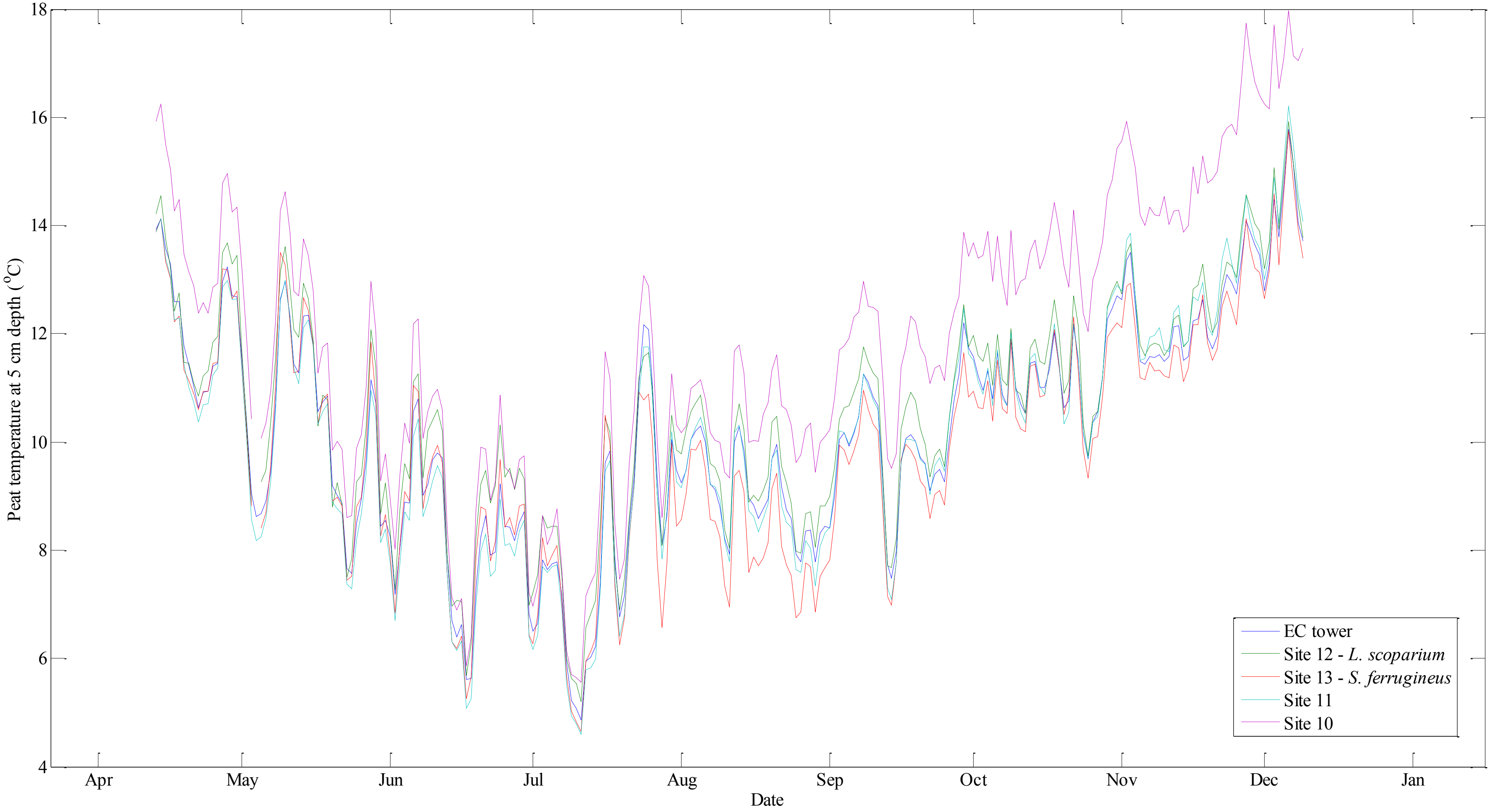

Figure 5.12: Daily mean peat temperature (°C) at 5 cm depth of five sites within Kopuatai bog.

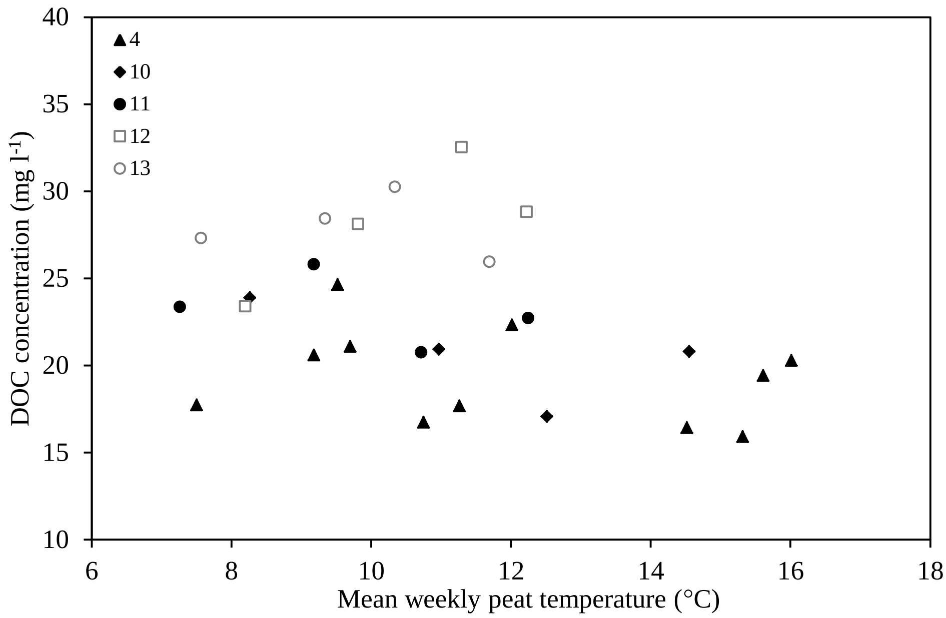

Figure 5.13: DOC concentrations from 0–0.3 m plotted against the mean weekly peat temperature at 5 cm depth from the week preceding sampling.

5.3.4 Spatial variability

5.3.4.1 Effect of vegetation type on DOC concentrations

Long term sites

Sites 1 to 11 were located at sites dominated by *E. robustum* and sites 12 and 13 were located in *L. scoparium* and *S. ferrugineus* stands respectively. Variations of DOC concentrations were compared to determine whether vegetation has an influence.

DOC concentrations for *L. scoparium* (site 12) and *S. ferrugenius* (site 13) were higher than for *E. robustum* (site 4) over the six sampling periods where they were all sampled on the same day (Figure 5.14). There was a significant difference between groups as determined by one-way ANOVA. A Tukey *post-hoc* test revealed that DOC concentrations were significantly higher at site 12 (27.6 ± 2.7 mg l^{-1}, p = 0.002) and site 13 (26.4 ± 3.1 mg l^{-1}, p = 0.008) compared to site 4 (19.5 ± 2.7 mg l^{-1}). There was no significant difference between sites 12 and 13 (p = 0.76) (Figure 5.15).

Figure 5.16 shows a box and whisker plot of all DOC concentrations for all sites categorised by vegetation, including different depth values and over time. This graph incorporates all variation caused by time, temperature, and depth. A one way ANOVA again indicated that *E. robustum* sites have significantly lower DOC than *L. scoparium* ($p < 0.01$) and *S. ferrugineus* ($p < 0.01$). There was no significant difference between *L. scoparium* and *S. ferrugineus* ($p = 0.1$).

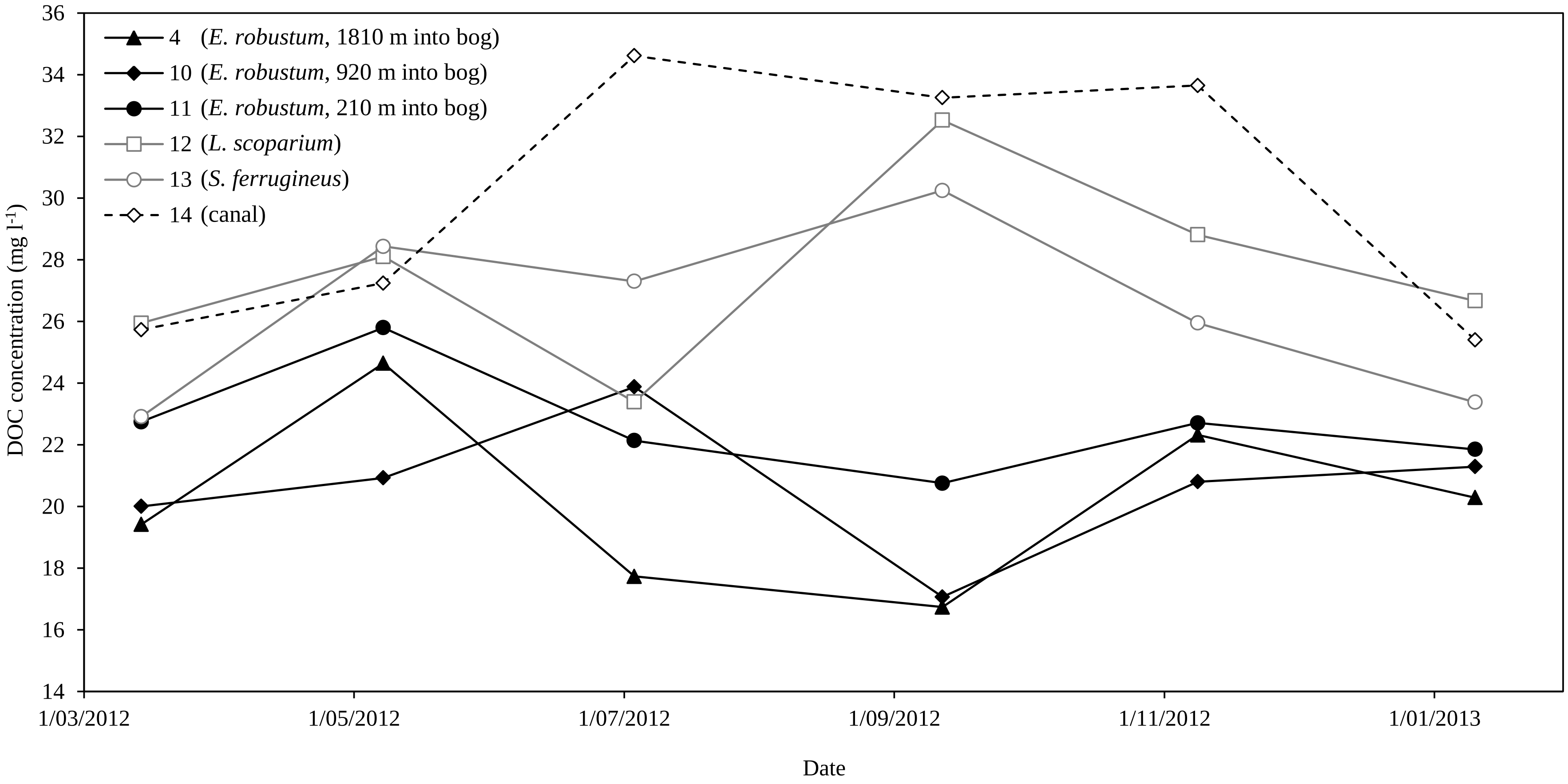

Figure 5.14: DOC concentrations at sites 4, 10 and 11 (*E. robustum*) and site 12 (*L. scoparium*), 13 (*S. ferrugineus*) and 14 (canal) over time. Data are only shown for sampling periods where all sites were sampled on the same day. Water samples were taken from each location once every two months and are a weighted average of samples taken from three different depths at each site.

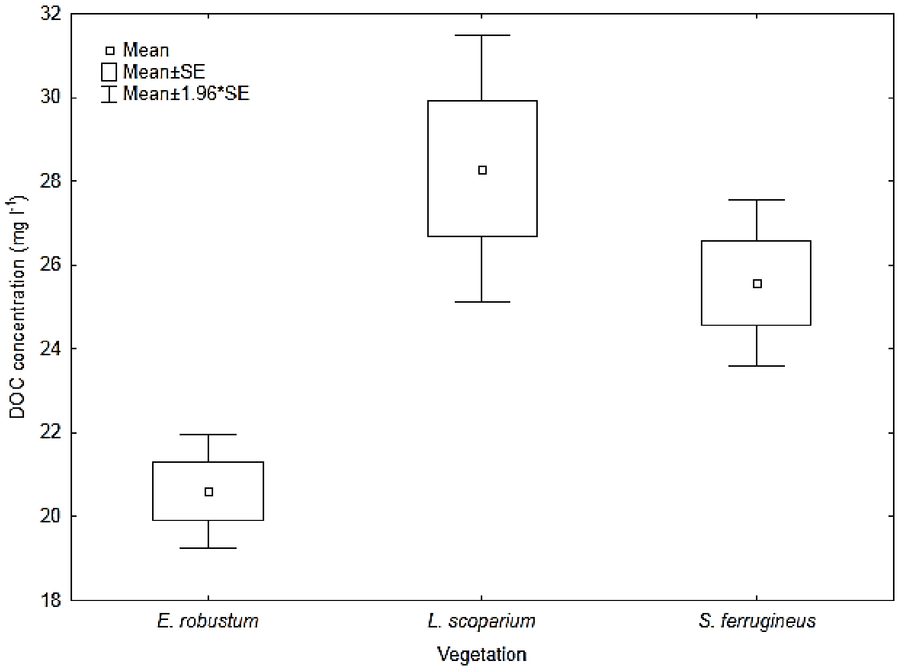

Figure 5.15: Box and whisker plots of DOC concentrations at sites 4 (*E. robustum*), 12 (*L. scoparium*) and 13 (*S. ferrugineus*) incorporating all variation caused by time, temperature, and depth. Mean ± 1.96*SE represents 95% confidence intervals.

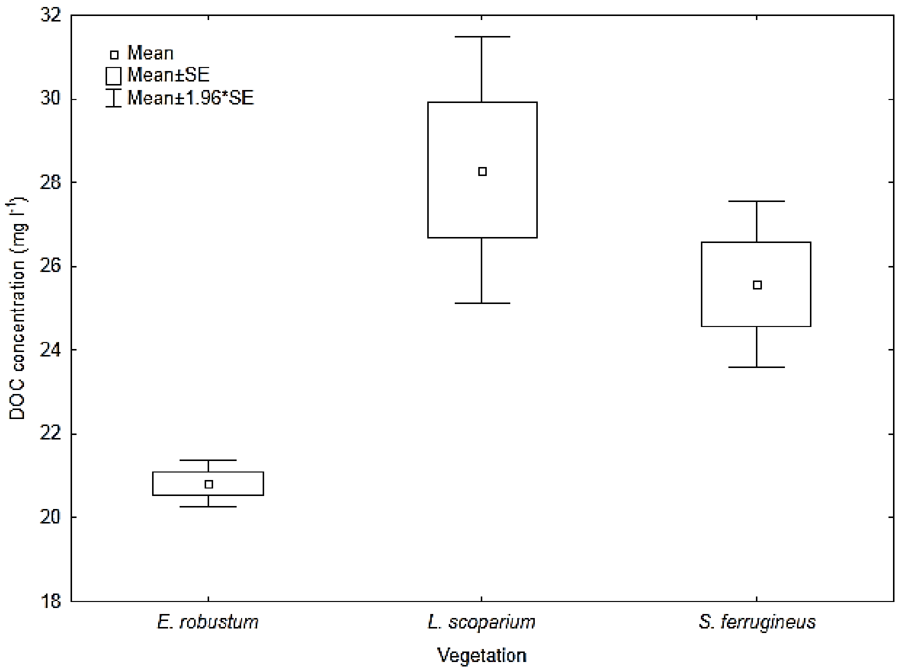

Figure 5.16: Box and whisker plots of all DOC concentrations for sites 1 to 13 categorised by vegetation type. This graph incorporates all variation caused by time, temperature, and depth. Mean ± 1.96*SE represents 95% confidence intervals.

