Environmental Considerations for Wet Mining Peatlands in Northwestern Ontario

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Abstract

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Significant changes in water quality were detected using a Before-After-Control-Impact (BACI) experimental design. Porewater showed increases in pH, alkalinity, conductivity (including Ca, Mg, K, Na), some metals (Sr, Ba, Mn, Fe) and total nitrogen (TN) in the mined and restored plot. Change in surface water total mercury (THg) was linked to total suspended solids (TSS) and limited to active phases of wet mining. The season mining ceased, TSS and THg concentrations in impacted surface waters were similar to reference site water (<5 mg L^{-1} and <4 ng L^{-1}, respectively).

Experimentally derived 28 day dry weight Biota-Sediment Bioaccumulation Factors (BSAFs) for THg using *Lumbriculus variegatus* exposed to site sediment ranged from 0.91 to 1.59, while indigenous benthos ranged from 1.2 to 6.8. The BSAFs for methylmercury (MeHg) ranged from 9.92 to 67.4 and benthos from 21.8 to 106. A kinetic trial with inorganic mercury (iHg) spiked sediment, showed tissue THg reached steady state (11.5 d, model BSAF=3.12). Both tissue and sediment MeHg for the same trial showed linear increases (model BSAF=8.38), suggesting an increase in MeHg concentration in sediment would result in a corresponding MeHg increase in *L. variegatus* tissue.

Sugar flotation methodology reduced recovery time and increased percent recovery of *L. variegatus* from site sediment. Tissue THg did not differ in aqueous only exposures to sugar solution and tissue MeHg did not differ when organisms were extracted from sediment by sugar flotation. However, MeHg tissue concentrations in aqueous only exposures were 27% higher than controls.

Mechanical dewatering of wet mined peat produced peat mining process water (PMPW) with low pH (5.55) and high TSS (432 mg L^{-1}), Al (1.39 mg L^{-1}), Fe (4.36 mg L^{-1}), Hg (37.1 ng L^{-1}), MeHg (0.485 ng L^{-1}), Zn (55 mg L^{-1}), TN (7.92 mg L^{-1}), total phosphorus (TP) (303 mg L^{-1}) and colour (532 TCU). In mesocosm studies, high removal efficiencies were calculated for acrotelm peat filters (TSS 45-83%, particulate organic carbon (POC) 47-89%, metals 52.9-100%, TN 84.4%, TP 80.8%), though leachate concentrations did not all achieve water quality guidelines. Colour and dissolved organic carbon (DOC) also leached from mesocosms. An initial removal of solids from PMPW is required before peatlands be considered further as primary treatment systems.

Dedication

To R.J., Brianne and Brian, for all your support when I was “bogged-down”.

How dreary – to be – Somebody!
How public – like a Frog –
To tell one’s name – the livelong June –
To an admiring Bog!

Emily Dickenson

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Contents

Acronyms

ANOVA analysis of variance

BACI Before-After-Control-Impact

BAF bioaccumulation factor

BD bulk density

BEP back of experimental plot

BSAF Biota-Sediment Bioaccumulation Factor

CWQG Canadian Water Quality Guidelines

DMW dechlorinated municipal water

DL detection limit

DOC dissolved organic carbon

DOM dissolved organic matter

DWT depth to water table

ELA Experimental Lakes Area

EP experimental plot

EPA United States Environmental Protection Agency

FeRB Fe(III)-reducing bacteria

Hg mercury

ICP-AES inductively coupled plasma atomic emission spectroscopy

iHg inorganic mercury

LIDAR light detection and ranging

LT lethal time

LOI loss on ignition

LUCAS Lakehead University Centre for Analytical Services

LUEL Lakehead University Environmental Laboratory

LUIL Lakehead University Instrumentation Laboratory

MDC means of the differences in concentration

METAALICUS Mercury Experiment to Assess Lake Loading in Canada and the United States

MeHg methylmercury

PHIM Peatland Hydrologic Impact Model

POC particulate organic carbon

POM particulate organic matter

PMPW peat mining process water

QC quality control

RP reference plot

SD standard deviation

SRB sulphate-reducing bacteria

SOM soil organic matter

TCU true colour units

THg total mercury

TN total nitrogen

TKN total Kjeldahl nitrogen

TOC total organic carbon

TP total phosphorus

TS total solids

TSS total suspended solids

USEPA United States Environmental Protection Agency

UV ultra-violet

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Chapter 1

Introduction, Literature Review, Site Description and Research Objectives

1.1 Introduction

Peatlands cover 2% of the world's total land area, and as carbon sinks, possess immense energy potential (World Energy Council, 2007). Unlike hydroelectric power generation, forest harvesting or mineral mining operations, a sustained peat energy industry never materialized in this country and peat extraction in Canada today is virtually non-existent (Warner and Buteau, 2000). It has been proposed that peat in northwestern Ontario be extracted using a wet mining technique and the pelletized biomass be used a fuel source (i.e. as biofuel). In 2008, the coal fired Atikokan Thermal Station (Ontario Power Generation) successfully combusted 100% biomass (OPG, 2011) and peat has been identified as the only biofuel of sufficient quantity within a 200 km radius to meet the stations needs (OME, 2006).

General hypotheses to date, as put forth in a review by Gleeson et al. (2006), suggested wet mining the peatlands in Ontario would cause aquatic and hydrological environmental consequences similar to traditional dry harvesting. Specifically, Gleeson et al. (2006) listed increased suspended sediments, ammonia, organics, total nitrogen (TN), total phosphorus (TP), Al, Fe and Hg and an increase in acidity to adjacent water bodies. Winkler and DeWitt (1985) predicted similar environmental impacts for peat mining

in the United States. However, Shotyk (1986b) and later Aström et al. (2001) noted that during the ditching phases of dry peat harvesting operations, large releases of basal peat porewaters resulted in increased pH and alkalinity, contrary to the acidity increase predicted by Gleeson et al. (2006). Therefore, Lakehead University, in collaboration with McMaster University, Ontario Centres of Excellence and Peat Resources Ltd., established a new peatland research field site in northwestern Ontario (Section 1.7) to test these hypotheses.

Environmental impacts associated with wet peat extraction are poorly understood compared to other peat harvesting techniques (Gleeson et al., 2006). Tibbetts (1986) suggested wet mining may alleviate detrimental environmental impacts associated with harvesting methods requiring peatland drainage and desiccation. Restoring a wet mined peatland by acrotelm transplant for this project, following methods for dry harvested ditches used elsewhere (Cagampan and Waddington, 2008b,a), was a first for Ontario (Waddington, pers. corr.). The novelty of both the peat extraction technique and restoration strategy were found to have little in common with published studies from dry harvested peatlands. A science based approach was used here to provide environmental considerations for industry and provincial regulators.

1.2 Peatlands: Definitions and Classifications

Peatlands are valuable ecosystems as they provide many functions. They are a carbon sink (McLaughlin, 2004), they have high biodiversity (Chapman et al., 2003), they influence the hydrology of areas beyond their delineation (Siegel and Glaser, 2006), they provide recreational activities (hunting, fruit picking) (Quinty and Rochefort, 2003), they support a complex mixture of ecological functions such as habitats for wildlife and other biological resources (Keys, 1992) and provide paleo-archives of our past environment (Frenzel, 1983; Benoit et al., 1998; Martinez-Cortizas et al., 1999; Mighall et al., 2006).

Peatland species have adapted to extreme conditions of high water, low oxygen content, toxic elements (acidity, humic substances) and low availability of plant nutrients. Their water chemistry may vary from alkaline to acidic (Joosten and Clarke, 2002). In addition to *Sphagnum* mosses, other Bryophytes, sedges (e.g. *Carex, Eriophorum spp.*), Ericaceous plants (e.g. *Vaccinium, Kalmia spp.*), carnivorous plants (e.g. *Sarracenia, Drosera spp.*) and tree species such as bog birch (*Betula pumila*) and tamarack (*Larix laricina*) may be present, each having developed strategies for survival in acidic and per-

sistently waterlogged ecosystems (Crawford, 1983; Newmaster et al., 1996; Rydin and Jeglum, 2006).

1.2.1 Peat Accumulation

Peat is simply the remains of plants and animals decomposing slowly due to anoxic conditions arising from a more or less water-saturated state (Clymo, 1983). Peat researchers define peat soils as possessing over 80% organic matter (Landva et al., 1983), whereas looser definitions exist in agriculture and engineering fields (Sparks, 2003; Rydin and Jeglum, 2006). Peatland ecosystems are characterized by their unique ability to accumulate and store dead organic matter from *Sphagnum* and other non-moss species as peat, making them immense carbon deposits.

Peat accumulation is the result of peat production exceeding decomposition, and involves an interaction between net primary productivity and losses through the process of aerobic and anaerobic decay, leaching, peat fires, wind abrasion, thermokarst erosion and deposition of organic material into mineral soils beneath peat layers (Kuhry and Turunen, 2006). Rates of accumulation are typically 10 to 20 cm per 1000 yr (Rydin and Jeglum, 2006), with rates reported in British peat as ranging from 20 to 60 cm per 1000 yr (Walker, 1970) and Canadian peatlands averaging values from 6 to 7 cm per 1000 yr (Daigle and Gautreau-Daigle, 2001). Complex models to reliably predict rates are required due to variations in vegetation, temperature, water tables, water movement, decomposition rates and compaction factors of lower layers (Rydin and Jeglum, 2006). Anthropogenic sources may also affect accumulation rates. A Finnish peatland treated with Ni (200 kg Ni ha^{-1}) ceased accumulating peat and emissions from a nearby Cu-Ni smelter were hypothesized to have negatively affected the accumulation rate at another site (Ukonmaanaho et al., 2006).

The slow renewal rate of peatlands lends debate on its consideration as a "renewable resource" (Tolonen, 1979; Foote and Krogman, 2006). The peat mining policy of New Brunswick classifies peat as a non-renewable resource because of the centuries required for peat accumulation (Department of Natural Resources, New Brunswick, 2010). The Intergovernmental Panel on Climate Change recently placed peat in its own category, intermediate fuel, being between fossil and renewable fuels (World Energy Council, 2007).

1.2.2 Peatlands as Wetlands

Wetlands are formally defined as "land that is saturated with water long enough to promote wetland or aquatic processes as indicated by poorly drained soils, hydrophytic vegetation and various kinds of biological activity which are adapted to a wet environment" and include five classes: bogs, fens, marshes, swamps and shallow water (Warner and Rubec, 1997). Bogs and fens are the only classes that form peat, and are collectively referred to as peatlands. Peatlands are distinguished from other wetlands by a water table that is, for the most part, just below the vegetative surface. Peatlands are defined in Canada as peat-covered terrain, with a minimum peat depth of 40 cm (NWWG, 1988), although other countries use a minimum peat depth of 30 cm (Rydin and Jeglum, 2006).

Delineations of wetlands, specifically bogs and fens, have been based on shape characteristics, porewater chemistry, hydrology, formation processes and plant species composition (Gore, 1983). Peatlands are not static, but exist in some stage of their formation process, which blurs the edges of any classification scheme. Nevertheless, general characteristics of common peatland types in northwestern Ontario are summarized in Table 1.1.