Autumn and spring large scale sampling

Peat pore water at ten sites within each vegetation type was individually sampled down to 0.3 m. These were described as ‘disturbed’ sites because sampling piezometers were inserted at the time of measurement. This sampling was carried out twice in the year, on 14 March (early autumn, mean peat temperature at 5 cm depth: 15.6°C) and on 12 September (early spring, mean peat temperature at 5 cm depth: 10.7°C) (Table 5.3).

Table 5.3: Table of mean, standard deviation and range of DOC concentrations (mg l^{-1}) of disturbed samples (n = 10).

Vegetation	*E. robustum*		*L. scoparium*		*S. ferrugineus*	
Month	Mar	Sep	Mar	Sep	Mar	Sep
Mean ± SD	23.0 ± 5.4	23.8 ± 6.7	30.3 ± 4.3	33.9 ± 9.7	25.3 ± 5.2	21.2 ± 2.7
Range	18.0 – 38.0	17.0 – 37.3	25.2 – 37.8	19.5 – 45.7	18.7 – 38.9	17.2 – 26.1

A box and whisker plot was constructed from DOC concentrations from the autumn and spring sampling periods (Figure 5.17). Using a one way ANOVA on the results of the autumn sampling it was found that DOC concentration in peat pore water under *L. scoparium* had significantly higher concentrations than under *E. robustum* (p = 0.008). DOC concentrations under *S. ferrugineus* and *E. robustum* and *S. ferrugineus* and *L. scoparium* were not significantly different (p = 0.57 and 0.08 respectively).

For the spring sampling period, DOC concentration in peat pore water under *L. scoparium* was significantly higher than both *E. robustum* and *S. ferrugineus* (p = 0.008 and 0.001 respectively). DOC concentrations under *S. ferrugineus* and *E. robustum* were not significantly different (p = 0.70).

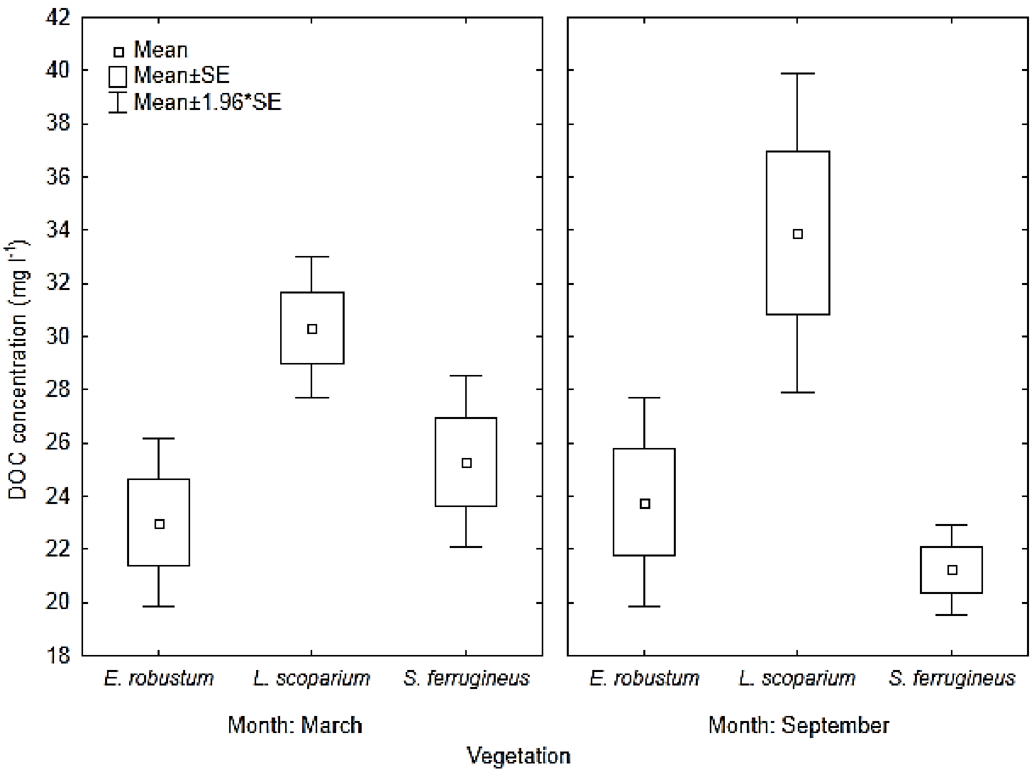

Figure 5.17: Box and whisker plots showing DOC concentrations between different vegetation types during the March and September sampling times.

5.3.4.2 Comparisons of DOC concentration from the middle to the edge of Kopuatai bog

Three sites were used to determine if there were any differences in DOC concentrations in peat pore water from the middle to the edge of the bog under *E. robustum*. This transect was from the eastern edge to the middle of the bog (approximately 2 km long) and consisted of site 4 (middle of the bog, 1810 m from the canal), 10 (920 m from the canal) and 11 (210 m from the canal).

DOC concentrations across the long term *E. robustum* sites were compared where samples were collected on the same day (Figure 5.14). Although DOC concentrations at site 11 tended to be higher than for sites 10 and 4, there was no significant difference between groups as determined by one-way ANOVA.

5.3.4.3 Comparisons with canal DOC concentrations

Canal DOC concentrations were compared directly back to DOC concentration within the EC footprint and at the edge of the bog (site 11) (Figure 5.14). An

ANOVA was conducted on DOC concentrations at the three sites where sample was collected on the same day. The canal had significantly higher DOC concentrations than site 11 ($p = 0.008$) and site 4 ($p = 0.003$).

5.3.4.4 Effect of depth on DOC concentration

In February 2012, sites 1 to 9 had significantly higher DOC concentrations closer to the surface (between 0 and 0.30 m from the surface) than at depth (0.3–1.0 m). Using an ANOVA it was determined that there were significantly lower DOC concentrations in piezometer B (18.1 ± 3.8 mg l^{-1}, $p = 0.049$) and C (18.2 ± 3.9 mg l^{-1}, $p = 0.055$) compared to piezometer A (23.1 ± 5.0 mg l^{-1}). There were no significant differences between piezometer B and C ($p = 0.998$).

In other sampling periods, there was no significant difference in DOC concentrations with depth down the peat profile at site 1 to 9 (Figure 5.18). This was determined by one-way ANOVA for all time periods ($p > 0.23$).

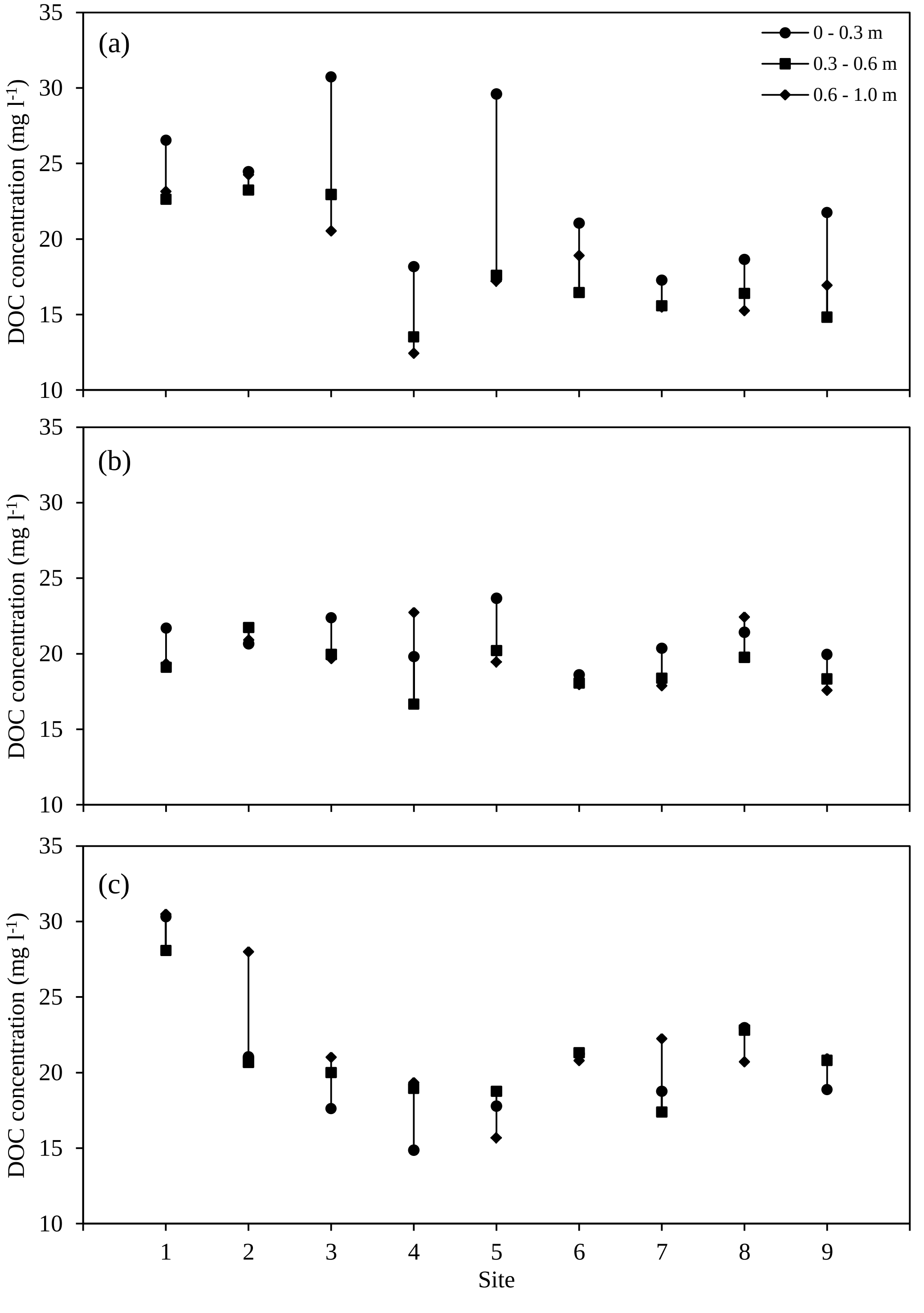

Figure 5.18: DOC concentrations at three depths for sites 1 to 9 for (a) February, (b) March and (c) September.

5.4 Discussion

5.4.1 Comparisons of DOC concentrations at Kopuatai with Northern Hemisphere peatlands

Kopuatai had DOC concentrations (12.4–46.4 mg l^{-1}) within the range or lower when compared to concentrations of 20–60 mg l^{-1} from northern peatlands (Blodau, 2002). Kopuatai had an average DOC concentration of 22.1 ± 4.7 mg l^{-1} from all sites within the bog over the year. Waddington and Roulet (1997) measured DOC concentrations of 21.0–29.0 mg l^{-1} at Stor-Amyran mire in Sweden. Worrall *et al.* (2006) measured DOC concentrations from Trout Beck blanket peat catchment in the UK of 5–18 mg l^{-1}. Kopuatai DOC concentrations were at the lower end of the range measured by Roulet *et al.* (2007) of 20.0–76.6 mg l^{-1} at Mer Bleue peatland in Canada. The mean DOC concentration at Mer Bleue measured in stream outflow was 47.5 ± 12.6 mg l^{-1} (Roulet *et al.*, 2007). At a blanket bog in south west Ireland, DOC concentrations ranged from 2.7 to 11.5 mg l^{-1} for the year of 2007 with a mean of 6.5 mg l^{-1}. This was considered very low when compared to other peatland sites published data (Koehler *et al.*, 2009).

5.4.2 Seasonal variability of DOC

Seasonal variability was not apparent in DOC concentrations from all sites. DOC concentrations at site 4 (*E. robustum* site) was at a maximum in May (winter) and minimum in September (spring). In contrast, site 12 (*L. scoparium* site) had maximum concentrations in September and minimum in July (winter). DOC concentration was at a maximum in September and a minimum of March (autumn) for site 13 (*S. ferrugineus* site).

Highest DOC concentrations at Kopuatai were expected to be in summer due to higher temperatures, higher primary productivity and increased decomposition, and lower precipitation, whereas, the lowest values were expected in winter coinciding with lower temperatures and higher precipitation. It was assumed that peat pore water from the shallowest depth (piezometer A at 0–0.3 m) would be more likely to show trends from precipitation and air temperature. However, there appeared to be no obvious trend in DOC concentration with temperature

(Figure 5.9). This is surprising as higher temperatures have been shown to increase microbial activity and accelerate the production of DOC more than the consumption of DOC leading to increases in concentration (Freeman *et al.*, 2001b; Moore & Dalva, 2001). Koehler *et al.* (2009) found that DOC concentration at Glencar, a temperate blanket bog in south-west Ireland, was higher in summer and lower in winter. McKnight *et al.* (1985) found that the ombrotrophic Thoreau's Bog in Concord, Massachusetts and had an average DOC concentration of 32 mg l^{-1} which varied seasonally, with the greatest concentration in the late spring and lowest in late winter.

DOC concentrations at Kopuatai seem to be little affected by the amount of rainfall that occurred before sampling took place (Figure 5.10). This again is in contrast to the literature. pH results also showed that the addition of rainfall resulted in higher pH in the shallow peat pore water in comparison to the deeper peat pore water (section 4.3.3) but this was not reflected in the lowering of DOC concentration. Waddington and Roulet (1997) found that DOC concentrations in a boreal peatland in Sweden were 6–8 mg l^{-1} higher at the surface than in peat greater than 2 m depth, during dry periods, as a result of evaporation and negligible precipitation. Under wet conditions the DOC concentration was lower at the surface by 6–8 mg l^{-1} than at depth due to dilution by precipitation. Roulet *et al.* (2007) determined that there was a seasonal pattern in DOC concentrations at Mer Bleue, being lower in the spring when runoff was greatest due to snowmelt, and higher in summer during periods of negligible flow. In contrast, Billett *et al.* (2004) found that extremely low DOC concentrations at Auchencorth Moss peatland (south-east Scotland) all coincided with periods of low flow from the outflow stream. Similar to Kopuatai findings, a study on tropical peatlands in south-east Asia by Moore *et al.* (2013) found DOC concentration was relatively constant over the study periods.

The lack of clear seasonal trend at Kopuatai may have been confounded by relatively infrequent sampling. Nevertheless, it would be expected that high rainfall paired with cold temperatures during winter would exacerbate a seasonal trend in DOC concentration but this was not apparent. Seasonal temperature variations in New Zealand are small owing to the temperate maritime climate.

From the 30 year climate record (1981 to 2010) at nearby Paeroa the average temperatures for spring, summer, autumn and winter were 14.0, 19.1, 15.2, and 10.2ºC respectively. The difference between the average temperature in summer and winter is approximately 9ºC. It appears that the temperature at Kopuatai might not have a large enough range from winter to summer to create seasonal DOC variations. In contrast Mer Bleue bog in Canada has a 28°C mean temperature range from winter to summer[7].

Kopuatai bog also experiences fairly consistent rainfall throughout the year and this may be a reason why precipitation does not have an obvious effect on DOC concentration. In most studies, DOC concentrations are measured from waterways and therefore precipitation effects are more easily seen with the influx of DOC poor water from direct precipitation and overland flow (Koprivnjak & Moore, 1992). Throughfall and stemflow water can lead to high DOC concentrations reflecting the dense foliage and the high interception rate of the canopy (Koprivnjak and Moore, 1992). Throughfall through the dense *E. robustum* canopy may increase DOC concentration from rainfall to peat pore water. Dalva and Moore (1991) reported concentrations of DOC in precipitation, throughfall, stemflow, and soil, peat and stream water in a 50 ha catchment with a central 5 ha swamp in Canada. DOC concentrations in precipitation were low (2.0 mg l^{-1}), but increased after passage through the tree canopies as throughfall (9.1–14.6 mg l^{-1}) and stemflow (23.1–30.1 mg l^{-1}). There was a large increase in DOC concentration as water moved through the vegetation and onto the soil surface and this could also be occurring at Kopuatai.