Table 1.1: General characteristics of peatland types typically found in northwestern Ontario as adapted from (Gore, 1983; Daigle and Gautreau-Daigle, 2001; Rydin and Jeglum, 2006)

Peatland Type	Peat pH	Water Quality	Water Origin	Vegetation
Rich-Fen	5.0–7.0	Elevated [Ca]; Minerotrophic, eutrophic to oligotrophic	Meteoric and geogenic: Topo-, soligenous, sometimes limnogenous	Sedges, grasses, reeds, brown mosses, certain *Sphagnum* species, ericaceous shrubs and trees
Poor-Fen	4.0–5.5	Low cations; Minerotrophic, oligotrophic	Meteoric and geogenic: Topo-, soligenous, sometimes limnogenous	
Bog	3.5–4.2	Ombrotrophic, oligotrophic	Ombrogenous; meteoric only as isolated from incoming minerogenous water	Treed or untreeded, limited diversity due to lack of nutrients, *Sphagnum* mosses and ericaceous shrubs are common

Ombrotrophic fen waters, as found at this study location, have been described as having a calcium:magnesium ratio less than one, few bases and low pH, suggesting that so long as some ground water reaches a peatland, the reaction of the water remains above

pH 4.5 (Bellamy, 1959). Transitional peatlands reflect characteristics of both fens and bogs, receiving minimal groundwater when compared to water supplied as precipitation. Their pH levels and mineral status are intermediate between those occurring in bogs and fens. Transitional vegetation is a characteristic mixture of species found in both poor fens and bogs (Washburn & Gillis, 1982).

1.2.3 Peatland Features

Peatlands possess some unique self assembling topographic features (Couwenberg and Joosten, 2005) that require definition. Northwestern Ontario peatlands between Thunder Bay and Upsala, the location of this research, possess alternating hummock-hollow microtopography (Fig. 1.1). Descriptions of each are adapted from Quinty and Rochefort

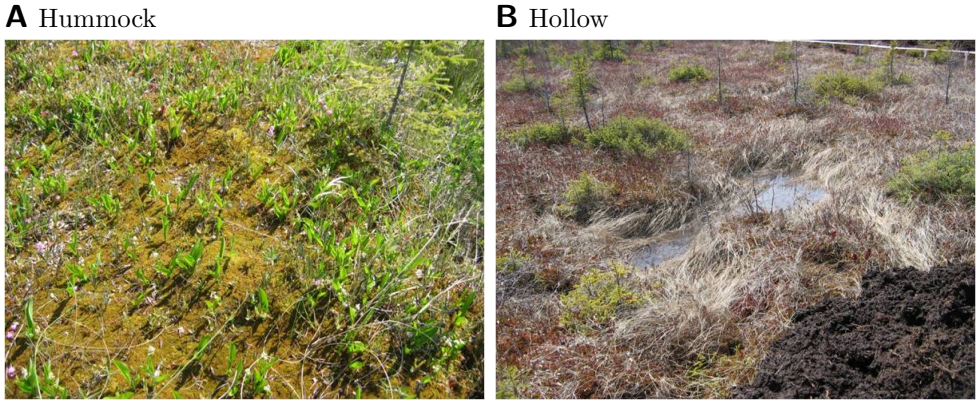


Figure 1.1: Microtopography of the study peatland, northwestern Ontario.

(2003) and Rydin and Jeglum (2006):

Hummocks: Large plateaus, raised 20–50 cm above the lowest surface level, characterized by dwarf shrubs as facilitated by drier conditions. *Sphagnum* species of the group Acutifolia (*S. fuscum, S. rubellum*) are more common, and grow in dense colonies that allow efficient water retention and supply. Specific *Sphagnum* species occupy niches at various levels on the hummock, correlated to water level and pH gradient.

Hollows: Habitats formed in depressions (0.5–2 m diameter) with a water table close and periodically above the surface, thus often persistently wet. Plant communities are typically comprised of sedges or graminoid species as well as *Sphagnum* from

the group Cuspidata (*S. fallax, S. angustifolium*) which grow in loose colonies and are not adapted to retain water.

The secondary development of peatland microtopography has been attributed to biotic factors amplified by physical mechanisms. Hollows probably result from small differences in the rate of peat accumulation (Kuhry and Turunen, 2006). It has been hypothesized that hummocks arise due to an extreme intrinsic decay resistance of the common circumboreal species *S. fuscum* (Johnson, 1987). Once formed, hummocks and hollows may exhibit chemical differences. For example, porewater methylmercury (MeHg) concentrations in shallow hollows had concentrations 3.5× higher than deep hollows and both hollow types had higher MeHg than hummocks (Branfireun, 2004).

The measure depth to water table (DWT) is an important peatland parameter and is defined as the distance from the peat surface to the water table. It controls not only vegetation features, plant occurrence and growth (Crawford, 1983) but also influences the subsurface pore water chemistry, especially redox conditions (Ingram, 1983; Devito and Hill, 1999). The water table creates two zones within the peat profile, referred to as diplotelmic stratification (Ingram, 1978). The terms "active layer" for the upper layer which is periodically aerated and "inert layer" for the lower anaerobic layer were first given explicit recognition by Soviet mire hydrologists (Ivanov, 1953), although their use in English was confusing. Alternative terms "acrotelm" and "catotelm" (Ingram, 1978) are used today.

The catotelm is permanently below the water table and experiences permanent anoxia. It is characterized by low microbial activity resulting in slow organic matter decay. The catotelm is composed of dead macroflora except for a few roots, consists of relatively decomposed compacted peat, has slow non-Darcyan movement of water, sees only slow exchanges of energy and matter and is typically the peat of interest for power generation (Ingram, 1983; Quinty and Rochefort, 2003; Rydin and Jeglum, 2006).

The acrotelm overlays the catotelm and sees fluctuations in DWT. Thus, both oxic and anoxic conditions periodically exist. As such, the acrotelm has higher microbial activity, rapid exchange of energy and matter, water transmission is Darcyan and facilitates root growth of plants (Ingram, 1983). This living layer is loose in nature. *Sphagnum* mosses with their empty hyaline cells are able to store and release large quantities of water, thus stabilizing the hydrology of adjoining areas (Quinty and Rochefort, 2003). Acrotelm peat is of lower calorific value and not valued for energy. Acrotelm peat is a

valued horticultural soil amendment (Rydin and Jeglum, 2006).

As stated by Whitfield et al. (2009), peatland hydrology, chemistry and ecology are intertwined and inseparable from the biology of *Sphagnum* and other peatland vegetation. Therefore, hydrology and chemistry are further reviewed.

1.3 Peatland Hydrology

Hydrology plays a defining role in peatland formation processes (Ingram, 1983). The major processes of recharge, evaporation, storage and discharge of water determine vegetation types and decomposition factors of peatlands. Over the long term, hydrology dictates peat chemistry and peat interstitial water (porewater) chemistry. Eventually, the water chemistry of surrounding ecosystems may be affected (Boelter and Verry, 1977; Gorham et al., 1985; Daigle and Gautreau-Daigle, 2001). Therefore, changes in hydrology may alter flows and concentrations of metals, nutrients and organic constituents. Wet peat mining activities have been hypothesized to alter surrounding ecosystem hydrology and chemistry (Brooks and Predmore, 1978; Winkler and DeWitt, 1985; Monenco, 1986; Gleeson et al., 2006).

Water table relates to the free energy status or potential of soil water. Water table is defined as the surface at which the hydrostatic pressure of soil water is zero (i.e. equal to atmospheric pressure) (Ingram, 1983). Indirectly, the water table marks the zone of saturated soil pores, but capillary fringe more correctly marks the upper limit of saturation, which may be 20-40 cm in peatlands (Päivänen, 1973). A comprehensive water table study at Wicken Fen (near Cambridge, England) by Godwin (1931), found sudden water table rises were in response to rainfall, while daily decreases were attributed to transpiration. True fens however, are not dependent on meteorological variables alone, but depend on surrounding catchment hydrology. In general, large catchments with long retention times will have slowly oscillating water tables remaining at high levels for longer periods (Ingram, 1983).

If water storage is W and positive for increasing amounts, the water balance of a peatland ecosystem is simply represented as

$$influx - efflux - \Delta W = 0 \tag{1.1}$$

However, elaborate equations with terms representing compartmented processes within each influx and efflux term (Eq. 1.1) are required to fully describe a peatlands intri-

cate hydrology (Ingram, 1983). Peatland systems may be viewed as consisting of four compartments; atmosphere, peatland, mineral soils/parent material and local surface streams. By definition, bog systems have an influx value directly related to precipitation (meteoric water: rain, snow, hail, fog or dew) without contributing inputs from the other three compartments. Fen influx values are related to meteoric and telluric (terrestrial) inputs. Influx waters may differ not only in their origin, but also in their chemical quality, which often exhibit seasonal trends (Ingram, 1983). Peatland Hydrologic Impact Model (PHIM) was developed to answer questions concerning the effects of drainage and peat mining on streamflow response (Guertin et al., 1987).

The study peatland for this dissertation, near Upsala, ON (40°57′33″N, 90°6′20″S), was once the ancient glacial Lake Agassiz (Upham, 1895; NWWG, 1988; Watts, Griffis and McOuat Ltd., 2004). Extensive hydrogeological work on L. Agassiz peatlands in Minnesota was done by Siegel (1983). They included ground water levels in observation wells, studies of soil types and thicknesses and a computer model experiment that simulated ground water flow. They concluded that:

1. Most ground water circulates along flow paths several kilometers long that pass through the peat column and into the underlying mineral soil;

2. Most ground water flow is probably caused by the development and persistence of large raised bogs, and occurs because of ground-water mounds (elevated water tables) under the bogs; and

3. Lateral bog growth may be limited by the neutralizing of bog water acidity by ground water discharge (artesian flow) at raised bog margins.

The specific peatland (fen) in the Upsala corridor used here (labeled Goodfellow/Gibbard Study Area (GG3) by DST (2005)) was part of several "water track" fen complexes in the area (McLaughlin, pers. corr.). As summarized by Rydin and Jeglum (2006), such a soligenous system is characterized as a sloping peatland, without distinct open water channels, but laminar flow at or below the peat surface, and occasionally (i.e. during rapid snow melt or heavy rain) as even sheet flow at the surface. The water track fen represents a primary peat formation, typically not beginning with aquatic plants, but rather by direct colonization of peat-forming plants on sloping ground following land uplift or glacial retreat. Water for GG3 is derived from a catchment (Muskeg L.) and headwater wetlands (Fig. 1.2). Further detail is provided in Section 1.7. The particular

mining site chosen here, was estimated in OME (2006) to possess the greatest amount of standing water (>2 m) following peat extraction, as a consequence of the peatlands basin topography and water flow paths.