Water that percolates down into the peat until it reaches the water table will accumulate DOC and the increase in water table after rain may accumulate more carbon. Contact of peat with water poor in DOC (such as rain water) can release DOC from the peat matrix (Blodau, 2002). Therefore the addition of water through rainfall may not have an obvious dilution effect on DOC concentrations at Kopuatai.

[7] *Canadian climate normal or averages 1971 – 2000*, Environment Canada website, http://www.climate.weatheroffice.gc.ca/climate_normals/index_e.html, 04/02/13.

5.4.3 Water level regime

Sites 12, 13 and the western side of the footprint had the highest water tables (WT) with the largest variation. Sites 4, 10 and the eastern side of the footprint had the lowest WT with the smallest variation. As the same amount of precipitation fell at each site, the range in WT depths was due to the hydraulic conductivity of peat in each area or the amount of water movement, e.g. areas with flow convergence might have a higher WT. Site 12, dominated by *L. scoparium*, may have been in an area of flow convergence due to the higher WT along with greater concentrations of TP and TN in the peat substrate. Site 12 also had a higher bulk density and humification index which is inversely related to hydraulic conductivity. The western side of the footprint was also likely to be an area of flow convergence as conditions were wetter in this area, with more standing water during the winter and increased prevalence of *Baumea spp*.

Water table position is an important factor controlling DOC production and loss. The WT depth also controls the volume of source peat in which production of DOC can occur (Laiho, 2006). Aerobic conditions can cause the enzyme phenol oxidase to remove phenolic compounds that inhibit biodegradation resulting in increased decomposition (Freeman *et al.*, 2001a). DOC production can occur above the WT in the acrotelm and this DOC is released from the peat when it is mobilised following rehydration (Freeman *et al.*, 2001a; Laiho, 2006). This suggests that there might be increased decomposition rates and increased DOC release at sites where the WT is very deep or has greater fluctuations. However, sites with the deepest WT (4 and 10) did not have significantly higher DOC concentrations than site 11 which had a higher WT. Other sites with a relatively higher and more variable WT (12 and 13) did have significantly higher DOC concentrations but this is likely due to a difference in vegetation types. Site 6 and 3 within the EC footprint also had high WT (western side of footprint) but had similar DOC concentrations to site 4 and site 10 also in *E. robustum* vegetation.

There is conflicting evidence over the role of WT draw down on DOC production (Clark *et al.*, 2009). A study by Mitchell and McDonald (1992) indicated that peat dewatering through lowering of the WT increases decomposition and net DOC production. Other studies such as Pastor *et al.* (2003) and Freeman *et al.*

(2004b) indicated that under aerobic conditions there is increased biological activity and therefore increased DOC consumption as a substrate for respiration. This results in a lowering of the observed DOC production rate (Moore & Dalva, 2001). The latter reason could be a possible reason why there was no discernible increase in DOC concentrations at Kopuatai during the summer when the WT dropped. Any DOC that was produced due to the aerobic conditions may have been consumed by microbes.

5.4.4 Spatial variability

5.4.4.1 Effect of vegetation type on DOC concentration

The different species of vegetation dominant within a peatland can influence peatland conditions that contribute to the production and export of DOC. Effects include: changes in the geochemistry of soil water (Agnew *et al.*, 1993; Kuder *et al.*, 1998; Clarkson *et al.*, 2009), the physical environmental conditions such as temperature and water table depth, the biological decomposer communities (Neff & Hooper, 2002), and the quality and quantity of plants and litter (Moore & Dalva, 2001; Wickland *et al.*, 2007).

DOC concentrations at the three different vegetation types of the long term sampling sites at Kopuatai (Figure 5.14) suggested that there was no significant difference in DOC concentration under *S. ferrugineus* and *L. scoparium* sites but these sites had significantly higher concentrations than under the *E. robustum* sites. In contrast, during the autumn and spring large scale sampling period it was found that there were higher DOC concentrations (at 0–0.3 m depths) under *L. scoparium* (32.1 ± 7.5 mg l^{-1}) compared to both *E. robustum* (23.4 ± 5.9 mg l^{-1}) and *S. ferrugineus* (23.3 ± 4.6 mg l^{-1}) sites. DOC concentrations under *E. robustum* and *S. ferrugineus* were similar. The difference in results suggests that site 13 (the long term *S. ferrugineus* site) may be less representative of *S. ferrugineus* compared to the spatially sampled sites. Nevertheless, these results show that there was a definite difference between *L. scoparium* and *E. robustum* and a difference between *L. scoparium* and *S. ferrugineus* when large scale sampling was conducted.

L. scoparium had higher DOC concentrations because the peat appears to be more decomposed (indicated by the high von Post index). Restiads have allelopathic properties which provide decay resistance along with the inherent inertness of lignin and tannin within their tissues (Kuder *et al.*, 1998). *L. scoparium* tissues and leaf litter may not have the same inhibitory effect on microbial activity and not be as resistant to decay as *E. robustum* and *S. ferrugineus*. Microbes and soil fauna decompose organic matter and their quantities and types will influence the concentration of DOC in soil pore water (Armstrong *et al.*, 2012). Microbial communities and soil fauna species have been found to change with different vegetation (Artz *et al.*, 2007) and they are likely to be inhibited by the allelopathic properties of the restiad plants and litter resulting in lower decomposition rates under this vegetation.

5.4.4.2 Comparisons of DOC concentration from the middle to the edge of Kopuatai

There was no difference in DOC concentration at site 11 compared to the other *E. robustum* sites in the bog. However, site 11 was different in some peat characteristics, such as a higher dry bulk density and a higher TN and TP concentrations. Schipper *et al.* (1998) conducted a study on Kopuatai bog that showed there was no effect of drainage or fertiliser drift further than 200 m into the bog. DOC concentrations at site 11 reflect that this site does not appear to be affected by drainage or agricultural activities at 210 m into the bog from the canal.

5.4.4.3 Canal DOC concentration compared to peat pore water

Processes such as adsorption, precipitation, oxidation, photodegradation and microbial degradation of DOC can lead to general decreases in DOC concentration within streams or canals draining peatlands (Worrall *et al.*, 2006). The DOC concentrations within Carter’s Canal were compared to peat pore water from the middle and the edge of the bog (site 4 and site 11 respectively) (Figure 5.14). These sites had similar values during some months (March and May in 2012 and January in 2013) but at other times DOC concentrations within the canal were higher. Overall, the canal had significantly higher DOC concentrations than peat pore water from the middle and the edge of the bog. This was probably due to the large amount of vegetation in the canal that was undergoing decomposition producing DOC. The canal was also closed off in the summer months in order to maintain a high water table in the bog and this would have increased the residence time of the water in the canal, concentrating DOC through evaporation, when water was stagnant. The canal also would be receiving water inputs from parts of the wetland dominated by *L. scoparium*.

5.4.4.4 Effect of depth on DOC concentration

In February there were higher DOC concentrations at sites 1 to 9 (of, on average, 5 mg l^{-1}) in the surface layer of the peat (0–0.3 m) than 0.3–0.6 and 0.6–1.0 m depth intervals. This may be due to the dry period or associated with increased primary production by *E. robustum*. Higher temperatures at shallow depths in the peat could have led to higher DOC production through accelerated microbial breakdown of peat (McKnight *et al.*, 1985). In Thoreau's Bog in Concord, Massachusetts, DOC varied with depth, with mean concentrations in the upper 1 m at 60 mg l^{-1} reducing to 30 mg l^{-1} deeper in the bog (McKnight *et al.*, 1985).

The lack of difference in DOC concentration with depth for other months may have been because there was regular rainfall causing dilution or because increased microbial oxidation of dissolved organic material had occurred.

5.4.4.5 Comparison to the Moore and Clarkson (2007) study

The study by Moore and Clarkson (2007) determined that the average concentration of DOC from samples of water collected at Kopuatai in late February in 2006 was 53.0 ± 37.7 mg l^{-1} (n = 12). This was considerably higher than DOC concentrations found in the present study where an average over 14 sites for one sampling period in early March 2012 was 21.3 ± 2.2 mg l^{-1}. Figure 5.5 indicates that laboratory error was not responsible for the differences between studies. An examination of the raw data of Moore and Clarkson (2007) showed their average was skewed by a rather large value of DOC concentration obtained by squeezing a sample of peat (170.8 mg l^{-1}). Their values also included sites within *S. ferrugineus* and the canal. On removing the outlier their mean DOC concentration became 42.2 ± 7.1 mg l^{-1}. Although this is still higher than the present study's mean, DOC concentrations have been obtained within *E. robustum*, *S. ferrugineus* and *L. scoparium* over 40 mg l^{-1} at sites where peat was disturbed beforehand. There was no statistical difference between means of disturbed and undisturbed samples in this study but there were large outliers in Figure 5.4 due to peat disturbance.

The difference in DOC concentrations obtained in the Moore and Clarkson (2007) and the present study is probably due to sampling differences. Moore and Clarkson (2007) collected samples in a number of different ways and averaged the resulting DOC concentrations. Examples of their sampling methods were: taking samples from the upper 25 cm of peat by digging holes, gently squeezing peat and sampling the expelled water, collecting from open water bodies such as streams pools, and drainage ditches and streams within or leaving the peatlands. These methods may have mobilised more DOC to be released into the water and the authors warn that caution should be exercised for those comparing results due to the number of different sampling techniques used. In the present study, piezometers were pushed into the peat and left in place for the duration of the study. Water sitting in the sampling tubes was expelled and left to fill up again before a sample was collected.

Moore and Clarkson (2007) sampled Kopuatai bog in March 2006 during a dry period. 2006 was generally warmer in January, February and March at 19.4, 19.3 and 17.5 °C respectively compared to 2012 mean monthly temperatures of 18.5, 19.2 and 16.7 °C. Total precipitation for January, February and March in 2006 was 206 mm and these were relatively dry months compared to 2012 which had a total of 323 mm for these months. Studies suggest that DOC concentrations in peat pore water is usually highest following periods of warm, dry conditions when DOC has built up due to higher evaporation rates and plant tissue decomposition (Waddington & Roulet, 1997; Blodau, 2002; Limpens *et al.*, 2008). Although DOC concentrations in this present study could not be correlated with temperature or rainfall, the relatively hotter and drier period in 2006 may have had an influence on DOC concentrations in the Moore and Clarkson (2007) study.

5.4.5 Impact of freezer storage on samples

Filtered samples from September and October were stored in a freezer for up to five months while the AgResearch TOC analyser was being repaired. This may have caused a decrease in DOC concentrations within the samples (Giesy & Briese, 1978; Fellman *et al.*, 2008). Fellman *et al.* (2008) found a significant decrease in DOC when stream water samples were frozen compared to samples that were analysed immediately with a mean decrease in DOC concentration in frozen samples of 14%. The proportional loss of DOC increased with increasing DOC concentrations and the primary mechanism of DOC removal was abiotic particle formation during freezing. They recommend that surface water samples with high DOC concentrations (> 5 mg l^{-1}) should be analysed immediately and not frozen although this was not possible in this case. However, in the present study, the absence of a significant difference between samples that were frozen and samples that were not frozen suggests that this was not causing an obvious impact on this study's DOC concentrations.

5.4.6 Summary

- All variables measured throughout the year, such as air temperature, precipitation, peat temperature and RWL, show seasonality in data but a seasonal trend in DOC concentration was not reflected.
- The absence of a seasonal trend in DOC concentrations at Kopuatai was presumed to be because of the relatively small seasonal variation in temperature at Kopuatai.
- DOC concentrations were not able to be correlated with air temperature, precipitation, peat temperature or water table regime.
- There was a difference in DOC concentration under different vegetation types. Significantly higher DOC concentrations were found under *L. scoparium* compared to *E. robustum* sites and DOC concentrations were higher under *L. scoparium* sites than the *S. ferrugineus* sites in the autumn and spring large scale sampling. This is likely due to the differing chemical properties of plant materials leading to higher decomposition rates under *L. scoparium*.
- Canal DOC concentrations were significantly higher than peat pore water concentrations under *E. robustum*.

- February 2012 had higher DOC concentrations at shallower peat depths due either the lack of rain before sampling or increased microbial decomposition due to warmer temperatures. There was no significant variation in DOC concentration with depth during other sampling periods.
- The difference between DOC concentrations reported by Moore and Clarkson (2007) and the present study is likely explained by differences in sampling methods.

Chapter Six
Annual DOC export

6.1 Introduction

Annual DOC export from Kopuatai was estimated using a water balance based approach. This approach is similar to the method applied to mineral soils by Sanderman & Amundson (2008), but does not appear to have been directly applied by the published literature.

In order to determine the complete waterborne carbon budget for Kopuatai, other forms of aquatic carbon must be considered such as the input of DOC through rainfall, and POC, DIC and dissolved CO_2 and CH_4 export. These alternative carbon forms will be discussed in this chapter.

6.2 Methods

6.2.1 Water balance of Kopuatai bog

The period of DOC sampling occurred from 1 February 2012 to 1 February 2013 for which evaporation and precipitation measurements were also available. Water discharge from the eddy covariance (EC) footprint was calculated from the water balance.

$$Q = P - E - \Delta S \qquad 6.1$$

where water loss (Q) is solved given inputs of precipitation (P), changes in water storage (ΔS) and evaporation (E). Evaporation is defined here to include transpiration, evaporation from the moist peat surface, as well as evaporation of intercepted rain water.

Q usually consists of Q_{vertical} and Q_{lateral}. Q_{vertical} is assumed to be negligible because hydraulic conductivity in peat decreases with increasing depth (King, 1999; Campbell & Jackson, 2004) and Kopuatai is underlain with marine silts and clays (Newnham *et al.*, 1995).

6.2.1.1 Evaporation measurement

An EC tower measures CO_2 and water vapour exchange at Kopuatai bog. Evaporation estimates were derived from EC measurements of the latent heat flux, *LE*. Briefly, the EC system at Kopuatai consisted of a sonic anemometer (CSAT3, Campbell Scientific Inc. (CSI), Logan, UT) and an open path infrared gas analyser (LI-7500, LI-COR, Lincoln, NE) mounted on a triangular steel lattice tower at a height of 4.25 m. 10 Hz raw measurements were stored on a compact flash card attached to a data logger (CR3000, CSI). Ancillary measurements were recorded by this and another data logger (CR1000, CSI) as half-hourly means. For calculating and quality-controlling *E*, the most important measurements were net radiation (NR01, Hukseflux, Delft, Netherlands), soil heat flux (HFT3, REBS, USA), and air temperature and humidity (HMP155, Vaisala, Helsinki, Finland). The soil heat flux was corrected for heat storage in the peat above the level of the soil heat flux plates, and vegetation canopy heat storage was calculated, both following Thompson *et al.* (1999).

Raw eddy covariance data were post-processed into fluxes (including *LE*), using the EddyPro software package (Version 4, LI-COR). Raw fluxes were filtered to exclude periods when the CSAT3 and LI-7500 reported interference due to liquid water droplets (rain, dew). Extremely large magnitude fluxes that were energetically impossible were also removed.

Frequent gaps in the *LE* dataset were gap-filled using the online gap-filling routine of Reichstein *et al.* (2005) (http://www.bgc-jena.mpg.de/~MDIwork/eddy proc/) to give continuous values over day and night. Gaps were filled with averages under similar meteorological conditions (7 or 14-day window), or the mean diurnal variation (starting with window size of 0.5 days), depending on availability of meteorological data.

Gap-filled 30-minute *LE* (W m^{-1}) were converted to 30-minute evaporation totals (kg m^{-2} ≡ mm) as

$$E = \frac{LE.t}{\lambda} \qquad 6.2$$

where t=1800 s and λ is the latent heat of vaporisation (≅2.45×10^6 J kg^{-1}), then *E* was summed over 24-hour periods.