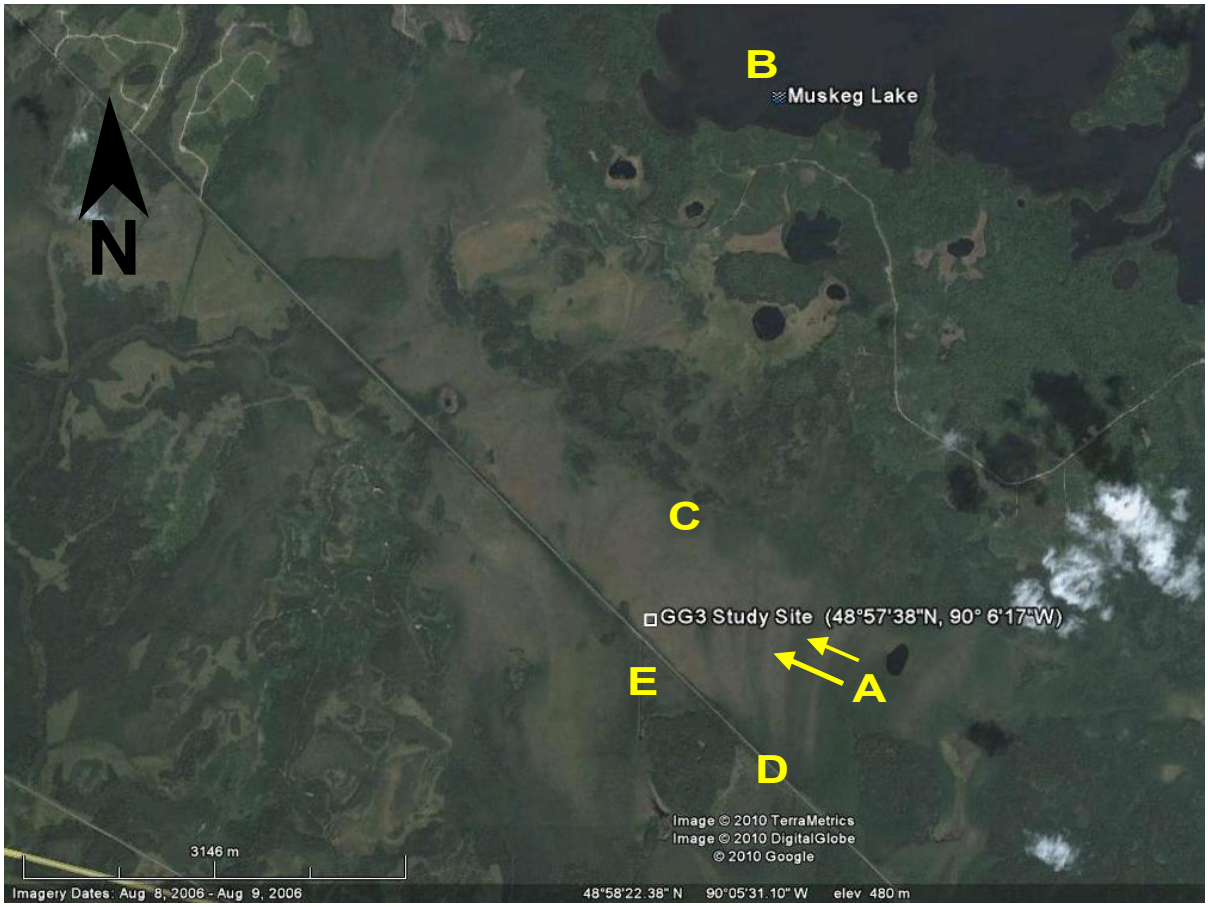


Figure 1.2: The GG3 peatland showing patterning typical of water track fens (A). Water flows from the height of land at Muskeg Lake (477 m B) south, through headwater wetlands (C) to the GG3 study site (labeled). Road access (D) and main drainage point (471 m E) are indicated.

Boreal lakes hydraulically connected to wetland and peatland systems typically have a characteristic brown, "tea-stained" appearance. Known to limnologists as dystrophic lakes, colour is imparted by high concentrations of humic substance originating from decomposition of vegetation within the watershed. Elevated organic components within the lake highly influence all physical, chemical and biological processes (Keskitalo and Eloranta, 1999). Hydrology governed both the flow and flux of MeHg as well as maintained Hg methylating environments in a boreal catchment of the Experimental Lakes Area (ELA) near Kenora ON (Branfireun and Roulet, 2002).

1.4 Peatland Chemistry

1.4.1 Water Quality

Wetlands are unique aquatic ecosystems, with waters possessing more dissolved organic matter (DOM) than dissolved inorganic matter. Peatland water chemistry is generally acidic (pH 3 to 6) due to organic acid accumulation. With an average pK_a of 4.2 for organic acids, buffering of water occurs from pH 3 to 5, in contrast to most aquatic environments where buffering is dominated by carbonate and bicarbonates (Thurman, 1985). Furthermore, a high exchange of metal ions onto peat releases hydrogen ions, thus decreasing pH (Gore and Allen, 1956; Lakatos et al., 1972; Rashid, 1974; Urban and Bayley, 1986).

Although the chemistry of influx water may influence peatland biology and chemistry, peat chemistry and biology influences influx water quality. Paine and Blakeman (1987) found water entering a peatland becomes characterized by acidic pH, elevated DOM, low concentrations of alkaline earth elements (Ca, Mg, Na, K), elevated Fe and Mn concentrations and dissolved CO_2. *Sphagnum* mosses are known to release chemicals that create cation exchange sites, with uronic acids active in bogs and polyphenolic compounds active in higher pH fens (Richter and Dainty, 1989). Therefore, while the bioavailability of minerals and nutrients in influx water may decrease as inflow waters are assimilated to peatland porewater, others minerals and nutrients may increase.

The first publication on the chemical composition of *Sphagnum* bog porewater by C.A. Weber (1902) summarized a single peat sample (1 m×1 m×20 cm) from which water was collected, filtered and analyzed (Shotyk, 1987). Since then, Clausen et al. (1980) published a peatland classification system based on water chemistry from streamflow

from Minnesota peatlands (n=49; Table 1.2). Their range in water quality showed no evidence of regional gradients after one year. Conversely, researchers studying water in Finnish peatland pools found regional gradients for pH and calcium that were likely related to industrial activity (Tolonen and Seppanen, 1976).

Table 1.2: Water quality indicators of streamflow from Minnesota bogs, fens and transition peatlands, summarized from Clausen et al. (1980).

	Peatland Type		
Parameter	**Bog**	**Transition**	**Fen**
pH	<6.0	6.0–6.5	>6.5
Conductivity (μS cm^{-1})	<50	35–65	>60
Acidity (mg L^{-1})	>16	10–30	<30
Alkalinity (mg L^{-1})	<15	15–40	>15
Calcium (mg L^{-1})	<7.0	4.5–15	> 7.5
Colour (TCU)	>250	—	< 350

For Finnish peatlands, Tolonen and Seppanen (1976) noted mean concentrations of most analytes in porewater changed very little over a season (June to September), except for suspended sediment, which was substantially higher in the fall, and Hg, which was lower in the fall. However, inter-porewater concentrations between fens and bogs were quite different. Tolonen and Seppanen (1976) noted fens had higher pH, conductivity, alkalinity, suspended sediment, Ca, Mg, Fe, Na, Mn and TN, while bogs had higher colour, acidity and Hg. They found no difference for TP. Earlier work in Minnesota (Verry, 1975) found similar trends, though TN was higher in bogs than fens. Therefore, though differences in bog and fen porewater and streamwater quality exist for basic parameters such as pH, alkalinity, conductivity and organic constituents, similar trends for metals and nutrients cannot be assumed. Processes determining the availability of N and P in peatlands are not well understood (van Breemen, 1995).

Gorham et al. (1985) analyzed ombrotrophic peatland pools, puddles, depressions and pits along a broad belt transect (midcontinental forest/prairie border in Minnesota and Manitoba to extremely oceanic sites in Newfoundland) and identified important sources of major ions in atmospheric deposition that contributed to peatland water quality. These were sea spray, soil dustfall and air pollution. They noted a marked variability in sulphate

concentrations, with sulphate reduction being very significant in these bog waters. A trans-American regional study by Pakarinen (1987) reported peat bulk density increased and ash content (i.e. mineral content) decreased towards eastern coastal areas. They noted Na concentration in peat was particularly high in oceanic sites, while Al showed an opposite regional pattern. Furthermore, Pakarinen (1987) found Mn and K in peat had a distinct surface maximum and observed leaching of Mn in wet microsites and in anaerobic peat. Sub-surface maxima were observed for Pb, Zn and Fe. Mercury was not studied.

Intra-peatland water quality over distances as small as 10 cm and with progress of the growing season were found related to variability in position and rooting depth of vascular plants (Summerfield, 1974). Although main processes on the peatland surface, including evaporation, uptake by plants and cation exchange can alter water chemistry, other factors, such as the rate of peat accumulation and flow rate of water through a peatland are equally important (Damman, 1987). Stagnanted peat accumulation caused increased concentrations of many elements near the surface (especially N, P, Fe, Al, Pb, Si and Zn), although mobile elements (K, Na) occurred in lower concentrations (Damman, 1987). Such stagnation may occur locally on hummocks, for example, if one is shaded and one is not. Damman (1987) also found the supply of nutrients from bogs tended to increase downslope, being highest in peatland features such as water tracks. Their research noted that either natural or anthropogenic disturbances tended to increase nutrient supply by accelerating the release of nutrients stored in peat.

The oxidation-reduction (redox) potential of natural water systems is an important geochemical parameter which may directly control speciation and solubility of chemical elements (Bohn, 1971). The DWT at a particular location within a peatland will dictate the oxygen status and control the redox potential of the surrounding peat. Although direct measurement of redox potential (E_h) is often of questionable quality (Lindberg and Runnells, 1984), it has been reported in many peatlands (Urquhart and Gore, 1973; Shotyk, 1987) and was measured here. Indirect measures of redox using reduced gasses (e.g. sulphide, methane, carbon dioxide), solid mineral phase presence (e.g. pyrite) or dissolved redox indicator species (e.g. sulphate, nitrate, oxygen) are possible. Total and reduced Fe were determined here to support E_h data and redox status of the measured waters, since sulphide/sulphate and nitrite/nitrate concentrations were below detection limits.

It is important to note that peat porewater pH is not necessarily related to the pH of

the peat itself. Peat pH is generally lower than its corresponding porewater pH, perhaps by orders of magnitudes in H^+ activity (Shotyk, 1987). The two should not be confused.

1.4.2 Peat Chemical Composition

Concentrations of inorganic chemical substances in peat are shown to vary according to vegetation type, bog type, depth in bog, location in bog, degree of decomposition, bedrock geology and anthropogenic inputs (Washburn & Gillis, 1982). Stewart and Robertson (1968) described the vertical and horizontal variation in peat chemistry, attributing differences to (i) degree of decomposition, (ii) diversity of specific plant groupings, and (iii) proximity of the underlying mineral soil. They suggested certain elements occurred in surface peats due to adsorption by metabolically active root tissues and biotic activity of surface flora and fauna, especially evident for biophilic elements such as P and S. Aluminum and Fe concentrations were found to be higher in basal peats than in surface layers and attributed to changes in peat formation rates throughout the life of the bog Stewart and Robertson (1968).