6.2.1.2 Change in storage measurement

The absolute water level (AWL) was measured continuously for a year from 1 February 2012 to 2 February 2013 at the EC tower site. AWL was measured with a vented pressure transducer (4580–2v-2.5, Geokon, Lebanon, NH) connected to a datalogger (CR10X, CSI). A steel rod was inserted into the peat through to a firm base at the EC site and the pressure transducer was attached to the rod (Figure 6.1). Water level was measured at 1 minute intervals and averaged for 30 minute periods. The change in storage (ΔS) over a time period was calculated as the change in AWL (ΔAWL) over the period multiplied by peat specific yield.

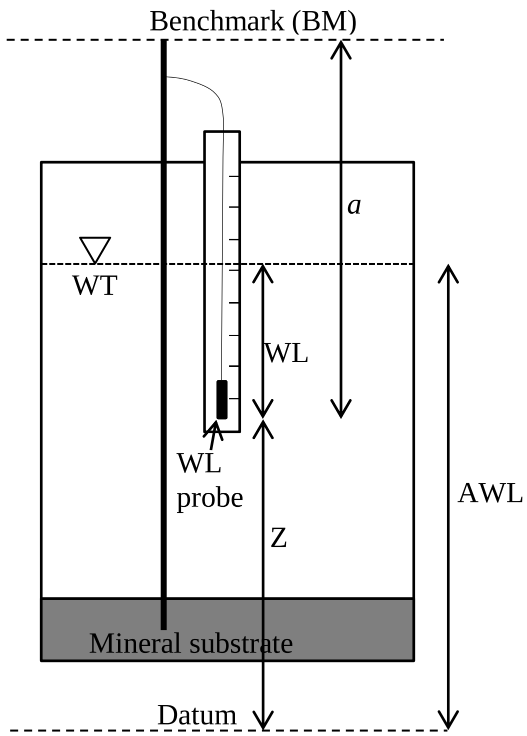

Figure 6.1: Diagram showing how absolute water level (AWL) was measured at Kopuatai. The water level probe was attached to a steel rod that was inserted into the mineral substrate below the peat. The top of the pole provided a fixed benchmark. AWL was derived from the pressure transducer measuring the height of the water table (WT) above it, as AWL = Z + WL, where the height of the probe above the datum, Z = BM – *a*, where *a* is the vertical distance from the benchmark to the probe.

Specific yield (*Y*) is the discharge of groundwater that takes place when the water table is lowered through a unit distance (Ingram, 1983). *Y* of peat at Kopuatai was estimated from the change in AWL caused by isolated large rainfall events. Each rainfall event had to be large enough to overcome canopy storage (or preferably was already wet) to ensure that interception losses were negligible. Rainfall amount and associated water table increase were recorded from the period of February to July 2012 and these data were graphed. The slope of the line of best fit gave *Y* of peat. Once *Y* was calculated, the water level change over a month can be converted to ΔS by multiplying it by *Y*. A negative ΔS indicates a reduction in storage whereas a positive ΔS indicates an increase in storage.

6.2.2 DOC concentration

DOC sampling took place over a year from the start of February 2012 to the end of January 2013. Water was sampled at sites 1 to 9 within the EC footprint once every two months from piezometers at three different depths. These samples were bulked across depth (e.g. by 0–0.3, 0.3–0.6, 0.6–1.0 m depths) to obtain average DOC concentrations as it was assumed that the position within the peat profile may have an impact on DOC production. Site 4 (located at the EC tower) was sampled individually every month and on months where bulked values were not available, site 4 DOC concentrations were used. Monthly DOC concentrations were calculated using a weighted average from King (1999) model (see section 5.2.1).

DOC concentrations from site 4 were compared with bulked DOC concentrations to determine whether there was a significant difference between them. This was also used to examine whether it was feasible to only sample from site 4 to reduce costs in the future. A regression equation between the two sets of data was calculated (Figure 6.8) but very little of the variation was explained by the regression (R^2 = 0.03). This likely resulted because of the small seasonal variation within the peat bog (Chapter 5). A paired t-test showed that there was no significant difference between the means of both sets of samples (p = 0.20). Despite this, site 4 DOC values were corrected by a factor of 1.087 to match bulked values (the average DOC concentration of bulked samples divided by the average of site 4).

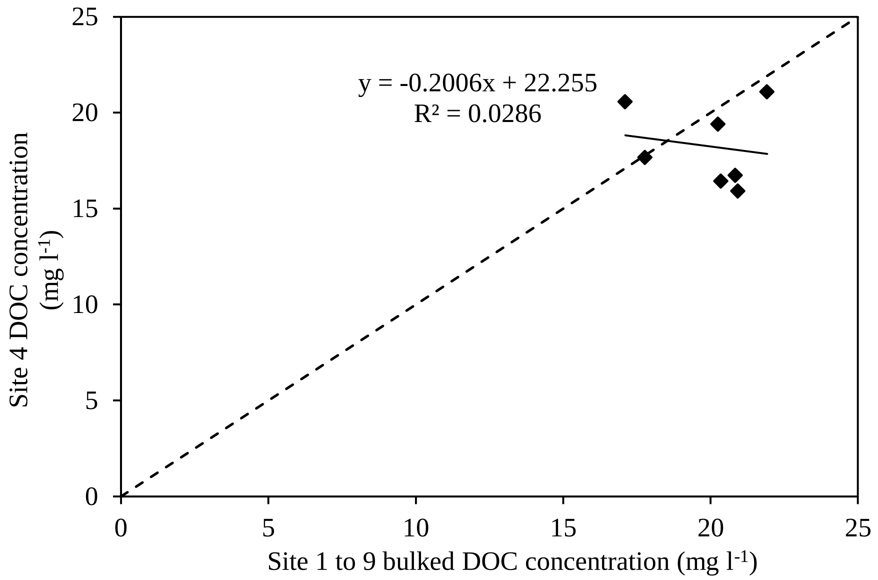

Figure 6.2: Scatterplot of site 4 DOC concentrations versus bulked DOC concentrations. Dashed line represents the 1:1 line. The solid black line is the trend line of the plots.

Three times in the year (February, March and September) water samples from each piezometer in the EC footprint were analysed individually to determine variability in DOC concentrations. From these data, weighted averages for sites 1 to 9 were calculated and from this an average EC footprint DOC concentration for months February, March and September was calculated. For the three months where DOC from individual sites were analysed, the standard error (SE) ranged from 0.41 to 1.36 mg l^{-1} (mean 1.1 mg l^{-1}).

Of the 12 months of DOC concentrations used to calculate annual DOC export: three months were averaged from individual samples of sites 1 to 9, five months were samples from site 1 to 9 that were bulked by depth in the field, and four months were the adjusted site 4 values (Figure 6.3).

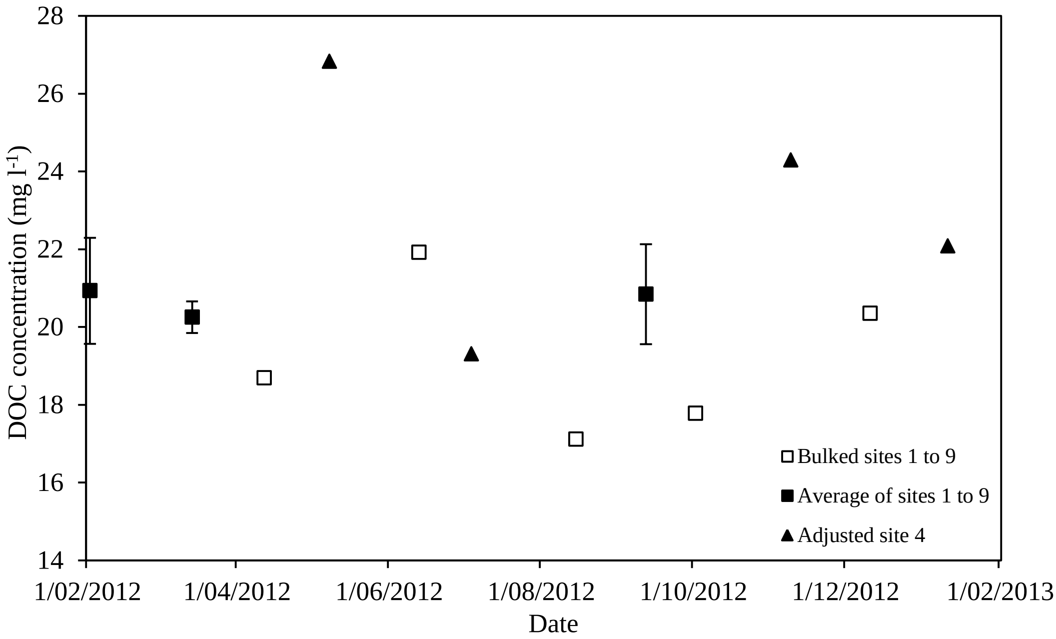

Figure 6.3: Vertically weighted average DOC concentrations per month following King (1999) model. Standard error values were only able to be calculated for three months when each site was sampled individually (averaged sites). Five months are bulked data and four months are adjusted site 4 data.

6.2.2.1 DOC in rainwater

To estimate DOC inputs to the bog via rainfall, the DOC concentration in rainwater was analysed and multiplied by the total amount of precipitation received at Kopuatai during the period of study. As DOC can degrade over time it was not feasible to leave a collecting device out in Kopuatai and retrieve it later. Rain samples were collected at a site on the southern edge of Hamilton city, with only a small fetch across the urban area (37º48'08.60"S 175º17'03.80"E). The site was approximately 50 km south west of Kopuatai and was expected to have rainfall of similar DOC concentrations to those found at Kopuatai. Rainwater samples were collected by putting a glass funnel and glass bottle in the rain to obtain a sample. Rainwater was collected on two days over the study period (14/08/12 and 10/12/12). The samples were stored in the fridge until it was filtered and analysed at AgResearch within one or two days.

6.2.3 DOC analysis and errors

For details of DOC laboratory analysis refer to section 5.2.2.

To check that the variation in DOC measurements was low the TOC analyser at AgResearch was set up to do 3–5 injections until coefficients of variance (CV) below 2% were obtained. The limit of detection for the TOC analyser was 0.6 mg l^{-1}. It was assumed that the TOC analyser random error was negligible compared to the spatial variation in DOC within the EC footprint. There were three sampling periods where samples were analysed separately for each of the nine EC footprint sites, 02/02/12 14/03/12 and 12/09/12, yielding a SE of 1.36, 0.41, and 1.29 mg l^{-1}. A conservative estimate of SE was applied to all months of 1.5 mg l^{-1}.

6.2.4 DOC export

The export (flux) of DOC for a time period is calculated as

$$F_{\mathrm{DOC}} = Q \times C_{\mathrm{DOC}} \qquad 6.3$$

C_{DOC}, the average DOC concentration of the time period of interest (mg C l^{-1}), was multiplied by Q (l m^{-2} $period^{-1}$) to get DOC export (F_{DOC}, g C m^{-2} $period^{-1}$). For this purpose Q had units l m^{-2} $period^{-1}$ where units of mm depth (from equation 6.1) are equivalent to l m^{-2} (assuming the density of water is 1000 kg m-3). Two methods (method 1 and 2) were used to calculate monthly and sampling interval DOC export and summed to calculate annual DOC export. A third method (method 3) was used only to calculated annual DOC export.

Method 1: Q was calculated from equation 6.1 by calendar months. DOC concentration was calculated by interpolating between DOC sampling periods to the start of each month. DOC concentrations across each month were calculated as the means of the bounding values and this was multiplied by monthly Q to obtain F_{DOC} for that month (an example of this is shown in Figure 6.4).

Method 2: The water balance was calculated between DOC sampling dates to give Q. DOC concentrations averaged across the two bounding dates, and this was multiplied by Q to obtain F_{DOC} for the period between sampling dates (an example of this is shown in Figure 6.5).

Method 3: Annual DOC export was calculated using *Q* calculated from annual totals of *P*, *E* and annual Δ*S*. DOC concentrations from each of the 12 sampling periods were averaged and multiplied by annual *Q*

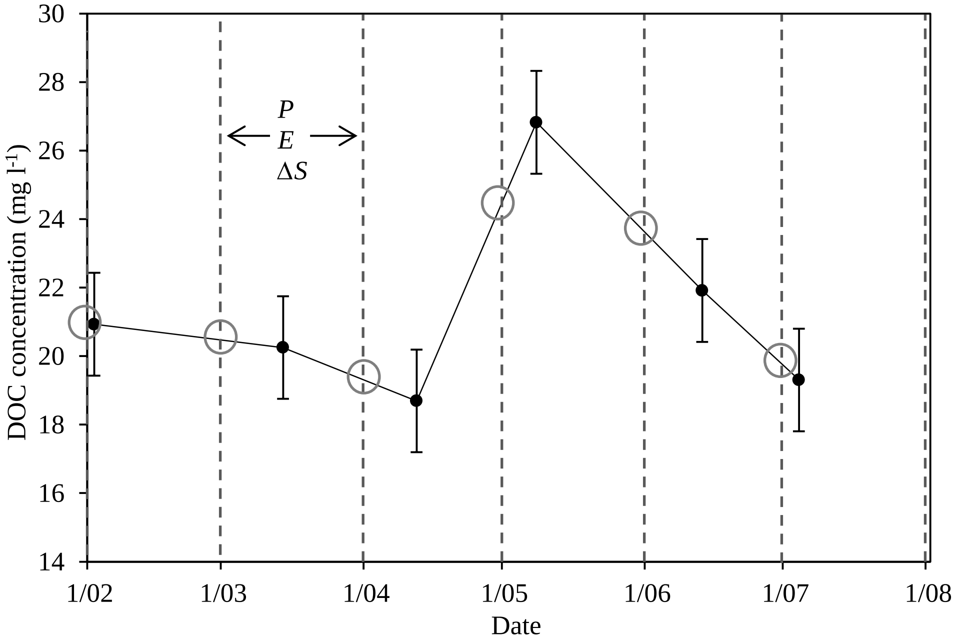

Figure 6.4: Method 1 used to calculate monthly DOC export at Kopuatai. Total precipitation (*P*), evaporation (*E*) and change in storage (Δ*S*) were determined over calendar months to obtain discharge (*Q*) and DOC concentrations were interpolated to the first of each month (circles). The estimated DOC concentrations of the start and end of each month were averaged and used as the average DOC concentration for that month and this was multiplied by *Q*. The same DOC concentrations from Figure 6.3 are used in this figure with an applied SE of 1.5, but not all measured monthly DOC concentrations are shown.

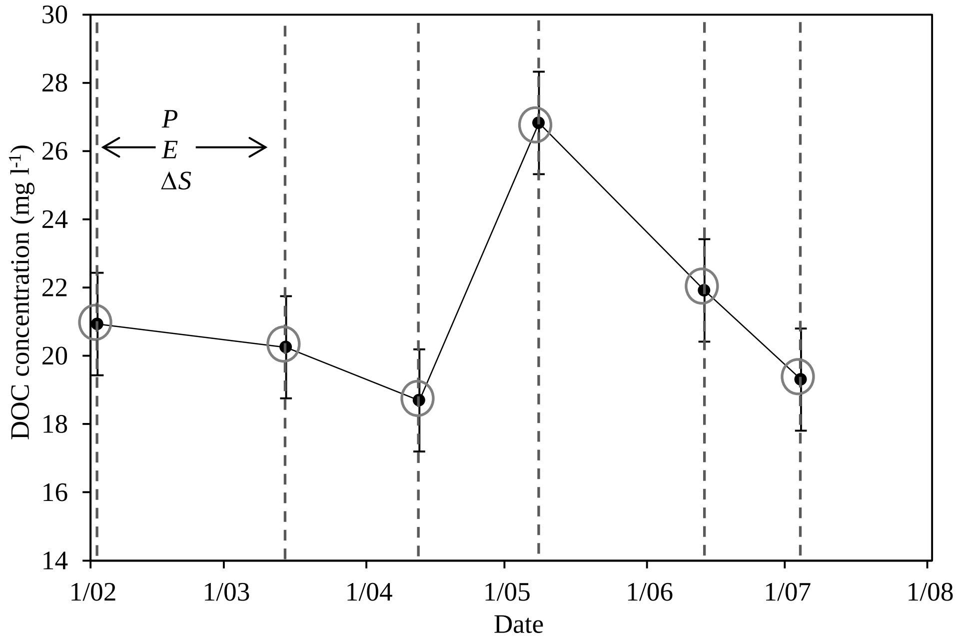

Figure 6.5: Method 2 used to calculate monthly DOC export at Kopuatai. Total precipitation (*P*), evaporation (*E*) and change in storage (Δ*S*) were determined between sampling periods to obtain discharge (*Q*). DOC concentrations were averaged between sampling periods and multiplied by *Q*. The same DOC concentrations from Figure 6.3 are used in this figure with an applied SE of 1.5, but not all measured monthly DOC concentrations are shown.