Sillanpaa (1972) followed the vertical distribution of 13 elements in peat profiles, finding notable concentrations at surface peat (0-30 cm), decreasing to minimums by mid profile (80 cm), followed by strong increases in the peat-mineral transition zone. Higher concentrations in surface peat were attributed to element-lifting activity in plants. They also noted mineral subsoil chemical concentrations are 10 to 25-fold higher for Pb, Sn, Mo and Zn, 30 to 80-fold higher for Ni, Mn, Sr and Cu, and over 100-fold higher for Al, Fe, Cr and V. Authors reported that if metal concentrations were calculated on a per volume (i.e. bulk density) rather than per weight basis, differences between mineral sub-soils and peat concentrations would differ a further 10-15 times. Glooschenko and Capobianco (1982) conducted an analysis of trace metals in northern Ontario peat, reporting average concentrations of Zn, Pb, Cu, Cr, Cd and Hg of 31, 16, 7, 3, 1 and 0.06 mg kg^{-1} (dw), respectively, and no significant variation in terms of peatland type or depth, with the exception of Pb, being significantly higher in surface peats and fens, than bogs. Their study was limited to the top 40 cm of profiles and bulk density was not reported.

Failure to report bulk densitys (BDs) existed in most literature, as criticized by Grigal et al. (2000). It is important to include BD with concentration data for peat analysis to allow interpretation of results on a per volume basis rather than solely on a per dry weight (dw) basis, as conventionally done for soil testing. Peat has only a small amount of

solid matter present. The unique, biologically produced pore architecture of *Sphagnum* hyaline cells results in large volumes made with small masses of tissue (van Breemen, 1995). As Grigal et al. (2000) noted, an emphasis on concentrations by mass distorts perceptions about Hg abundance in peatlands, which would similarly apply to other such analytes. Although higher Hg concentrations are usually associated with higher soil organic matter, soil bulk density and soil organic matter are inversely related, so soils with high Hg concentrations often have low mass per area (Grigal et al., 2000), or similarly, per volume.

Mercury in peat is of recent concern (1990's) with Hg results appearing only sporadically in extensive peatland research programs of older literature. Even then, Hg analysis was conducted on a fraction of total samples collected. Reliable methods for accurate quantification of total mercury (THg) and MeHg that is free of interferences has come about during the 1990's (Bloom et al., 1997). Data prior to this time should be viewed with skepticism. Reliable Hg data have been summarized (Grigal et al., 2000; Grigal, 2002, 2003; Biester et al., 2006) and extensive research conducted at the ELA (near Kenora ON; Mercury Experiment to Assess Lake Loading in Canada and the United States (METAALICUS) project). Positive relationships between atmospheric loadings of inorganic mercury (iHg) to watersheds and concentrations of MeHg in fish tissue have been established (Munthe et al., 2007) with Hg transformations in peatlands, including methylation, researched (St. Louis et al., 1994, 1996; Branfireun et al., 1998, 1999, 2001; Ullrich et al., 2001; St. Louis et al., 2004). Glooschenko and Capobianco (1982) suggested peat presents the same concerns as coal in terms of trace metal emissions to the atmosphere when combusted in thermal generating stations. Based on dry weight comparisons, they noted trace metals in peat fuels were at similar concentrations to some coal types.

1.4.3 Peat Organic Matter

Peat in the peatlands of northwestern Ontario generally arose from some ecological combination of *Sphagnum* sp. and *Carex* sp. (Section 1.2.3). *Sphagnum* peat, typical of bogs and poor fens, consists of more than 99% organic matter (Rydin and Jeglum, 2006). *Sphagnum* peat is different from other moss peat due to its formation under ombrotrophic and oligotrophic conditions. *Carex* peat in more characteristic of fens. *Carex* peat is usually denser, of higher ash content and inorganic solutes, and generally has formed under

the influence of mineral soil water (Rydin and Jeglum, 2006). Decomposition processes in peatlands and the resulting forms of organic matter in peat and peat porewater are important in understanding the transport of analytes, including Hg, within and from the ecosystem.

Decomposition

Peat starts as recently dead plant matter and begins a series of changes, usually occurring in three phases (Johnson, 1987): (i) an initial slow decay, (ii) a relatively rapid decay, and (iii) a final slow decay. Physical properties and the chemical composition of peat changes as it decomposes. Terms used interchangeably to describe this phenomenon include decay, decomposition, breakdown and humification. Peat decomposition is characterized by a loss of organic matter via any combination of processes (Clymo, 1983): (a) as a gas, (b) in solution due to leaching and/or microbial activities, (c) loss of physical plant structure and/or (d) a change in chemical state .

The H scale of humification devised by von Post and Granlund (1926), is often used to describe the state of peat decomposition. The numeric scale is based on objective observations in the field when the peat is squeezed in the hand. Criteria include the colour of exuded fluid and the proportion and character of the peat material which remains in the hand (Table 1.3). Unhumified peat is light in colour, has low bulk density and high adsorptive values. Conversely, humified peat is darker in colour, has higher bulk density and low adsorptive values. Ideal biofuel peat, both technically and economically, would be classified as H5 or higher on the von Post H scale (Monenco, 1978). A linear relationship between degree of humification and heat value has been shown for a series of Newfoundland bogs (Scott et al., 1980).

Table 1.3: Von Post, H scale of humification as adapted from (von Post and Granlund, 1926; Ekono, 1981; Washburn & Gillis, 1982).

Scale	**Description**	**Bulk Density (kg m^{-3})**
H1	Completely undecomposed peat. When squeezed, releases almost clear water. Plant remains easily identifiable. No amorphous material present.	45
H2	Almost entirely undecomposed peat. When squeezed, releases clear or yellowish water. Plant remains still easily identifiable. No amorphous material present.	60
H3	Very slightly decomposed peat. When squeezed, releases muddy brown water, but from which no peat passes between the fingers. Plant remains still identifiable and no amorphous material present.	75
H4	Slightly decomposed peat. When squeezed, releases very muddy dark water. No peat is passed between the fingers but the plant remains are slightly pasty and have lost some of their identifiable features.	90
H5	Moderately decomposed peat. When squeezed, releases very muddy water with a very small amount of amorphous granular peat escaping between the fingers. The structure of the plant remains is quite indistinct although it is still possible to recognize certain features. The residue is very pasty.	105
H6	Moderately highly decomposed peat with a very indistinct plant structure. When squeezed, about one-third of the peat escapes between the fingers. The residue is very pasty but shows the plant structure more distinctly than before squeezing.	120
H7	Highly decomposed peat. Contains a lot of amorphous material with very faintly recognizable plant structure. When squeezed, about one-half of the peat escapes between the fingers. The water, if any is released, is very dark and almost pasty.	135
H8	Very highly decomposed peat with a large quantity of amorphous material and very indistinct plant structure. When squeezed, about two-thirds of the peat escapes between the fingers. A small quantity of pasty water may be released. The plant material remaining in the hand consists of residues such as roots and fibres that resist decomposition.	150
H9	Practically fully decomposed peat in which there is hardly any recognizable plant structure. When squeezed it is a fairly uniform paste.	165
H10	Completely decomposed peat with no discernible plant structure. When squeezed, all the wet peat escapes between the fingers.	180

Types and Definitions

The chemistry of organic matter can vary from an empirical formulation of $C_{1200}H_{813}O_{389}N_5S$ for poorly decomposed peat to $C_{293}H_{409}O_{20}N_5S$ for a well decomposed peat, where the C/N ratio decreases with increasing decomposition (Morita, 1980). Gaseous carbon dioxide and methane are also released when peat decomposes (Hogg, 1993; Valentine et al., 1994). Organic matter is not a single homogeneous substance, but a complicated mosaic of organic structures, consisting of carbohydrates (cellulose, hemicellulose, sugars), nitrogenous compounds (proteins, amino acids), polyphenols (lignins, humic acids, fulvic acids), and lipids (waxes, resins, steroids, terpenes), in addition to smaller amounts of nucleic acids, pigments, alkaloids and vitamins, among others (Rydin and Jeglum, 2006).

Typically, soil organic matter (SOM) is 52-58% carbon, has a high cation exchange capacity and high surface area (Sparks, 2003). The SOM consists of both non-humic and humic substances, of which the later make up the major components of DOM and particulate organic matter (POM). Non-humic substances are recognizable plant components, and generally have names and defined chemical formulae (e.g. proteins, steroid). Humic substances are "a category of naturally occurring biogenic, heterogeneous organic substances that can be generally characterized as being yellow-to-black in colour, of high molecular weight and refractory" (Aiken et al., 1985).

Humic substances are divided into sub-categories, functionally defined by fractionation on the basis of solubility. Fulvic acid is soluble in both acidic and alkali, making it quite mobile in all aquatic environments. Humic acid is insoluble in acid but soluble in alkali, making its mobility dependent aquatic system pH. Humin is insoluble in both acids and alkalis, making it a relatively stable particulate form in aqueous environments (Sparks, 2003). It has been suggested that wetland DOM is nearly 90% fulvic acid (Thurman, 1985).

Organic matter leached from soil may eventually enter an aqueous environment. As outlined in Thurman (1985), the water quality parameters dissolved organic carbon (DOC) and particulate organic carbon (POC) quantify inputs of SOM to streams, rivers and lakes. Organic carbon that passes through 0.45 μm filters is defined as DOC, with swamps, marshes and bogs possessing DOC concentrations from 10 to 60 mg L^{-1}. Varied operational definitions exist for POC, which consists of organics retained by either 0.45 or 0.70 μm pore size filters. The POC is generally 0.02 times the total sus-

pended solids (TSS), although wetland environments may possess up to 40% of TSS as POC. Geochemical processess that affect DOC include (Thurman, 1985): (a) sorption/partition, (b) precipitation, (c) volatilization, (d) reduction/oxidation (biochemical and chemical) and (e) complexation.

Complexes, Adsorption and Binding Coefficients

Mechanisms by which trace elements form complexes with humic and fulvic acids in peatlands have been investigated extensively (Washburn & Gillis, 1982). Lakatos et al. (1972) found humic and fulvic acids from peat formed complex chelate bonds of significant ionic character, mainly coordinated by carboxyl groups in very distorted octahedral, tetrahedral or square-planar arrangements of polynuclear structure. Early geochemical modeling by Shotyk (1986a) found, at pH 4, citric, oxalic and salicylic acids complexed more than 50% of total dissolved Fe, with nearly 20% of Al as organically bound. A Russian study revealed concentrations of humic and fulvic acids in oligotrophic peatlands vary dramatically when they are drained and mined, whereas cultivation of eutrophic peatlands resulted in minimal concentration changes of humic and fulvic acids (Largin, 1976). Such changes would influence the mobility and bioavailablity of minerals and nutrients.

Bunzl et al. (1976) demonstrated *Sphagnum* peat adsorbed metals in the following sequence of rates: $Pb^{2+}>Cu^{2+}>Cd^{2+}\approx Zn^{2+}>Ca^{2+}$ from pH 3.5 to 4.5. Thus, Pb is bound strongly and its rate of release due to desorption is low, whereas desorption of Cd, Zn and Ca can be rapid. Earlier work by Bunzl (1974) with Pb suggested a film diffusion-limited model to describe binding . Later, Kadlec and Keoleian (1986) suggested adsorption and desorption of metal cations to peat are better described by equilibrium transfer processes between the cations in bulk solution exterior to peat particles and the intraparticle liquid phase, with control either by diffusion rate through the surface film, or by diffusion through interstices of the particles. Precise dynamics of metal binding by organic components in peat is daunting and common geochemical modeling programs lack accurate organic binding algorithms, mainly due to a lack of good quality data sets for model calibration (e.g. WHAM (Windermere Humic Aqueous Model), VMINTEQ(Visual chemical equilibrium model); pers. corr. Gustafsson, 2007).