6.2.5 Error analysis of DOC export

Uncertainties were calculated using error models from Watts and Halliwell (1996).

F_{DOC} has uncertainty δF_{DOC} which was estimated as

$$\delta F_{\mathrm{DOC}(i)} = FE_{F_{\mathrm{DOC}_{(i)}}} \times F_{\mathrm{DOC}_{(i)}} \qquad 6.4$$

where $FE_{F_{\mathrm{DOC}(i)}}$ is the fractional error in F_{DOC} for the time period *i*. This is calculated from the error model for equation 6.3 as

$$FE_{F_{\mathrm{DOC}}} = \sqrt{\left(\frac{\delta Q}{Q}\right)^2 + \left(\frac{\delta C_{\mathrm{DOC}}}{C_{\mathrm{DOC}}}\right)^2} \qquad 6.5$$

where δQ is the uncertainty of Q and δC_{DOC} is the uncertainty of DOC concentration (C_{DOC}).

6.2.5.1 Error analysis of *P*, *E* and Δ*S*

To find δQ, the uncertainty model for equation 6.1 is

$$\delta Q = \sqrt{\delta P^2 + \delta E^2 + \delta \Delta S^2} \qquad 6.6$$

We assumed appropriate conservative values of the component uncertainties. The uncertainty of *P* (δP) was estimated at ±5%. The rain gauge was calibrated prior to installation and wind speeds at Kopuatai were relatively light so there was less chance of underestimation. There was potential underestimation of *E* due to lack of closure of the energy balance but *E* could be adjusted accordingly for this. Therefore, uncertainty in *E* (δE) was caused mainly by random measurement and gap-filling errors and estimated at ±10%.

Instrument errors in determining ΔAWL were considered to be very small. The pressure transducer has accuracy ±0.4 mm and a precision of ±0.2 mm. The major uncertainty in Δ*S* was its spatial variation, which was unknown. However, AWL probably varied little over most of the footprint, except when the water table intersected the peat surface over some parts during winter. If the peat properties were reasonably spatially homogeneous, then Δ*S* was probably conservative in its variation. The uncertainty in Δ*S* ($\delta\Delta S$) was estimated at ±20%.

6.2.5.2 Error analysis of DOC concentration

As the uncertainty in EC footprint DOC concentrations, δC_{DOC}, is mostly caused by spatial variation, the standard error of the means used to calculate DOC concentration (C_{DOC}) for each time period was adopted as an appropriate estimate. Since two values of C_{DOC} were used to calculate a monthly average, δC_{DOC} was calculated as

$$\delta C_{\mathrm{DOC}} = \sqrt{2 \times (\mathrm{SE}_{C_{\mathrm{DOC}}})^2} \qquad 6.7$$

where $\mathrm{SE}_{C_{\mathrm{DOC}}}$ is the standard error value chosen to represent spatial variation in C_{DOC}.

6.2.5.3 Annual flux of DOC error analysis

Since the annual flux of DOC, $F_{\mathrm{DOC(annual)}}$, is calculated from the sum of the component period fluxes, $F_{\mathrm{DOC}(i)}$ (equation 6.3), the uncertainty in $F_{\mathrm{DOC(annual)}}$ will be

$$\delta F_{\mathrm{DOC(annual)}} = \sqrt{\sum \delta F_{\mathrm{DOC}(i)}{}^2} \qquad 6.8$$

6.2.6 POC concentration

Water samples were extracted from the peat in the same way as DOC samples in order to determine the importance of POC export within the EC footprint. At three times during the year (August, October and December 2012) 100 ml POC samples from sites 1 to 9 were bulked across depth (0–0.3, 0.3–0.6, 0.6–1.0 m). 1 litre samples of water for POC analysis were also taken from the canal site.

A method from Hope *et al.* (1994), Moore *et al.* (2011) and Worrall *et al.* (2003b) was used to derive POC concentration. Filters (0.45 μm cellulose acetate membrane filters) were rinsed through with 500 ml of deionised water under vacuum and then oven dried at 40°C for 24 hours. The water samples (along with a control of deionised water) were filtered through the (pre-weighed) filters under vacuum. The filters were retained and oven dried (24 hours at 40 °C) to quantify particulate matter which was assumed equal to particulate organic matter (POM) due to the dominance of peat. POM was then converted to a POC value by assuming organic matter to be 50% carbon (Hope *et al.*, 1994). POC concentrations were averaged and multiplied by annual *Q* to determine annual POC export from the bog. The error model of DOC export (equation 6.4) was also applied to the calculation of annual POC export.

6.3 Results

6.3.1 Water balance of Kopuatai Bog

Monthly *P*, *E* and ΔS were calculated to yield monthly *Q*.

6.3.1.1 Precipitation

Annual *P* for the start of February 2012 to the end of January 2013 totalled 1026 mm. Annual *P* was 225 mm lower than the 30 year average (1981–2010) of 1251 mm measured at NIWA's long term site at Paeroa, approximately 10 km to the east of the sites. *P* was similar to the 30 year average for the months May, September and October (Figure 6.6). Wetter than average months were March, July and August with 156%, 137% and 128% higher than the 30 year rainfall average for each month respectively. Drier than average conditions occurred in April and June with monthly *P* values of 27% and 44% respectively of the 30 year monthly average. Lower *P* also occurred from November 2012 to January 2013, totalling 37% of the 30 year mean for the 3 months. Temperatures were generally lower in 2012 than the 30 year average.

6.3.1.2 Evaporation

Annual *E* for the period February 2012 to January 2013 totalled 527 mm. Maximum monthly *E* was 67.4 mm in December and the minimum was in July when *E* totalled 22.1 mm. *E* exceeded *P* for November, December 2012 and January 2013 (Figure 6.7).

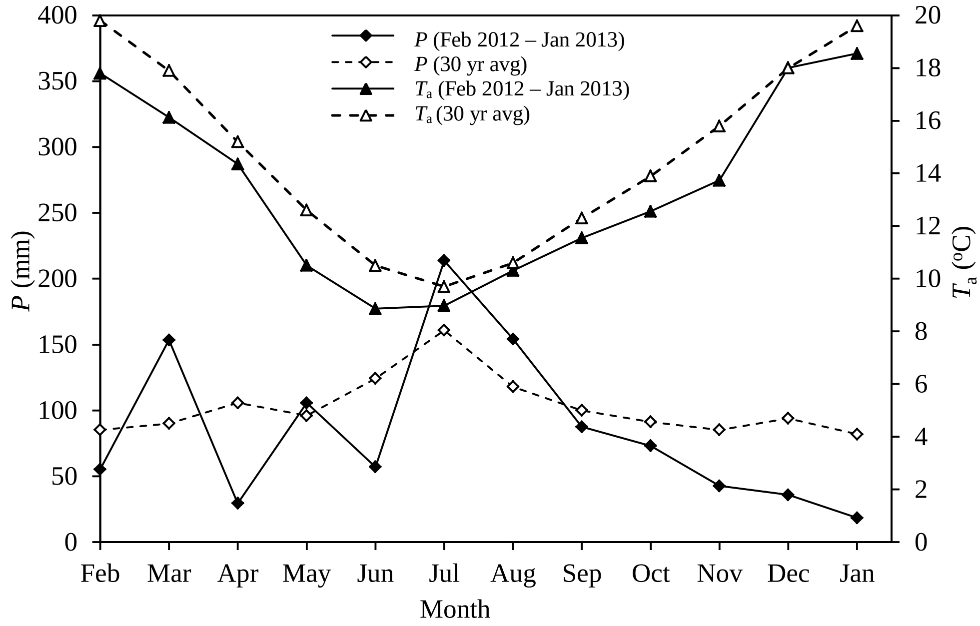

Figure 6.6: Monthly averages of air temperature (T_a) and monthly totals of precipitation (*P*) at Kopuatai bog from February 2012 to January 2013 compared to 30 year averages of monthly *P* and T_a recorded at Paeroa.

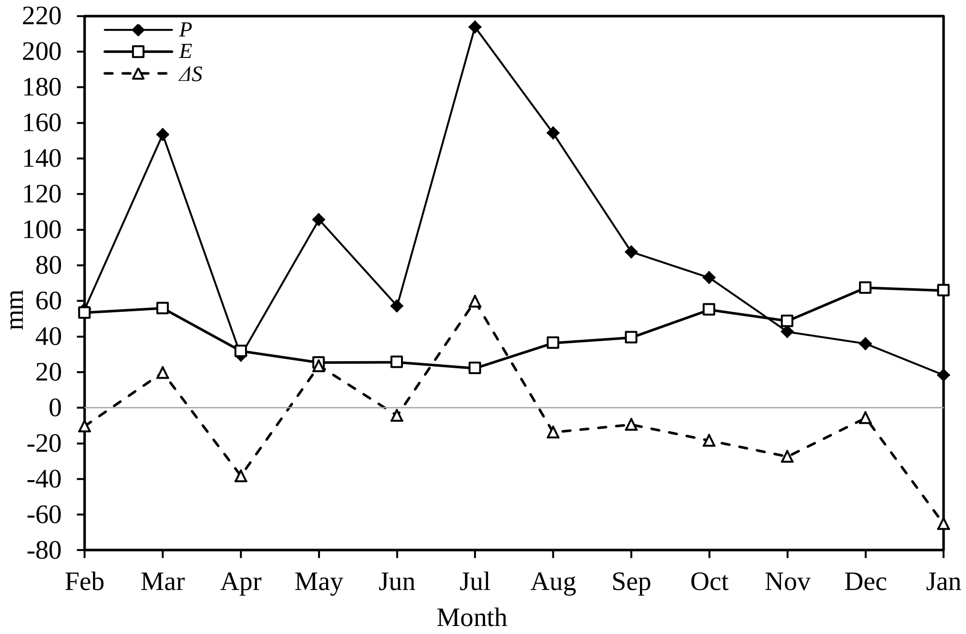

Figure 6.7: Monthly totals for precipitation (*P*), evaporation (*E*) and change in storage (ΔS) at Kopuatai bog for the annual period February 2012 to January 2013.

6.3.1.3 Change in storage

The change in AWL during selected isolated precipitation events was plotted against the event precipitation totals (Figure 6.8). The trend line was an excellent fit with an R^2 of 0.96. The slope this relationship was used as the value for specific yield (*Y*) which was calculated at 38% volume yield of water. *Y* was multiplied by the monthly change in AWL to obtain *ΔS* for the month (Figure 6.7).

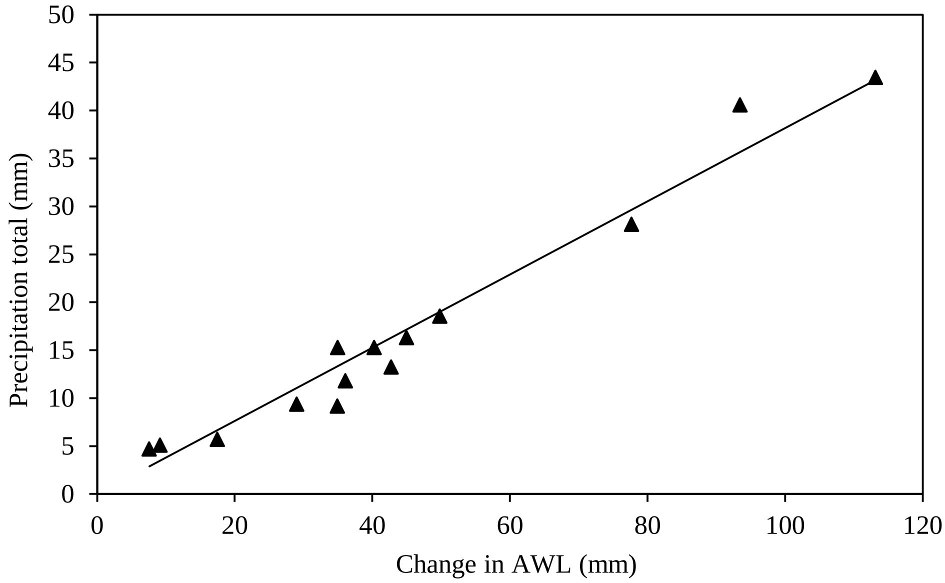

Figure 6.8: Specific yield was determined as the slope of the relationship between rain event size and the change in AWL. The equation of the regression was y = 0.38x (R^2 was 0.96). The slope of the line (0.38) gives the specific yield of the peat.

6.3.1.4 Discharge

Method 1: Highest *Q* occurred in July and August during the winter and the lowest *Q* occurred in December, January and February during the summer. December had a negative *Q* which resulted from low *P*, high *E* and a small negative Δ*S*. A negative *Q* implies a net water input into the EC footprint (Figure 6.9).

Method 2: Highest *Q* occurred from 4 July to 15 August in the winter during a very wet period. The lowest *Q* occurred from 9 November to the end of the year during the summer. Only one period (11 November to 11 December) had a negative *Q* (Figure 6.9).

The annual Q for all three methods was 588 l m^{-2}.

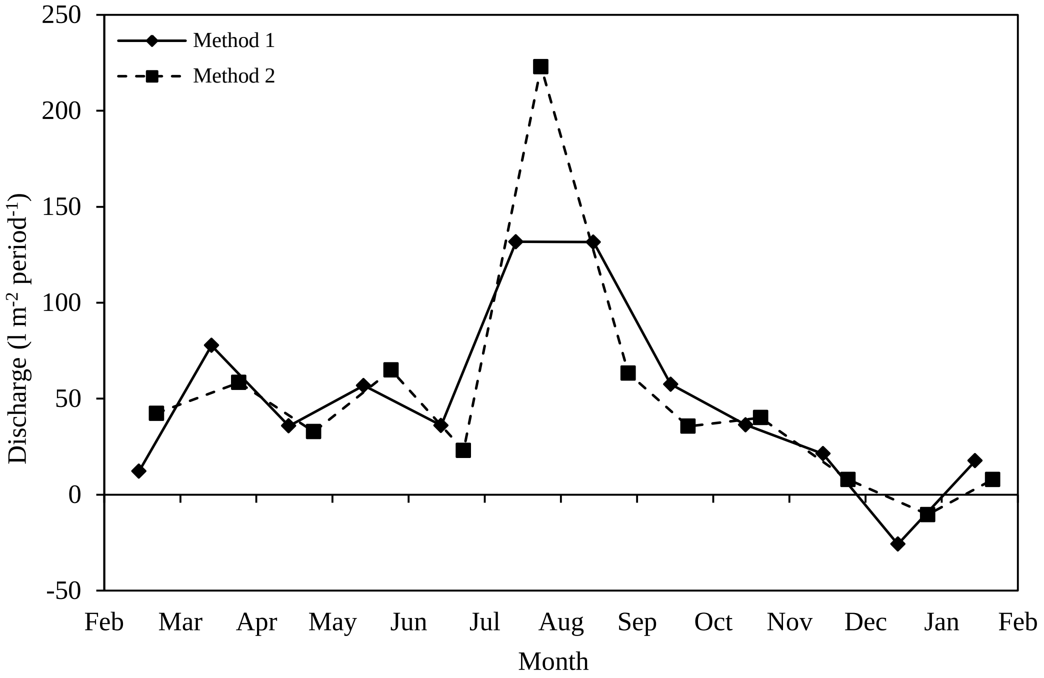

Figure 6.9: Monthly discharge from the EC footprint using method 1 and method 2.

6.3.2 DOC concentration

Monthly DOC concentration ranged from 17.1 to 26.8 mg l^{-1} from February 2012 to January 2013 and the annual average DOC concentration (± SE) was 20.9 ± 2.72 mg l^{-1}. To calculate DOC export, DOC concentrations from Figure 6.3 were interpolated between sampling periods using two methods (see section 6.2.4). The comparisons of DOC concentration for method 1 and method 2 are shown in Figure 6.10.

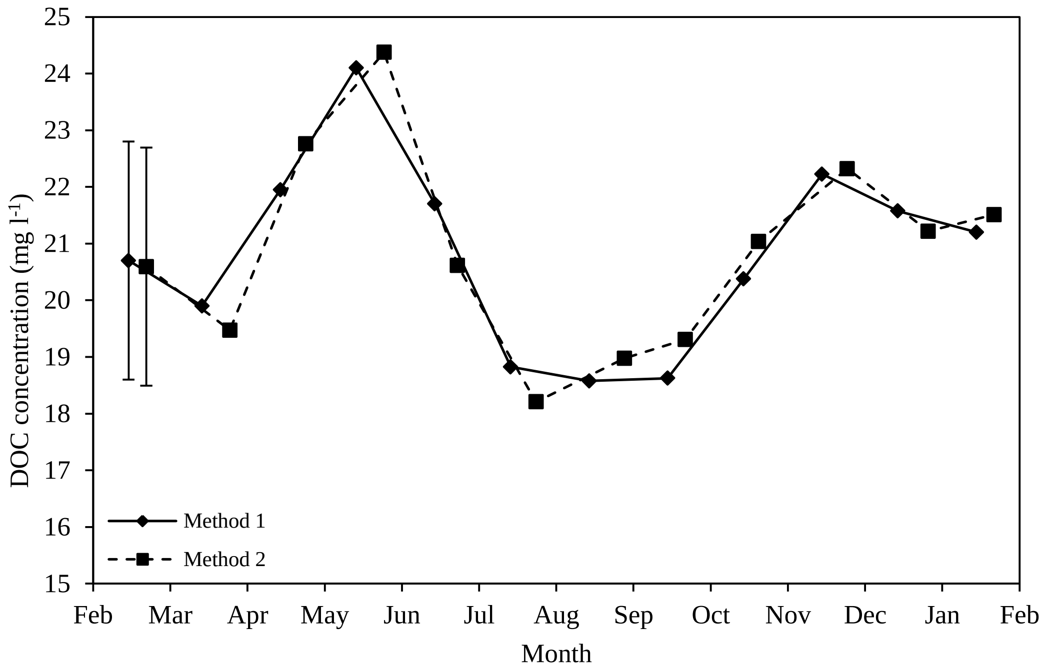

Figure 6.10: DOC concentrations interpolated between sampling points and used for methods 1 and 2. Example error bars are shown of SE = 2.1 mg l^{-1} (determined using equation 6.7).

6.3.3 DOC export

Monthly export for method 1

Monthly average DOC concentrations were multiplied by monthly *Q* to calculate DOC export from the footprint over a calendar month (Figure 6.11). DOC exports ranged from –0.56 ± 0.16 to 2.50 ± 0.41 g C m^{-2} $month^{-1}$ over the year from February 2012 to January 2013. There was seasonal variability with high exports in winter and low (and negative) exports in summer. Monthly DOC exports summed up over the year equalled 11.7 ± 0.82 g C m^{-2} yr^{-1}. A negative export occurred in December 2012 due to the negative *Q* that was calculated. This negative value implies an import of water and DOC into the EC footprint.

Monthly export for method 2

DOC exports ranged from –0.23 ± 0.2 to 4.08 ± 0.59 g C m^{-2} between sampling dates from February 2012 to January 2013 (Figure 6.12). DOC exports summed over the year equalled 11.7 ± 0.87 g C m^{-2} yr^{-1}. The negative DOC export from

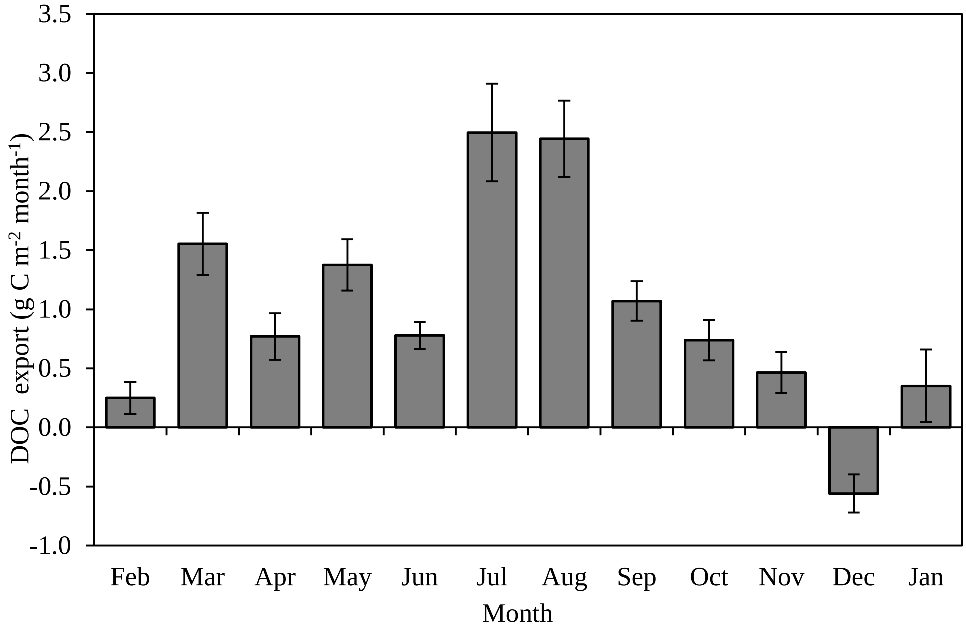

Figure 6.11: Monthly DOC export from Kopuatai bog using method 1. Error bars indicate the uncertainties calculated from equation 6.4.

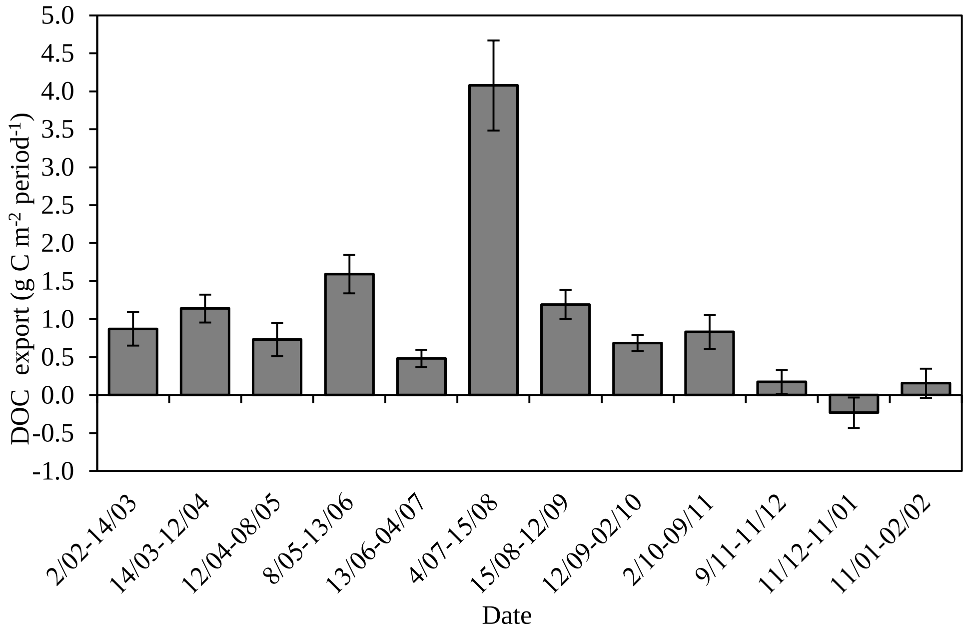

Figure 6.12: DOC export between sampling periods. Error bars indicate the uncertainties calculated from equation 6.4.

the time period 11/12/12 to 11/01/13 implies an import of water and DOC into the EC footprint. The large spike in DOC export from 04/07/12 to 15/08/12 occurred due to the larger than usual spacing of time between sampling dates coupled with high rainfall. This spike is spread across two months in method 1 (July and August).

Method 3

The third estimate of annual DOC export was calculated by averaging monthly DOC concentrations over the year (20.9 ± 0.79 mg l^{-1}) and multiplying by Q (588 ± 76 l m^{-2}). Annual DOC export by this method was 12.3 ± 2.01 g m^{-2}.

6.3.3.1 Drivers of DOC export

Strong relationships were found between monthly DOC export values (from method 1) and monthly totals of P (Figure 6.13, R^2=0.80) and monthly totals of P–E (Figure 6.14, R^2=0.86). Given that there was little seasonal variation in DOC concentration these relationships suggest a relatively simple way to estimate DOC export.

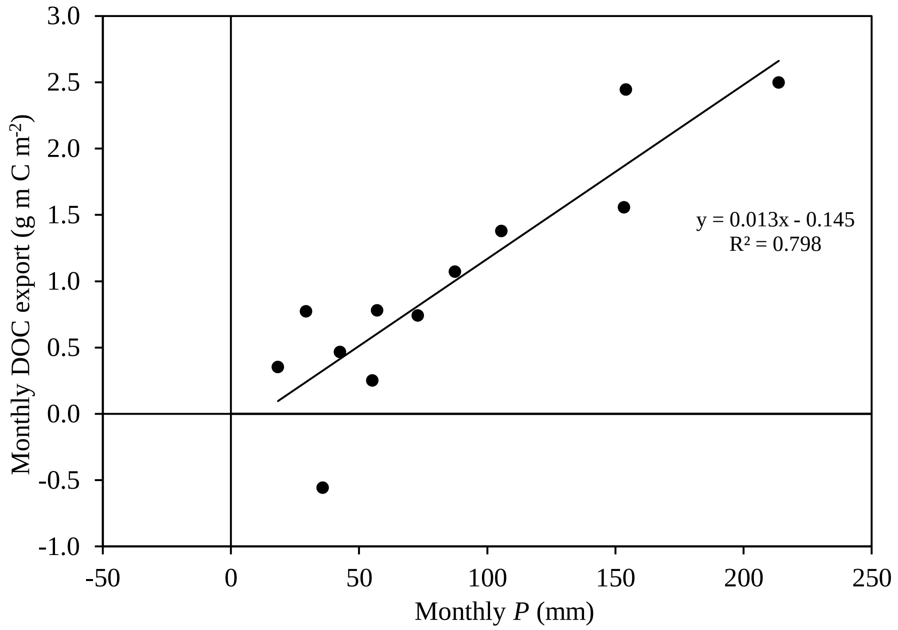

Figure 6.13: Regression of monthly DOC export (using method 1 values) and monthly *P*.

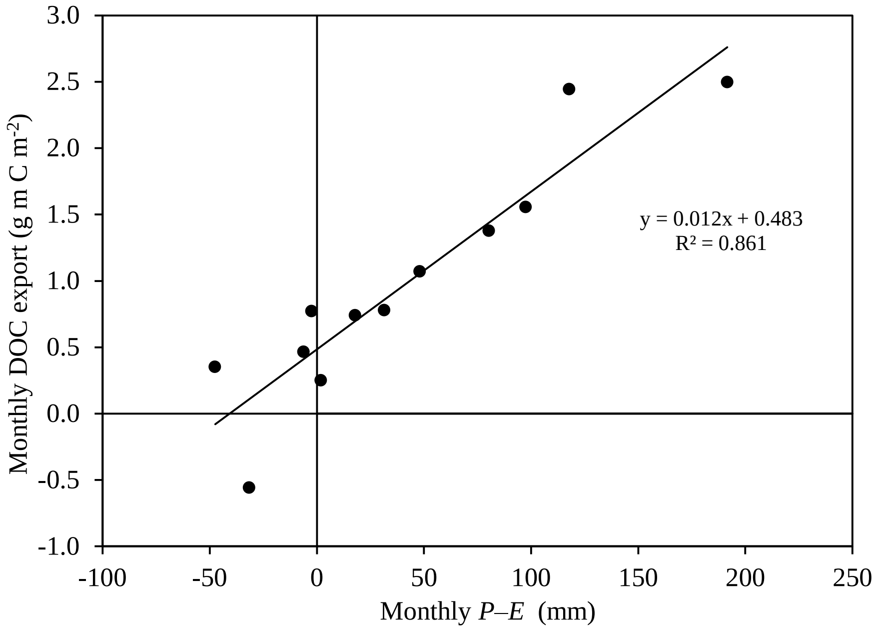

Figure 6.14: Regression of monthly DOC export (using method 1 values) and monthly *P–E*.

6.3.4 Annual import of DOC through precipitation

DOC concentration in rain water (1.23 mg l^{-1}) was an average of two samples of rainwater (0.66–1.80 mg l^{-1}). This was multiplied by total *P* over the year resulting in an estimated addition of DOC to the bog by rain of 1.26 ± 0.83 g C m^{-2} yr^{-1}.

6.3.5 Annual export of POC

POC concentrations of peat pore water within the EC footprint were bulked for three different depth ranges (0–0.3, 0.3–0.6, 0.6–1.0 m) and compared to POC concentrations from the canal (Figure 6.15). The lowest measurements of POC concentration were found in the canal (1.0 ± 0.2 mg l^{-1}). The highest POC concentrations were found at 0.6–1.0 m depth (11 ± 2.0 mg l^{-1}), followed by 0–0.3 m depth and 0.3–0.6 m (5.7 ± 0.7 mg l^{-1} and 2.2 ± 0.7 mg l^{-1} respectively).

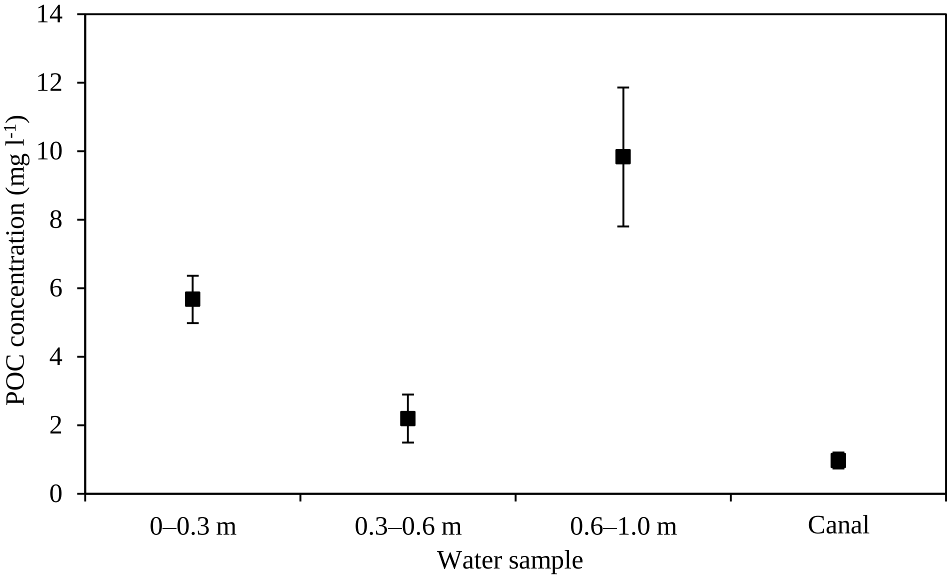

Figure 6.15: POC concentrations (mg l^{-1}) of peat pore water bulked for 0–0.3, 0.3–0.6, 0.6–1.0 m depths and for water from the canal (n = 3, ± SE).