Humic acids and their carboxyl and phenolic hydroxyl groups are considered the primary metal complexing components of peat (Kadlec and Keoleian, 1986). Solution

pH plays a pivotal role in metal binding by determining the charge characteristics of these functional groups, as well as the hydrolysis of metal ions. Functional groups and metal ions may be protonated or deprotonated by adsoption of H^+ or OH^- from water molecules in aqueous environments. Positively charged species will associate with negatively charged species, forming stable molecular entities (surface complexes). Various but finite geometric configurations are possible (Sparks, 2003).

The affinity of a metal for its organic ligand may be described by its stability constant. If

$$M + L_i \rightleftharpoons ML_i \tag{1.2}$$

where M is the metal ion and L_i is the ith deprotonated ligand, then the conditional stability constant can be expressed as

$$K_i^{cond} = \frac{[ML_i]}{[M][H_{xi}L_i]}, \tag{1.3}$$

where $[H_{xi}L_i]$ is all forms of the ith ligand not bound to M, since, it is not possible to measure L_i directly. Note conditional stability constants are only valid for the conditions stated (pH, temperature, ionic strength, mixture of humic ligands). Due to the complexity of mixed systems, average values are determined from experimental data. Therefore, interpretation of binding coefficients in literature must be done with consideration of experimental conditions and metal concentrations used for derivation (Sparks, 2003).

Extensive experimental measurements have been made for various metal ions and humic substances and the range of conditional stability constants can be used for generalizations. Thurman (1985) notes in coloured waters where humic substances may be present at concentrations of 10 to 30 mg L^{-1}, there may be from 10 to 30 μeq L^{-1} of metal binding sites for ions of Cu and Fe. Therefore, for every mg L^{-1} of DOC, there is about 1 μeq L^{-1} of metal binding capacity.

The binding of Hg species by DOM has undergone review, with literature DOM–Hg conditional stability constants ranging from $10^{4.7}$ to $10^{32.2}$ (Ravichandran, 2004). Older research tended towards unrealistic Hg:DOM ratios, with lower stability constants, more consistent of Hg complexation to oxygen functional groups (Haitzer et al., 2002), as found for other metals binding to organic matter in peat (Kadlec and Keoleian, 1986). Generally, a soft acid such as Hg^{2+} preferentially binds to soft bases such as thiol (-SH) functional groups (EPA, 2007). Elevated DOM:Hg ratios used in early experiments, likely saturated reduced sulphur binding sites, as demonstrated by x-ray spectroscopy

(Skyllberg et al., 2000). Gasper et al. (2007) published Hg^{2+}–DOM conditional stability constants from 10^{25} to 10^{30} at environmentally relevant Hg:DOM concentrations, also consistent with complexation to reduced sulphur binding sites. Other metal speciation in water, porewater, peat and/or sediment may influence binding coefficients. Zhong and Wang (2009) demonstrated the complexity of predicting bioavailability, demonstrating that different sulphur species and Hg:S ratios significantly affect the partitioning and binding of Hg in anoxic sediments.

Karlsson and Skyllberg (2003) confirmed MeHg also binds to reduced sulphur groups in SOM, controlling its biouptake, toxicity, demethylation and transport, by lowering concentrations of free MeHg, its neutral halide and hydroxyl species. Their log K_{CH_3HgSR} values for DOC and soil organic carbon ranged from 15.6 to 17.1. Hintelmann et al. (1995) published the first binding capacities and conditional stability constants for MeHg–pure humic solution (by dialysis membranes), finding values for 2 binding sites of 1.3×10^{12} (binding 0.2 ng CH_3Hg^+ per mg humic acid) and 5.0×10^{10} (binding 1.2 ng CH_3Hg^+ per mg humic acid). Karlsson and Skyllberg (2003) suspected those results were underestimations. Nonetheless, though fewer published binding constants for MeHg to organic matter exist than those for Hg, data suggests MeHg would be more bioavailable than Hg in similar organic matter environments.

As immense carbon reservoirs, peturbing peatland systems through wet mining may release dissolved and particulate organic matter and its associated analytes to downstream ecosystems. The positive relationship between organic matter and Hg has been implicated in mobilizing Hg from contaminated floodplains (Wallschlager et al., 1996), after clear-cutting and forest fires (Pinheiro, 2000), in temperate and boreal terrestrial ecosystems (Grigal, 2002) and in runoff episodes in a northeastern USA watershed (Schuster et al., 2008). The cycling of Hg and organic carbon was coupled to hydrology in a forested upland bog watershed of the Marcell Forest in Minnesota, with 70% of THg transported with POC and 30% associated with DOC (Kolka et al., 2001). Authors suggested that watershed disturbances that stimulate the transport of particulates and/or cause higher water yields would lead to higher THg in runoff, thus influencing adjoining surface waters. Verta (1984) noted receiving waters of particulates can act as sinks or sources of Hg, and found greater than 99% of THg in a lake ecosystem existed in sediment.

1.5 Peat Excavation

1.5.1 History in Canada

Within the first two decades of the 20^{th} century, Canada identified a lack of energy resources in the centre of the country (noteably Ontario and Québec), as being a detrimental to the growth of the nation (Haanel, 1925). He stated, "large fuel resources lying dormant in the numerous peat bogs strategically distributed throughout the inhabited portions" of those provinces, could solve the problem. However, he also pointed out that prior to the war in 1914, numerous attempts by individuals and small companies for fuel peat manufacture had failed for reasons ranging from inefficient machinery to lack of knowledge for dewatering. To collate European knowledge, investigate local barriers and conduct further research, a Canadian Joint Peat Committee was appointed in 1918, being equally financed by the federal and Ontario governments (Haanel, 1925). The committee was tasked with investigating the ways and means for converting the peat content of Canadian bogs into a marketable fuel.

Since then, each energy crisis has shown renewed interest in Canadian peatland resources, most recently during the 1980's when "biomass peat" was a popular discussion topic. Numerous studies were conducted by the National Research Council of Canada and summarized by Tibbetts (1986). Peat energy potential was evaluated in Ontario (Monenco, 1981b). Laboratory methods for testing peat for Ontario inventory projects were standardized (Riley, 1986). Technologies were developed for peat slurry pumps and macerators (Monenco, 1985). Methods to convert peat to other liquid fuels were engineered (Lindstrom, 1980; Tibbetts and Ismail, 1980). A "double use" system was proposed, suggesting dry peat extraction be followed by forest plantations (Hinrichsen, 1981). Thunder Bay, ON hosted the International Peat Society conference in 1981 (IPS, 1981). Today, an emerging biofuel/bioproduct industry has raised interest in peat fuels again.

In reference to peat extraction, the terms "peat mining" and "peat harvesting" have been used interchangeably, and may be misinterpreted as reflecting ones bias on the subject. Historically, the terms have arisen from the means used to extract peat and the aesthetic qualities of the impacted area (Monenco, 1978). Peat harvesting involves peat drainage and removal of peat by machinery resemblant of harvesting equipment used for agriculture (Fig. 1.3A). The site itself is flat, being barren of vegetation unless intensive

restoration is undertaken. Peat mining involves extraction of peat while wet (≥90% moisture), using machinery typical of mining operations (backhoes, dump trucks). The site remains wet, mucky and uneven (Fig. 1.3B). The term "peat mining" was used here.

Figure 1.3: Contrasting techniques used to extract peat. **A** Dry harvesting as observed during a peatland restoration tour in northern Minnesota (2008). The "hockeys" (see text) are exposing a new peat layer for drying (foreground), while harvested peat is stored in piles (background). **B** Wet mining as employed during this research (2008). A backhoe sits atop a floating mat and extracts higher energy, catotelm peat.

1.5.2 Local and Global Peat Resources

Wetlands are an integral part of the Canadian landscape, covering 148 million ha, of which 113 million ha (76%) are peatlands (Daigle and Gautreau-Daigle, 2001). Indicated peat volumes are 3 trillion m^3 for all of Canada and, assuming 50% water content, are estimated at 507 billion tonnes (NWWG, 1988). Over 50 million tonnes of peat are estimated to accumulate in the natural environment each year in Canada while current applications utilize an average of 700,000 to 800,000 tonnes annually (Daigle and Gautreau-Daigle, 2001). Thus, peat continues to accumulate in Canada.

With less than 0.02% (16,000 ha) of Canada's peatland area being used, revenues for horticultural peat in 1990 exceeded $90 million (CND$), providing employment for thousands of residents, especially those in rural areas (Keys, 1992). Revenues in 1999 were $170 million (CND$) (Daigle and Gautreau-Daigle, 2001). During the course of this research and stated earlier (Daigle and Gautreau-Daigle, 2001), there was no peat use for energy in Canada. This is in sharp contrast to other countries.

The World Energy Council (2007) estimates 3 million km^2 of peat exists worldwide and consumption for energy outside Europe is negligible (17 million tonnes per year). Asplund (1996) reported about 50% of extracted peat was used for energy worldwide, although in some countries this was the major use (Ireland, 90% of extracted peat for energy; Finland, >66% of peatland area extracted for energy). For comparison, global peat for energy is estimated to be 5 to 6 million tonnes of oil equivalent per year, which is only 0.1% of the energy used globally (World Energy Council, 2007). Bord na Móna in Ireland is an example of a current and highly organized peat fuel industry, employing various processing techniques (http://www.bnm.ie/corporate/index.jsp).

Peatlands cover 31.3 million ha (29.3% of area) in Ontario (Rubec, 2000; Tarnocai et al., 2000). In 1980, the potential/inferred peat resource of Ontario was 16 million ha or 27,580 million tonnes (at 50% moisture), although only 62,000 ha (103 million tonnes; 0.4%) were properly evaluated (Washburn & Gillis, 1982). The volume of peat within the Western Shield region (below permafrost) described in Monenco (1981b) were quantitatively calculated as 22.86 billion m^3 and 6.86 billion tonnes (at 50% moisture) by Watts, Griffis and McOuat Ltd. (2004). Estimates consolidated by Gleeson et al. (2006), using data from Riley and Michaud (1989) for some northwestern Ontario sites (Rainy River, Dryden-Lac Seul, Sioux Lookout, Ignace, Armstrong, Longlac-Nakina), were 13 billion m^3. As noted by Gleeson et al. (2006), significant variability in estimates exist due to variable inventory techniques. Total peat production in Ontario during 1944 by six companies was reported to be about 10,000 tonnes. Less costly energy generation (e.g. hydroelectric) was cited as partially responsible for poor peat fuel development in Ontario.

Peat Resources Ltd. contracted a detailed regional study of their property in the winter of 2004/2005 (DST, 2005). They estimated that indicated resources could differ by as much as 20% and measured resouces by 10%. The study peatland (GG3) was assessed at 4.01 million tonnes of indicated resource and 2.96 million tonnes of measured resource, both at 10% moisture. Peat Resources Ltd. calculated that northern Ontario has an allowable harvest potential of 8.8 million bone dry tonnes per year (Peat Resources Ltd., 2009). They had planned to extract a million tonnes per year of dry fuel-grade peat pellets, consuming roughly 500 ha of peatland per year from their property (OME, 2006). The same report found peat to be the only biofuel within a 200 km radius of sufficient quantity and quality to sustain northwestern Ontario's two coal fired generating stations for any length of time. The Atikokan Generating Station, being historically coal

combustion, was re-equipped to burn 100% biofuel (OPG, 2011). However, the plant was accepting only bio-resources deemed renewable at the time of this dissertation (Jane Todd, pers. corr.).

1.5.3 Peat Extraction Methods

Dry harvesting is the current, popular and cost effective industrial scale extraction method for peat products. It involves draining the peatland over 3 to 5 yr. As explained in Washburn & Gillis (1982), moisture in peat severely undermines its heating capacity and water removal to less than 30% moisture is required at some stage between the peatland and combustion furnace. Three common dry extraction methods were milled-peat harvesting, sod peat harvesting and block cutting.

Dry peat harvesting site preparation was described by Washburn & Gillis (1982), Monenco (1986) and observed in Minnesota in 2008. Briefly, initial peatland dewatering is accomplished with a series of strategically spaced ditches (1×1 m, 20 m spacing, 500 m ditch per hectare) and a perimeter ditch (2 to 4 m deep). A decrease in water table coupled with natural solar irradiation results in sufficient drying after several years. Drying and peat subsidence enables the area to support heavy machinery. Trees and other woody vegetation must be cleared before harvest. The top peatland surface is contoured and stripped of its lower calorific value mosses which further facilitates drying. Peat is extracted as either peat sods or milled peat. Vacuum harvesters are often used to draw up the top dried layers (12 to 15 mm) of peat material while turning over the next layer for air exposure. Minnesota peat harvesters refer to these devices as "the hockeys" (Fig 1.3A). Milled peat may be formed into windrows and allowed further drying in the field, whereas vacuum peat is piled for drying. Caution must be taken to prevent spontaneous fires. Other dry harvesting methods after initial peatland dessication involve block cutting or sod cutting of the peat. Alternatively, one metre depths may be macerated and extruded as large cylinders (8-10 cm×25-30 cm) which are field dried. All weather access roads to peat areas are necessary for dry harvesting methods. Potential dry harvested yields for Canada were estimated as 100 to 180 tonnes of fuel peat per hectare.

Wet mining of peat differs significantly from dry harvest methods. Three techniques were described by Monenco (1978): (i) slurry ditch system, (ii) slurry pond system, and (iii) a combination of slurry pond and sod peat production (hydro peat). After removal of surface vegetation, dredging of raw wet peat as a slurry, either by heavy machinery

such as backhoes or with a piping and pumping network, can be conducted. Wet mining techniques are uncommon, though reported in Russia for over 40 years (Tibbetts, 1986).

The advantages of wet harvesting over dry harvesting include the potential to mine difficult to drain peatlands, lower costs associated with reduced handling of peat material and an increased harvest season (Monenco, 1981a; Washburn & Gillis, 1982). Minimal or no peatland desiccation is initially required (Päivänen, 1973; Monenco, 1986). Some site preparation (clearing, ditching) may occur (Washburn & Gillis, 1982).

Wet mining methods were not popular since the colloidal content of peat remained an economic barrier to full scale dewatering operations (Monenco, 1981a). Mechanical pressure is required to remove a large portion of the water, which expedites the drying process (Schnitzer, 1986; Gleeson et al., 2006). Dewatering to 35-50 wt% water content was achievable after exposure to elevated temperatures and pressures (Monenco, 1986). However, such dewatering methods are energy intensive. As reported by Haanel (1925), "every form of press has been tried ... apparently promising results have been obtained in laboratory experiments, [but] no success in commercial production has been achieved".

Wet extraction methods were deemed not economically feasible by the early Canadian Peat Committee (Haanel, 1925). As reported in Carncross (1980), Western Peat Moss Ltd. used wet harvesting methods beginning in the 1930's at its 6000 acre bog near Vancouver, mainly due to wet climatic conditions unsuitable for dry harvest methods. Their experiences were wrought with logistical and mechanical issues, culminating in low scale production. Costs were estimated as 3 to 4.5 times that of dry vacuum harvested milled peat. Heterogeneity of the peat fuel also cast further doubt on the overall effectiveness of their wet excavation methods (Washburn & Gillis, 1982).

Today, Peat Resources Ltd., a private sector partner with Lakehead University through the Ontario Centres of Excellence Atikokan Bio-energy Research Centre, has developed wet mining peat methods with a proprietary upgrade step. Their mechanical dewatering is undertaken with a continuous high pressure press once peat has been extracted as a wet slurry. Their equipment is portable and can readily be moved from site to site on the back of a flat bed truck (Fig. 1.4). Portability may decrease transportation costs and associated greenhouse gas emissions (pers. corr., Telford). Peat Resources Ltd. would establish a piping-pumping network, reducing the need for heavy machinery. Pelletization of peat occurs on-site, and process water was proposed to be discharged onto an adjacent intact peatland for natural filtration (pers. corr., McLellan, Telford). A comparable system was outlined in Monenco (1985). Restoration of mined sites is planned. It

has been suggested that wet mining methods would alleviate detrimental environmental impacts associated with peatland drainage and desiccation associated with dry harvesting methods (Tibbetts, 1986). This study appears the first to provide environmental considerations for wet mining northwestern Ontario peatlands.

Figure 1.4: Proprietary mechanical dewatering equipment used by Peat Resources Ltd. to pelletize wet peat is transportable to a site via a flat bed truck.

A similar peat mining proposal was originally viewed in 1982 as an "ambitious project for the Fort Frances area" (Washburn & Gillis, 1982). Peat Resources Ltd. planned to initially produce 100,000-500,000 tonnes per year of pelletized peat, mainly for space heating, with supplies to Ontario Hydro a long term goal (Washburn & Gillis, 1982). Project viability hinged on their specific wet harvesting/wet carbonization technology success and peat production would need to be a million tonnes per year (Washburn & Gillis, 1982).

The restoration strategy for this research is unique to wet mined peatlands. The acrotelm layer (of lower calorific value) was set aside, catotelm peat was mined, then acrotelm pieces with living vegetation were replaced (Fig. 2.3). This type of peatland restoration was used for peatland drainage ditches at dry harvested sites (Cagampan and Waddington, 2008a,b). Wet mining would leave open areas subject to flood under certain hydrological conditions, forming lake habitats for fish, cranberry production or wild rice cultivation as options for land reuse (OME, 2006).

1.5.4 General Environmental Concerns

Walters (1980) stated that peat extraction for energy products requires the disturbance of far greater land areas than other fossil fuel extractions (e.g. coal) of an equivalent size.

They suggested that impacts may alter lands of greater terrestrial habitat, aquatic habitat and environmental value at distances beyond the mined site. Furthermore, Walters (1980) identified point source wastewater discharge from both wet and dry extraction methods would require treatment to site-specific effluent standards to maintain water quality of receiving waters. After reviewing local, regional and national environmental and economic impacts of mining peat for energy in the United States, Winkler and DeWitt (1985) concluded the unique biophysical attributes of peatland ecosystems and their importance internationally in carbon cycling, make them valuable, diverse and irreplaceable habitats of more value to society when left undisturbed. Winkler and DeWitt (1985) noted a shortage of American peer reviewed studies, stating "peat mining on a large scale was not identified in the scientific literature as a possibility and therefore not identified as an environmental problem". A need for local studies as conducted here are warranted.

Since early impact statements, research showed dry harvesting environmental effects to include increased evaporative losses and runoff from harvested sites (Seters and Price, 2001), long term hydrological changes (Holden et al., 2006b), changes to hydrological function (Siegel, 1988), alterations in water quality of the local water shed (Monenco, 1986), including increased MeHg (Westling, 1991), increased cations, sulphate, chloride and nitrogen species (Wind-Mulder et al., 1996), increased suspended sediment loading (Pavey et al., 2007), increased CO_2 emissions (Waddington et al., 2009), subsidence and erosion (Quinty and Rochefort, 2003; Rydin and Jeglum, 2006) and loss of wetland area including effects on large and small animals (Daigle and Gautreau-Daigle, 2001). Further reviews on impacts related to peat harvesting/mining have been published (Carpenter and Farmer, 1981; Osborne, 1982; Gleeson et al., 2006; Holden et al., 2006a).

The review by Gleeson et al. (2006) specifically focused on assessing peat harvesting and mining for Ontario, noting a lack of literature available to accurately assess wet peat mining impacts. Therefore, extrapolations from dry harvesting research predicted wet mining would (i) affect regional biodiversity through wetland loss, (ii) disturb unique hydrological functions of peatlands, (iii) affect local water quality, (iv) alter the natural carbon balance of peatland ecosystems, and (v) increase net greenhouse gas emissions over pre-disturbance values.

After peat removal, dry harvested lands may be reclaimed for both agriculture and forestry, as routinely done in Finland, Ireland, Sweden and Germany (Rydin and Jeglum, 2006). Dry peatlands may be suitable for blueberry cultivation (Haanel, 1925; Mol, 2009).

To reclaim wet mined peatlands, low lying areas may be allowed to reflood, becoming favourable sites for northern crop production (e.g. cranberries and wild rice; OME (2006), P.F.Lee, pers. corr.). Precise water content and water levels for adjacent peat and mined plots, respectively, were difficult to predict. Monitoring hydrology and water chemistry during peat extraction was recommended (Washburn & Gillis, 1982; OME, 2006). Gleeson et al. (2006) cited a lack of available knowledge and methods to restore/rehabilitate wet mined sites as problematic to mining activities proposed for northwestern Ontario by Peat Resources Ltd. Much research on restoring dry harvested sites has been done, culminating in methods outlined by Rochefort et al. (2003) and presented in the Peatland Restoration Guide (Quinty and Rochefort, 2003). Such methodology, however, seems inapplicable to wet mined sites.

Since this dissertation focuses on impacts associated with water quality and the potential for Hg species to bioaccumulate in benthic organisms, only those topics will be further reviewed. Gleeson et al. (2006) summarized direct and indirect hydrological and aquatic impacts of any peat extraction to include (i) increased sedimentation and loss of fish habitat, (ii) increased stream flow temperature, (iii) increased levels of ammonia, organics[original text "organisms"], TN, TP, Al and Fe, (iv) changes to evapotranspiration affecting heat flux and ground temperatures, (v) changes in turbidity and chemistry from peatlands to adjacent water bodies, (vi) increased release of heavy metals (i.e. mercury) and acidity to adjacent water bodies, (vii) eutrophication of neighbouring ecosystems from releases of stored phosphorus in peat into surface waters, (viii) sedimentation and contamination of watercourses as a result of runoff from extraction sites and potential loading of area watercourses/waterbodies with impurities and trace metals previously bound within the peat deposits, (ix) increases in runoff, peak flows, and base flows due to drainage, (x) flooding as a result of higher base flow contribution to area watercourses following harvesting, and (xi) potential loss of reservoir function and water storage capacity of peatlands as a result of removing the acrotelm layer and exposing the catotelm. As has been reviewed here, most impacts are interrelated.

1.5.5 Alterations in Hydrology and Water Quality

Wet and dry peat extraction may differ significantly in their effects on water yield following initial pre-development (Olkowski and Olesinksi, 1976). Impacts associated with wet mining are historically identified as mainly hydrological, including an increase in max-

imum discharge and total water yield from the excavated area (Brooks and Predmore, 1978). Lowering the local groundwater table as a result of wet mining, which extends to areas outside the peatland, can interfere with groundwater supplies resulting in soil conditions favourable to upland rather than wetland vegetation (Washburn & Gillis, 1982). Modeled hydrological changes associated with wet mining the GG3 study peatland , suggested water would pool at the specific location excavated and sampled for this research (Figs. 1.8, 2.1, 3.1), whereas upfield areas would be drier (OME, 2006).