POC values were higher than expected from the bulked samples within the footprint but the canal, draining a large area of the wetland, had very low values of POC. It is possible that the method used to collect water for POC analysis mobilised more POC than would normally move with pore water. Therefore, the annual POC export was estimated by multiplying the average POC concentration of the canal by annual *Q*. Average POC concentration of the canal (1.0 ± 0.2 mg l^{-1}) was multiplied by annual EC footprint *Q* (588 l m^{-2}), yielding POC export of 0.57 ± 0.21 g C m^{-2}.

6.3.6 Summary of results

Some published studies have reported annual DOC exports with DOC imported through rainfall subtracted from the total. Other studies include DOC and POC export together as a measure of total organic carbon (TOC export). In order to compare to other studies, the following table (Table 6.1) has DOC export values for all three methods summarised, along with values adjusted for rainfall import or with POC export added.

Table 6.1: DOC export values for all three methods summarised with values adjusted for rainfall import or with POC export added.

	Method 1	*Method 2*	*Method 3*
		g C m^{-2} yr^{-1}	
DOC export	11.7 ± 0.82	11.7 ± 0.87	12.3 ± 2.01
Adjusted for rainfall import	10.5 ± 1.17	10.4 ± 1.20	11.0 ± 2.18
TOC export (DOC+POC)	12.3 ± 0.84	12.3 ± 0.90	12.8 ± 2.02

* DOC import by P = 1.26 ± 0.83 g C m^{-2} yr^{-1}

** POC export = 0.57 ± 0.21 g m^{-2} yr^{-1}

6.4 Discussion

6.4.1 Water balance of Kopuatai bog

Total rainfall from February 2012 to January 2013 was 225 mm lower than the 30 year average at Paeroa suggesting that annual average DOC export may be larger than found in this study. ΔS followed patterns in P; if P was high in a month ΔS was also positive and if P was low in a month, ΔS was negative, indicating movement of water out of the footprint area.

Discharge was driven by P as E varied much less. In December 2012, Q was negative, implying net water (and DOC) import into the flux footprint.

6.4.2 DOC concentration

Average DOC concentrations for the EC footprint ranged from 17.1 to 26.8 mg l^{-1}. It was expected there would be some seasonal variability in DOC concentrations due to seasonal temperature changes but this was not obvious at Kopuatai (see section 5.4.2). It was also expected that rainfall would be a driver of DOC variability but there was no significant relationship found between precipitation and DOC concentrations (section 5.4.2). However, this relationship was not specifically tested as sampling was conducted regardless of rainfall events.

6.4.2.1 DOC in rainwater

DOC concentration of rainfall sampled in Hamilton averaged 1.23 mg l^{-1}. This falls in the lower end of the range of DOC concentrations for rainfall reported by Thurman (1985) of 1 and 3 mg l^{-1} in boreal environments. Rainfall DOC concentrations were slightly higher than reported by Kieber *et al.* (2002) on the south-eastern coast of the South Island of New Zealand, approximately 3 km from Dunedin. Their samples were collected from 54 rainfall events between April 1999 and March 2000. The volume weighted average concentration of DOC was 0.70 ± 0.1 mg l^{-1}, and DOC values ranged from 0.12 mg l^{-1} to 4.81 mg l^{-1} with an average concentration of 0.82 mg l^{-1} (Kieber *et al.*, 2002). In the present study, only two rainfall samples were collected over the year and therefore may not show the true variability of DOC concentration within rainfall.

Concentrations of DOC in throughfall and stemflow were not measured as the release of DOC from decaying peat was expected to be the largest influence of DOC in the system and any DOC leached from the vegetation canopy is captured in the measurement of DOC export.

6.4.3 DOC export

Comparisons between methods 1, 2 and 3

DOC export calculated using methods 1 and 2 gave very similar results meaning that either method could be used to calculate annual DOC export. Method 3, used only to calculate annual DOC export, was 0.57 g C m^{-2} higher than using method 1 and 2 and had a larger uncertainty. It is recommended that method 1 be adopted as the preferred method of DOC export calculation as calendar months are easier to use and more intuitive. The following DOC export values reported in the discussion will be method 1 values.

Monthly DOC export

DOC export ranged from –0.56 ± 16 g C m^{-2} month^{-1} in December 2012 to 2.50 ± 0.41 g C m^{-2} month^{-1} in July 2012. The variation in monthly DOC export was primarily caused by variations in Q, mainly driven by the amount of rain during each month. Months with the high P and Q resulted in high DOC export (Figure 6.11). This compares with results from other studies (Pastor *et al.*, 2003; Clark *et* *al.*, 2007; Koehler *et al.*, 2009; Moore *et al.*, 2013) where DOC export values were mainly driven by discharge volumes and consequently by rainfall. Moore *et al.* (2013) found that 94% of DOC export occurred during the wet season in tropical peatlands in south-east Asia. Koehler *et al.* (2011) found that there was no clear seasonal pattern found for DOC export at a temperate blanket bog in Ireland (Glencar), although the highest exports corresponded to the months with the highest precipitation. At Kopuatai bog, winter experienced the highest amount of precipitation and summer had the lowest amount of precipitation and this resulted in a seasonal pattern for DOC export (e.g. highest exports during the winter and lowest during the summer).

Koehler *et al.* (2009) and Clark *et al.* (2007) have shown that most DOC export occurs during storm events when the highest discharge occurs. Therefore the infrequent sampling of DOC concentrations at Kopuatai may lead to bias in overestimation of DOC export. This occurs because DOC concentrations were not sampled on the days of large storm events where it is possible that DOC concentrations could be lower due to dilution. We do not have evidence that this was occurring as the sampling programme was not specifically designed to test this. However, from our measurements, rainfall did not appear to be a significant driver of DOC variability.

In December 2012 there was an apparent negative DOC export. The negligible ΔS (–6.6 mm) coupled with relatively large E (68.4 mm) and smaller P (35.9 mm) suggested that water converged on the EC footprint area. This is feasible because the study site lies on the side slope of a domed bog (Figure 3.7) and water flows will cross surface elevation contours, meaning that water from higher on the dome moves down slope to the study site. The negative DOC export represents net DOC import from peat higher up on the domed part of the bog.

Annual DOC export

DOC export from Kopuatai bog of 11.7 ± 0.82 g C $m^{-2}yr^{-1}$ was less than estimates from the ‘typical’ Northern Hemisphere peatland of approximately 20 to 30 g C m^{-2} yr^{-1} as estimated by Gorham (1991) which is also of the same magnitude as the long-term carbon sink term of these ecosystems. Koehler *et al*. (2009) found the annual export measured from a stream draining Glencar in Ireland was 14.1 ±

1.5 g C m^{-2} for 2007. As reported by Worrall *et al.* (2009), the annual DOC export at the outlet of the Trout Beck stream in the UK varied from 10.3 to 25.2 g C m^{-2} from 1993 to 2005.

DOC export from Kopuatai adjusted for DOC input by rain equalled 10.5 ± 1.17 g C m^{-2} yr^{-1}. This is lower than the average export of DOC over a six year period estimated from a stream draining Mer Bleue bog in Canada of 14.9 ± 3.1 g C m^{-2} yr^{-1} by Roulet *et al.* (2007) (after subtracting DOC inputs through rainfall).

TOC export from Kopuatai bog was estimated at 12.3 ± 0.84 g C m^{-2} yr^{-1} (DOC + POC). This compares to the estimate of TOC export from a stream draining the Degero Stormyr mire complex, in northern Sweden, of 13.0 ± 1.5 g C m^{-2} yr^{-1}. Billett *et al.* (2004) measured TOC export from a stream draining the Auchencorth Moss peatland, south-east Scotland, to be 28.3 mg C m^{-2} yr^{-1}.

Kopuatai bog is largely still in a pristine state which may account for why DOC exports are lower than some other peatlands. This could also be due to the difference in decomposability of restiad peat compared to Northern Hemisphere peatlands, where the primary peat former is *Sphagnum*. In addition to the inertness of lignin and tannin, the allelopathic properties of the restiad tissues results in decay resistance due to the inhibition of microbial activity (Kuder *et al.*, 1998).

Measured *P* for the start of February 2012 to the end of January was approximately 225 mm or 22% below the 30 year average for the area. Therefore, measured DOC export may not reflect ‘normal’ DOC export from the bog under ‘normal’ hydrological conditions. This could be roughly estimated by using the annual average DOC concentration (20.9 mg C l^{-1}) and multiplying it by annual $P–E$ using *P* calculated from 30 year averages and estimating *E* as half of *P*. This gives DOC export of 13.1 g C m^{-2}, and this is only slightly higher than the measured DOC export during 2012/2013. Nevertheless, it is expected that runoff and therefore DOC export will vary from year to year, following differences in annual precipitation (Roulet *et al.*, 2007).

Fate of DOC

The fate of DOC that leaves the footprint of the EC tower and ultimately reaches streams and drains is uncertain. When it reaches a stream, in-stream processing is likely to become increasingly important as water moves downstream. As a result, both DOC and POC may be respired and lost through evasion (Dinsmore *et al.*, 2010). Research by Basiliko *et al.* (2012) showed that, despite high amounts of organic matter exported to the oceans by rivers, the contribution of this to marine dissolved organic matter is small. This means that there is a loss of this organic matter along the stream or river lengths through microbial degradation or flocculation or absorption onto suspended sediments in the estuarine environment (Dinsmore *et al.*, 2010). Further consumption of DOC can occur through photodegradation, where solar radiation causes conversion of DOC into DIC (Granéli *et al.*, 1998). Apart from the abiotic production of DIC, photodissociation can also break down DOC into low molecular weight carboxylic acids. As these are good bacterial substrates, this could lead to increased production in bacterial biomass and rates of respiration therefore increasing biotic production of CO_2 from DOC (Granéli *et al.*, 1998). DOC exported from an ecosystem like Kopuatai may ultimately end up as a source of CO_2 further downstream or incorporated into estuarine or oceanic sediments (Dinsmore *et al.*, 2010).

6.4.3.1 Error analysis

Evaporation error analysis

For the eddy fluxes such as *LE* there are large sources of random error that lead to uncertainty levels of 30–80% of the flux at half-hourly timescales (Hollinger & Richardson, 2005) However, when summed over daily, monthly and annual timescales the random error component decreases significantly (Hagen *et al.*, 2006; Baldocchi, 2008).

A common check on the quality of EC measurements is the ability to close the energy balance. However, most EC studies report incomplete energy balance closure (Wilson *et al.*, 2002), suggesting some of the measurements are deficient or that assumptions of the EC method are violated. Some studies have adjusted *LE* to correct for lack of closure. For instance, Twine *et al.* (2000) assumed the deficiency lay equally with the sensible heat flux (*H*) and *LE*, and both were adjusted upwards, preserving their ratio. Other authors recommend fluxes not be adjusted (Baldocchi, 2008). Leuning *et al.* (2012) substantially improved energy balance closure for OzFlux EC sites once energy storage terms were properly accounted for. At Kopuatai, preliminary analysis suggests energy balance closure of around 82% (D. Campbell, *pers. comm.*, February 2012), which is in the range commonly reported for EC studies (Wilson *et al.*, 2002). If a 20% underestimation of *E* is assumed, the DOC export from Kopuatai becomes 9.54 ± 0.80 g C m^{-2} yr^{-1}, a decrease of approximately 2.0 g C m^{-2} yr^{-1}

DOC sampling frequency error

Koehler *et al.* (2009) investigated the likely error of infrequent sampling and determined that the same annual DOC export measurement was calculated whether sampling was conducted at 30 minute, daily, weekly or monthly intervals. The only difference was when more frequent samples were taken the uncertainty of the export value was lower and the confidence in the export estimate was higher. An increase in the frequency of water sampling at Kopuatai is unlikely to change the annual DOC export value significantly but would reduce the uncertainty value.

6.4.3.2 Simple method to estimate DOC export

Strong relationships were found between monthly DOC export values (from method 1) and monthly totals of *P* (Figure 6.13, R^2=0.80) and monthly totals of *P–E* (Figure 6.14, R^2=0.86). Such strong dependence on these water balance components results from the observed lack of seasonal variation in DOC concentrations. This relationship may be used as a method to estimate DOC export from Kopuatai however its use is cautioned because it was developed over only one year, which was drier than normal.

6.4.4 POC export

POC export from Kopuatai bog was estimated to be 0.57 ± 0.21 g C m^{-2} yr^{-1}. It was expected that POC concentrations would be very low as in pristine wetland catchments nearly all organic carbon is exported as DOC (Hope *et al.*, 1994) whereas in actively eroding or drained peatlands the export of POC is generally high (Fiedler *et al.*, 2008; Pawson *et al.*, 2008; Pawson *et al.*, 2012).

Tipping *et al.* (2010) and Koehler *et al.* (2011) measured DOC input through rainfall and POC export from peatlands and as both measurements were similar, they were cancelled out in the C budget. At Kopuatai, DOC import through rainfall was estimated at 1.26 ± 0.83 g m^{-2} and POC export at 0.57 ± 0.21 g m^{-2}. The uncertainty of both values overlap and as they are both very low, in the future, it is probably sufficient to ignore both quantities and only focus on DOC export.

6.4.5 Other aquatic carbon export

Most literature agrees that DOC export is the largest export of carbon in discharge from an undisturbed bog (Waddington & Roulet, 1997; Dinsmore *et al.*, 2010).

DIC

As DIC is mostly derived from the products of carbonate dissolution and weathering of silicate materials (Hope *et al.*, 2004) the export of DIC is considered negligible at Kopuatai as the catchment is entirely peat and DIC coming in through rainfall is considered minor.

Dissolved CO_2 and CH_4

The dissolved CO_2 is CO_2 dissolved in water above and beyond that which could be expected from equilibration with the atmosphere. Dissolved CO_2 can come from both inorganic and organic sources (Worrall *et al.*, 2003b) although it is mostly the result of soil and root respiration (Dinsmore *et al.*, 2010). Measured DIC concentrations will contain minor amounts of CO_2, which has remained after degassing and regaining equilibrium with the atmosphere (Dawson *et al.*, 2001; Billett *et al.*, 2004). Dissolved gaseous CO_2 and CH_4 concentrations were not measured due to time and budget constraints but it was expected that dissolved CH_4 would be negligible (Dawson *et al.*, 2001), but dissolved CO_2 may not be. The aquatic carbon flux may be underestimated by just using DOC concentration and it is recommended that future studies at Kopuatai bog would include the analysis of dissolved CO_2 concentrations within peat pore water. Degassing at the surfaces of stream draining peatlands can be an important pathway for the release of C to the atmosphere (Dinsmore *et al.*, 2010).

6.4.6 Summary

- Annual DOC export from Kopuatai bog was 11.7 ± 0.82 g C m^{-2}, while DOC input from precipitation was estimated to be 1.26 ± 0.83 g C m^{-2} resulting in a total DOC loss from the EC footprint of 10.5 g C m^{-2} yr^{-1}.
- The main driver of variation in DOC export was *P* and *P–E*. There was seasonal variability in DOC export with high exports in winter due to high rainfall and low exports in summer due to low rainfall.
- A simple way to estimate monthly DOC export from Kopuatai was found by a linear regression between monthly DOC export and monthly *P–E*. The regression equation had a good fit with an R^2 of 0.87, likely due to the absence of seasonal variation in DOC concentrations.
- POC export from Kopuatai bog was small and was estimated at 0.57 ± 0.21 g m^{-2} yr^{-1} when measured using POC concentrations from the canal.

Chapter Seven

Conclusions

7.1 Introduction

This chapter will consider the importance of DOC export to the net ecosystem exchange of CO_2 (NEE) of Kopuatai bog and propose the method used in this study as a new method to be utilised by other peatland EC sites around the world.