Peat mining that primarily alters watershed hydrology and water quality has the potential to affect ecology in downstream aquatic habitats (Winkler and DeWitt, 1985; Gleeson et al., 2006). Knowledge of local aquatic environments are required to define their sensitivity to alterations caused by such changes (Monenco, 1986; Glooschenko et al., 1985). PHIM was developed to address questions concerning the effects of peatland drainage, peat mining and timber harvesting on streamflow responses in northern USA lakes (Guertin et al., 1987; Yu and Campbell, 1998). Recently, PHIM was integrated with the hydrological model HYDROTEL for prediction in the James Bay area, with suggested applications for northern Boreal watersheds (Jutras et al., 2009).

Some drainage ditches are required before wet mining the GG3 peatland (Waddington, pers. corr.). Impacts to receiving streams associated with construction of peatland drainage ditches can be attributed to suspended solids and colloidal matter, resulting in siltation of habitat, avoidance reactions by aquatic organisms and changes to biological productivity (Carpenter and Farmer, 1981; Winkler and DeWitt, 1985; Shotyk, 1986b; Boron et al., 1987; Gleeson et al., 2006). Ditching for dry peat excavation was found to increase amounts of POM to riffle beds in boreal streams of Finland, with the finest particles (<0.075 mm) carrying Fe (Laine and Heikkinen, 2000). The presence of DOM and nutrients released from drainage ditches may decrease levels of dissolved oxygen downstream, leading to anoxic conditions (Monenco, 1986).

Sallantaus (1984) noted the importance of including local climatic conditions in assessing peat harvesting impacts. At an active dry harvested fuel peat mining site with experimental catchments (Finland), they found suspended solids were discharged only with peak water flows that occurred only after rare heavy rainfall events. Concentrations were typically low, as peat was not easily eroded (Sallantaus, 1984). They speculated that erosion could become an issue once more decomposed catotelm peat becomes exposed. Such erosion likely occurred in Minnesota harvested sites, as Clausen and Brooks (1983) reported higher suspended solids concentrations from exploited bogs (mean 13.7 mg L^{-1})

than control bogs (mean 5.1 mg L^{-1}). When surface peat was dried below 30% moisture it exhibited a granular surface with hydrophobic characteristics (Olkowski and Olesinksi, 1976). This physical change may lead to reduced infiltration and increased surface runoff (Tallis, 1973).

Korpijaakko and Pheeney (1976) found bog drainage did not decrease pH in a receiving stream in New Brunswick. Later studies by Surette et al. (2002), also in New Brunswick, reported receiving water had low pH (3.9 to 4.7), higher concentrations of TP and total organic carbon (TOC) and peat sediments with high THg. Washburn & Gillis (1982), studying river water quality adjacent to actively mined bogs, found pH, alkalinity, conductivity and hardness (Ca, Mg) all declined below bog discharge points and approached normal (reference site) concentrations 1.3 km downstream. Nitrate, turbidity, suspended solids, TOC and Ba concentrations were elevated at discharge points, returning to reference levels downstream. Iron and Al were of intermediate concentrations at discharge points relative to other stations, and highest downstream. Though Washburn & Gillis (1982) found no elevated levels of metals in mined peatland water itself, they hypothesized elevated levels of suspended particles may provide a mechanism for release of metals to receiving waters, since binding capacity of humic substances is very high at pH 4 to 5. They theorized that once peat particles are transported downstream, decomposition may be fairly rapid. If pH increased and binding capacity weakened, a secondary release mechanism of metals from particles would occur.

Investigations of metal speciation would facilitate a better understanding of metal solubility and bioavailability in peatland ecosystems (Shotyk, 1986a), especially at impacted sites. When examining the organic geochemistry of bog drainage water in eastern Canada (one drained, one undisturbed), observed changes in DOM quality were extrapolated to cause increases in biochemical oxygen demand, changes in organic contribution to acidity and changes in metal complexation capacity (Bourbonniere, 1987). They reported 30% more DOC was released by the drained site.

Largin (1976) measured water quality associated with draining and mining of bogs in USSR, finding peat porewater had increased pH, Ca, Mg, bicarbonate, sulphate, humic acid and fulvic acid concentrations. They found similar operations in fens had increased pH, Mg, sulphate, nitrate, humic acid and fulvic acids. They hypothesized that increased aeration of the bog occurred as the drainage aged, leading to observed increases. However, little connection between chemistry of the peat ash and chemistry of aqueous solutions of the corresponding layer was noted. Water table alteration in immediate mined areas will

subsequently change the aerobic/anaerobic conditions at various depths in the peatland, altering redox sensitive geochemical processes. Washburn & Gillis (1982) suggested a peatland's well humified catotelm layer would likely be exposed to increased oxygen during extraction, leading to increased decomposition rates. They highlighted the need to assess concentrations and release rates of elements in exposed bog layers.

Wells and Williams (1996) found ditch spacing of 3 m in bog peats had higher bulk density and total contents (kg ha^{-1}) of N, P, K, Ca and Fe than bog peats with 15 m ditch spacing. However, authors found bulk density and most nutrient contents of fen peats were not significantly affected by drainage spacing. Specific changes in peat chemistry, decomposition rates and subsequent analyte leaching due to water table fluctuations were difficult to ascertain *a priori* for this research site. Holden et al. (2006a) found nitrogen mineralization due to a lowered water table was not always predictable, though likely related to peat decomposition rates. Changes to oxygen content in overlying water altered Hg methylation production in lake surface sediments, where MeHg decreased in sediment when redox potential increased from -200 mV to + 50 mV (DeLaune et al., 2004). This was consistent with Branfireun (2004), who found less MeHg on higher hummocks than in hollows.

Mercury was detected in peat harvesting runoff (Evans et al., 1984; DiGiulio and Ryan, 1987; Surette et al., 2002) and Gleeson et al. (2006) anticipated Hg release from such activities in Ontario. However, Surette et al. (2002) did not find higher tissue concentrations of THg in indigenous invertebrates from control and impacted sites, nor did introduced blue mussels accumulate significant amounts of THg. Surette et al. (2002) concluded that although relatively large amounts of peat particles with THg are discharged into the ecosystem, bioaccumulation of THg by biota does not occur. Similar conclusions were drawn by DiGiulio and Ryan (1987) studying soils, sediments and clams in a North Carolina peatland. Neither study included MeHg bioaccumulation. To properly address concerns of THg and MeHg raised by Gleeson et al. (2006), a review of Hg cycling in peatlands seemed required.

1.6 Mercury in Peatlands

Mercury and MeHg are commonly accepted as detrimental to ecological systems because of their persistence and ability to bioaccumulate and biomagnify in food webs to concentrations of concern. These metals are global pollutants of significant importance to

the health of fish and predatory animals, including humans (NRCC, 2000). The United States Environmental Protection Agency (EPA) has placed inorganic mercury on its metals and metalloids of primary interest (EPA, 2007). The main organometallic form of mercury (Hg) in nature is MeHg, being (i) bioaccumulated and bioconcentrated (EPA, 1984; WHO, 1990), (ii) a potent neurotoxin in vertebrates (Clarkson, 1994; Clarkson and Magos, 2006) and (iii) 100 times more toxic than inorganic forms of Hg (Environment Canada, 2003a).

Mercury from natural or anthropogenic sources is methylated to the more toxic MeHg as a byproduct of the activities of both sulphate and iron reducing bacteria under anoxic conditions such as lake bottoms and wetlands (Gilmour and Henry, 1991; Kerry et al., 1991; Pak and Bartha, 1998; Fleming et al., 2006; Kerin et al., 2006). Numerous reviews on Hg and MeHg history, poisonings, toxicity and cycling in a myriad of contaminated and uncontaminated ecosystems and organisms (including humans) are available (EPA, 1984; Stokes and Wren, 1987; Jackson, 1988; Zillioux et al., 1993; Clarkson, 1994; EPA, 1997a; NRCC, 2000; USGS, 2000; Ullrich et al., 2001; Environment Canada, 2003a, 2004; Biester et al., 2006; Kerin et al., 2006; Clarkson and Magos, 2006).

1.6.1 History and Basic Chemistry

Historic to modern uses of Hg include its use as red ink in China over 3000 years ago, carroting of felt hats, treatment of syphilis, extraction of gold and silver, tooth filling amalgams, preservative in vaccinations and antibacterial agents for crops. A comprehensive review, including toxicological studies past and present was covered by Clarkson and Magos (2006). Tragic Hg poisonings due to direct industrial discharges in both Minimata, Japan in the 1950's (Harada, 1995) and Grassy Narrows First Nation (in northwestern Ontario, an hour north of Kenora, ON) in the 1970's (CBC Archives, 1970; Shephard, 1976; Takeuchi et al., 1977) are classic case studies that resulted in severe tragedy for the people involved and garnered international media attention. Since those incidents, direct point sources have been identified and eliminated.

Persistent MeHg concentrations in fish have been linked to hydro-electric dam projects for energy production. The flooding of terrestrial soils, their vegetation and their detritus results in anoxic conditions conducive to microbial methylation of Hg (Stokes and Wren, 1987; Jackson, 1988) and higher MeHg in benthic species (Tremblay et al., 1996). The implication of wetlands as MeHg sources by St. Louis et al. (1994) has focused attention

towards Hg cycling in wetland ecosystems. Clarkson and Magos (2006) commented the major health dilemma with regards to fish consumption; "Despite almost 30 years of studies searching for adverse effects in human health from ingestion of methylmercury in fish, no clear answer has yet emerged. ... On the other hand, the cardiovascular benefits from fish consumption are well established".

Chemically, Hg may exist in three oxidation states Hg^0 (metallic, Hg(0)), Hg_2^{2+} (mercurous, Hg(I)) and Hg^{2+} (mercuric, Hg(II)), with Hg(I) rarely stable under environmental conditions (EPA, 1997a). The previous reference summarizes some common properties and behaviours of Hg, including;

- generally Hg forms covalent bonds, rather than ionic bonds characteristic of other metals;
- most Hg in the environment is present as inorganic mercuric salts and organomercurics, defined by the presence of a covalent C-Hg bond;
- common compounds found under natural conditions include:
  - mercuric salts: $HgCl_2$, $Hg(OH)_2$ and HgS,
  - methylmercury compounds: CH_3HgCl, CH_3HgOH,
  - small fractions of organomercurics, i.e. dimethylmercury ($(CH_3)_2Hg$) and phenylmercury,
- aqueous phase Hg compounds often remain undisassociated molecules and their solubilities are not based on their ionic products;
- most organomercurics are not soluble and do not react with weak acids or bases, with the exception of methylmercuric hydroxide (CH_3HgOH), which is highly soluble due to hydrogen bonding;
- mercuric salts vary widely in solubility; $HgCl_2$ is readily soluble in water, whereas HgS is unreactive due to high affinity of Hg for S.