7.2 Annual DOC export

The importance of DOC export to the carbon budget at Kopuatai

DOC export at Kopuatai for the annual period February 2012 to January 2013 was 11.7 ± 0.82 g C m^{-2}. For the same period, data suggests that NEE, was –176 g C m^{-2} (J. Goodrich, *pers. comm.*[8], February 2012), meaning that DOC export was only 6% of NEE. In contrast, DOC losses over a six year period at Mer Bleue bog in Canada were equal to, on average, 37% of the mean NEE. However, in three of those years the loss of C from DOC export resulted in there being a net loss of C from the peatland (Roulet *et al.*, 2007). DOC export from Trout Beck blanket bog in the UK was between 17 and 27% of mean NEE (Worrall *et al.*, 2003b). DOC export from Auchencorth Moss peatland in Scotland was 22% of annual NEE (Dinsmore *et al.*, 2010). DOC export from Degero Stormyr mire in Sweden was 25% of annual NEE (Armstrong *et al.*, 2012). While total DOC export at Kopuatai was similar to or slightly lower than bogs in North America and Europe, preliminary data suggests that NEE values are significantly higher at Kopuatai. This outcome is likely an effect of dominance by vascular plants and the year-round growing conditions. This study was only one year long, and firm conclusions require confirmation of the size and interannual variation of NEE. DOC losses are likely to vary less than NEE across years (Billett *et al*., 2010).

[8] Preliminary data only, representing quality controlled and gap-filled NEE.

Comparison to canal DOC concentrations

It is difficult to compare DOC concentrations reported in the literature. Some studies sample from catchments that are not solely comprised of ombrotrophic peatland or sample from streams draining peatlands and, as a result, water from other sources may be mixed into it or in-stream cycling of DOC may have resulted in changes in DOC concentration. Measuring DOC concentrations within peat pore water and using the water balance based approach adopted in this study is potentially a very accurate way of calculating DOC export. Any DOC that is decomposed by microbes within the footprint is measured as ecosystem respiration (CO_2 out) by the EC tower. Measuring DOC export within the flux footprint also means that all components of the carbon budget are being measured in the same area.

Discharge and DOC export from Carter's Canal draining part of Kopuatai bog were not able to be measured because of the hydrological setting and management practices. The outflow was blocked by steel gates in summer, there was difficulty establishing a catchment area and there was a possibility that water leaks from the canal to the adjacent farmland. DOC concentration was measured in Carter's Canal and values were significantly higher than the average DOC concentration measurements from the EC footprint (section 5.3.4.3). The higher DOC concentrations within the canal were likely due to decomposition of vegetation within the canal producing DOC, along with increased residence time concentrating DOC when water was stagnant and evaporation was occurring. These processes may have outweighed microbial utilisation of DOC and photodegradation occurring. Therefore, studies that have estimated DOC export by taking samples from canals and streams draining bogs have overestimated or underestimated export relative to the footprint of EC sites, depending on whether in-stream processes produce or consume DOC.

Water in Carter's Canal was also derived from a variety of bog vegetation types, including significant areas of *L. scoparium*, from a different catchment area to where the NEE was being measured. Peat pore water under *L. scoparium* was shown to have higher DOC concentrations and it could be influencing canal DOC concentrations.

If the average canal DOC concentration was multiplied by annual *Q*, from the EC footprint water balance, the annual DOC export becomes 16.01 ± 2.54 g C m^{-2}. This is 4.3 g C m^{-2} higher than the DOC export estimate from the EC footprint (11.7 g C m^{-2}) with a difference of 37%. Fraser *et al.* (2001b) found the difference between measuring DOC export within a stream draining Mer Bleue bog and a groundwater method within the bog to be a difference of 21% or 1 g C m^{-2}. In their case the stream resulted in lower export values due to a decrease in DOC concentration either by dilution of low DOC water or photodegradation or flocculation of DOC.

In December 2012 DOC export from the EC footprint was calculated to be negative due to an influx of water and DOC into the area from higher on the northern dome of the bog. Stream-based discharge measurements will always be positive and therefore produce positive DOC exports. At the spatial scale of EC measurements this may not be the case, especially during very dry periods.

Proposal of a new method for measuring DOC export

In this study, measurements of DOC concentration within Kopuatai bog were coupled to water discharge calculated from the water balance using measurements of *E*, *P* and ΔS made at the EC site, in order to estimate DOC export. To the best of our knowledge this method does not appear to have been directly applied by the published literature. For many EC sites, the location is chosen to minimise spatial heterogeneity and, while it incorporates the desired ecosystem signal, water ways and drainage networks are generally excluded (Dinsmore *et al.*, 2010). In many studies DOC measurements are obtained from these drainage networks that are separate from the sites where the CO_2 (and CH_4) flux is measured. The water balance approach ensures that all components of the C budget are measured from the same area.

7.3 Drivers of variability in DOC concentration and export

The literature recognises a number of factors that influence DOC concentrations in peat pore water. Factors that influence DOC concentrations include vegetation type (more specifically plant tissue and peat type), peat temperature (affects microbial production and utilisation of DOC) and hydrological regime (such as rainfall resulting in dilution and flushing of DOC or movement of the water table increasing or decreasing the thickness of the aerated zone of the peat profile) (Dalva & Moore, 1991). Other influences such as disturbance and atmospheric deposition of nitrates, sulphides and sea salt can affect DOC concentrations in peatlands. The influence of atmospheric deposition was not measured in this study and disturbance was not evident at any of the sites where DOC concentration was sampled at Kopuatai bog.

Precipitation and temperature

There did not appear to be any coherent seasonal variations in DOC concentrations at Kopuatai bog and DOC concentrations were also not correlated with air temperature or the temperature of peat at any of the sites. Concentrations of DOC may be decreased by rainfall events due to dilution but this was not observed. It is possible that DOC input from throughfall of precipitation through the dense *E. robustum* canopy might be obscuring a dilution effect, as found by Koprivnjak & Moore (1992) and Dalva & Moore (1991). Sampling design limited the overall conclusions about the role of rain dilution. Although a statistical relationship between DOC concentration and rainfall did not show up, it was observed that DOC concentration was generally lowest during sampling in July and August when there were large continuous rainfall events.

In the future, soil organic matter decomposition rates may become accelerated in response to warming of the climate (Carrera *et al.*, 2011). According to IPCC (2007), by the 2030s there is likely to be a warming of 0.1 to 1.4°C and by the 2080s a warming of 0.2 to 4.0°C is likely in New Zealand. There will also be a tendency for increased precipitation in New Zealand apart from in the eastern North Island and northern South Island. The frequency of heavy rainfall is likely to increase, especially in western areas of New Zealand (IPCC, 2007). It seems likely that future climate warming producing warmer and wetter summers could stimulate both plant productivity and decomposition rates as a rise in temperature would increase the rate of enzyme activity. This could result in increased production and release of DOC from peatlands (Moore, 2002; Wickland *et al.*, 2007). As rainfall was found to the significant factor controlling the export of DOC from EC footprint, an increase in rainfall could potentially lead to increased DOC export through high water flow out of the peatland. The lack of seasonality in DOC concentrations at Kopuatai bog shown in this study suggests insensitivity to the projected increase of temperature and an increase in rainfall could mean that Kopuatai escapes significant changes occurring despite a rise in temperature. It is possible, however, that the correlation between DOC export and *P–E* observed in this study might break down at longer timescales.

Vegetation type

Some of the spatial variability in DOC concentration throughout the bog may be explained due to differences in the main vegetation types across the bog. DOC concentrations in peat pore water beneath *L. scoparium* were significantly higher than under *E. robustum*. As DOC export was only calculated from the EC footprint area dominated by *E. robustum* vegetation, DOC exports may be higher under areas where *L. scoparium* dominates. Disturbance causing encroachment of *L. scoparium* into the bog could also result in higher DOC exports in the future. This is an important consideration if DOC export from the footprint were to be scaled up to the whole peatland as DOC export was estimated for just the EC footprint, an area of around 0.071 km^2, within the 90 km^2 bog. Ideally, water balances and DOC concentrations would be coupled with NEE of all other main vegetation types (such as *S. ferrugineus* and *L. scoparium*) to produce a full carbon budget for Kopuatai bog.

Neff and Hooper (2002) concluded that vegetation type was as important as climate conditions as a driver for DOC concentrations in soil pore water and Armstrong *et al.* (2012) suggested this may mean that managing vegetation could provide a way of lessening the increasing trend in DOC export to rivers, for example, encouraging the growth of lower DOC concentration species such as *Sphagnum* in Northern Hemisphere peatlands.

7.4 Recommendations on sampling scheme for DOC

A relatively simple way to estimate DOC exports from Kopuatai bog over the long term was found in this study. A strong linear relationship was established between monthly DOC export values and monthly values of *P*–*E*. From this relationship monthly DOC exports can be estimated when only *P* and *E* data are available. The equation for estimating monthly DOC export (F_{DOC}) was calculated as:

$$F_{\mathrm{DOC}} = 0.012(P - E) + 0.483 \qquad 7.1$$

However, it is recommended that three pore water samples are taken from site 4 once a month (one from each depth) and analysed to have a continuous record of DOC concentrations within the EC footprint.

7.5 Limitations of this study

It is possible that insufficient samples were analysed over the year to determine seasonal trends. This could have been overcome by using a spectrometer to measure absorbance in samples and working out DOC concentrations from that. By establishing a correlation between UV absorbance and DOC concentration, it could be used to calculate DOC concentrations for all days. This would have allowed for rapid analysis of a large number of samples but kept down the analysis costs, while allowing a highly detailed sampling scheme (Jager *et al.*, 2009). This could be used to do possible future research on DOC concentrations at Kopuatai bog.

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Appendix A

Table A.1: Peat humification index from Clymo (1983).

Level of peat decomposition	Characteristics
H1	Undecomposed: Plant structure unaltered. Yields only clear colourless water.
H2	Almost undecomposed: Plant structure distinct. Yields only clear water coloured light yellow-brown
H3	Very weakly decomposed: Plant structure distinct. Yields distinctly turbid brown water; no peat substance passes between fingers, residue not mushy.
H4	Weakly decomposed: Plant structure distinct. Yields strongly turbid water; no peat substance passes between fingers, residue rather mushy.
H5	Moderately decomposed: Plant structure still clear but becoming indistinct. Yields much turbid brown water; some peat escapes between the fingers; residue very mushy.
H6	Strongly decomposed: Plant structure somewhat indistinct but clearer in the squeezed residue than in the undisturbed peat. About half the peat escapes between the fingers, residue strongly mushy.
H7	Strongly decomposed: Plant structure indistinct but still recognisable. About half the peat escapes between the fingers.
H8	Very strongly decomposed: Plant structures very indistinct. About two-thirds of the peat escapes between the fingers; residue consists almost entirely of resistant remnants such as root fibres and wood.
H9	Almost completely decomposed: Plant structure almost unrecognisable. Almost all the peat escapes between the fingers.
H10	Completely decomposed: Plant structure unrecognisable. All peat escapes between the fingers

Appendix B

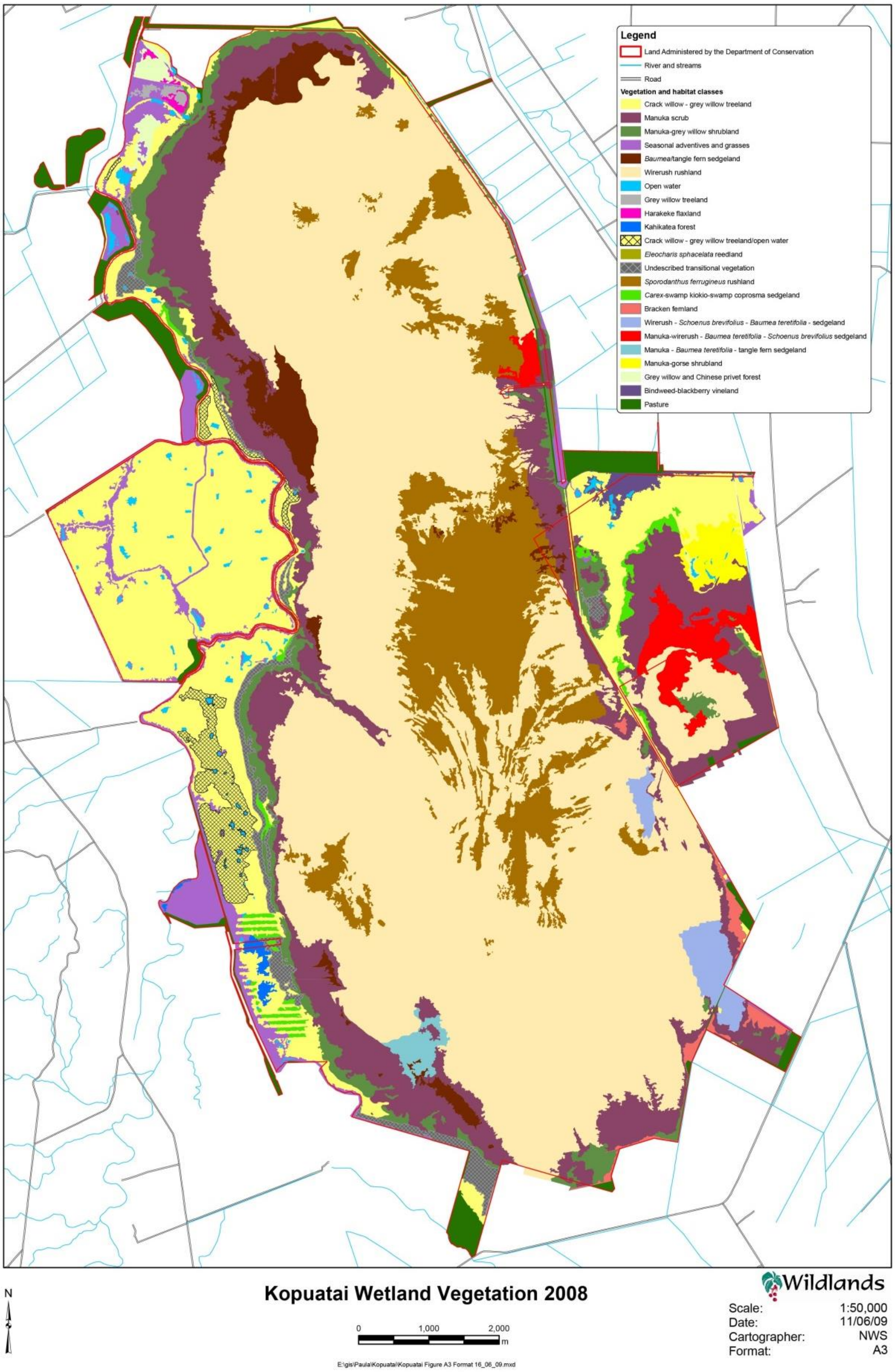

Figure B.1: Kopuatai wetland vegetation map 2008. From Department of Conservation (2009).

Appendix C

Table C.1: DOC sampling regime.

	Date											
Site	2/02/2012	14/03/2012	12/04/2012	8/05/2012	13/06/2012	4/07/2012	15/08/2012	12/09/2012	2/10/2012	9/11/2012	11/12/2012	11/01/2013
1												
2												
3												
4	Individual sampling of sites 1 to 9		Bulking of sites 1 to 9 and sampling of site 4	Sampling of site 4	Bulking of sites 1 to 9 and sampling of site 4	Sampling of site 4	Bulking of sites 1 to 9 and sampling of site 4		Bulking of sites 1 to 9 and sampling of site 4	Sampling of site 4	Bulking of sites 1 to 9 and sampling of site 4	Sampling of site 4
5												
6												
7		Individual sampling of sites 1 to 14						Individual sampling of sites 1 to 14				
8												
9												
10												
11												
12				Individual sampling of sites 10 to 14		Individual sampling of sites 10 to 14				Individual sampling of sites 10 to 14		Individual sampling of sites 10 to 14
13												
14												
		Spatial sampling of vegetation types						Spatial sampling of vegetation types				

Appendix D

A CD-ROM is enclosed containing the contents of Appendix D. All raw data from this project is contained on the CD-ROM.