Mercury is a global issue. Contemporary measurements of atmospheric Hg, together with historical records from lake sediments and peat, indicate that the global reservoir of atmospheric Hg has increased two to five fold since the beginning of the industrialized period (Klassen, 2001). Mercury pollution is often viewed as a global problem

that defies regional and national abatement efforts because Hg vapor has a long atmospheric residence time and Hg contamination of lacustrine food webs are often not from identifiable local sources (Klassen, 2001). The Hg cycle and chemical, geochemical and biogeochemical processes, as they relate to peatlands of northwestern Ontario, are reviewed (Figure 1.5).

1.6.2 Atmospheric Origins

Natural sources emitting Hg to the atmosphere include degassing of the earth's crust through volcanic eruptions and volatilization from land, exposed rocks and oceans (Boening, 2000). Coal combustion and solid waste incineration account for more than half of the total global Hg emissions (Pirrone et al., 2001). In 2003, reported atmospheric Hg emissions for Canada totaled 6,949 kg with electrical generation accounting for 34% (Environment Canada, 2004). According to the National Pollutant Release Inventory, in 2005, Ontario Power Generations's coal fired plants emitted over one-third of airborn Hg emissions of all Ontario's reporting facilities, with Atikokan releasing 39.7 kg and Thunder Bay releasing 37.2 kg (Ontario Clear Air Alliance, 2007). Data reported for 2008 and 2009 were lower, at 18 kg and 8.8 kg for Atikokan, respectively, and 31 kg and 3.7 kg for Thunder Bay, respectively (Environment Canada, 2009).

With two coal fired electrical generating stations within a 200 km radius of the GG3 study peatland (Thunder Bay, ON and Atikokan, ON; Fig. 1.7), THg and MeHg in precipitation, peat and peat porewater were anticipated to be above detectable concentrations. Modeling from the EPA National Atmospheric Deposition Program/Mercury Deposition Network predicted rainfall in the study area to have precipitation with THg concentrations in the range of 4-6 g m^3. (=ng L^{-1}). Fewer MeHg atmospheric data were available, with values of 0.05 ng L^{-1} for snow samples in Wisconsin and an average of 0.15 ng L^{-1} for a rain storm in Washington (Bloom and Watras, 1989). Lee et al. (2003) reported MeHg concentrations in background air (Gothenburg, Sweden) as 2-22 pg m^3. St. Louis et al. (1995) reported MeHg in precipitation collected in the ELA as 0.010-0.179 ng L^{-1} and THg ranged from 0.95-9.31 ng L^{-1}, being higher when rains originated from the west.

Mercury may be present in the atmospheric in several operationally defined forms. Areas near to Hg sources ($\approx$ 50 km) will see deposition of particulate Hg, reactive gaseous Hg and oxidized elemental Hg (Fig. 1.5). Areas more distant to point sources will see

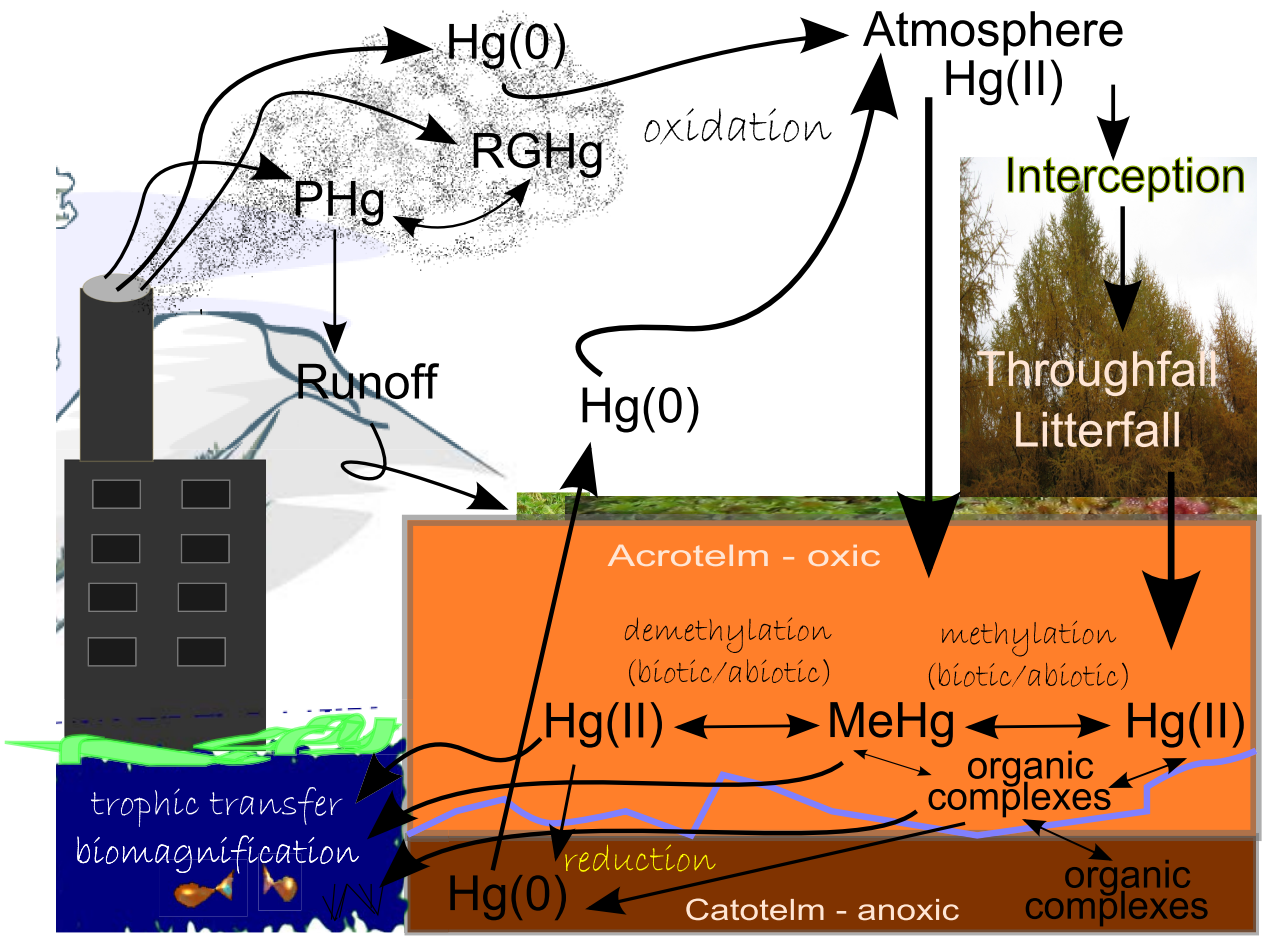


Figure 1.5: Cycling of mercury in northwestern Ontario peatlands, described clockwise from top-left. Mercury may be released to the atmosphere as elemental (Hg(0)), reactive gaseous (RGHg) or particulate (PHg) forms that deposit at varying distances from the point source dependent on its residence time. Oxidation converts atmospheric Hg species to Hg(II) where it will react with various atmospheric chemicals and fall as wet or dry deposition, possibly on a peatland. Removal of Hg species or conversion to MeHg may occur in vegetation if deposition is intercepted. Mercury may also pass through vegetation or be transfered to peatland soils as litterfall or from upland runoff. Once in the acrotelm, Hg species may be methylated or bound to organic complexes. Organic complexes may also be methylated. The redox potential and ensuing reactions will be dependent on the water table (blue wavy line), that likely fluctuates. Acrotelm peat eventually becomes buried and anoxic, thus catotelm Hg species would undergo reduction reactions. Depending on peatland hydrology, water movement may facilitate oxidation/reduction reactions, pH or physico-chemical driven association/dissociation phenomenon and the transport of Hg as ionic, organic or organically bound species to adjacent downfield aquatic ecosystems. Further methylation/demethylation reactions may occur in receiving water and sediment. Trophic transfer and biomagnification may occur in foodwebs. Not shown is a possible return of Hg to the atmosphere if peatlands are combusted for energy production, renewing the cycle.

lower deposition of particulate and reactive gaseous Hg, with remote areas seeing only Hg that originates from an oxidation of Hg(0). Whereas the lifetime of reactive gaseous Hg is short (hours to days), oxidized Hg may remain in the atmosphere for a year (Driscoll et al., 2003).

Treed bogs and fens may also receive Hg inputs from throughfall and litterfall (Fig. 1.5), which is greater in some terrestrial watersheds than precipitation (Grigal, 2002; Driscoll et al., 2003). Whether litterfall becomes a source or sink for Hg, or leads to the production MeHg, is dependent on initial Hg concentrations in tissue and whether tissue remains under dry or saturated conditions (Hall and St. Louis, 2004). Since peatlands are known sinks for atmospheric Hg (Grigal et al., 2000; Grigal, 2003) and bogs only receive inputs from atmospheric sources, peat cores have been used for tracing historic levels of human activity (Liu et al., 2003; Biester et al., 2006; Benoit et al., 1998).

It was concluded that combusting peat for energy would present the same concerns as coal in terms of trace metal emissions to the environment, including Hg (Glooschenko and Capobianco, 1982). Conclusions were based on twelve samples from 0-20 cm and 20-40 cm collected from several peatland ecosystems from the Kinoje Lake area in northern Ontario. Average Hg concentration of Ontario peat were 0.06 μg g^{-1} (dw), whereas Okeefenokee swamp peats (Georgia, USA) had 0.4 μg g^{-1} (dw), Illinois coal had 0.2 μg g^{-1} (dw), Appalachian coal had 0.2 μg g^{-1} (dw) and Western coal had 0.09 μg g^{-1} (dw).

1.6.3 Ground Water Origins

Mercury present in water discharged from any natural or impacted ecosystem would, by definition, influence fens. Controlled Hg loading studies in the ELA suggest that THg exported to a lake in any given year is derived largely from native soil pools of Hg, rather than new Hg deposition (Harris et al., 2007). Soil Hg may be perturbed by land disturbances, such as the formation of wetlands and/or flooding for reservoirs (Rudd, 1995), clear-cutting forests (Munthe and Hultberg, 2004) and fire (Grigal, 2002).

Natural rock formations containing Hg are generally sulphidic in nature. Such formations are commonly associated with Au, or other base metals of value (e.g. Cu, Ni, Zn). Thus, mining activities adjacent to peatlands may source Hg to them. Coal also has detectable levels of Hg, with concentrations dependent on coal type, ranging from 0.08 to 0.22 μg g^{-1} (mean=0.2, US Geological Survey's COALQUAL database) (Toole-O'Neil et al., 1999), making coal mining activities and discharged leachate of concern.

Another ground water source of Hg is landfill leachate, with THg concentrations reported as 0.05-50 μg L^{-1} (Baun and Christensen, 2004).

Ground water influences to Hg cycling in peatlands depend not only on concentrations of THg and MeHg, but also on biogeochemical phenomenon. It has been suggested that the interface between peatland and upland watersheds harbour MeHg hotspots (Mitchell et al., 2008b). Though mesocosm studies suggested the delivery of sulphate from upland areas may be a contributing factor, the type of carbon was not (Mitchell et al., 2008a). Therefore, disturbances to upland areas that alter the chemistry of upland waters, may alter the chemistry of peatlands and the cycling of Hg.

1.6.4 Transformations of Mercury Species

In Canada, 98% of all recent fish consumption advisory warnings are due to Hg (Environment Canada, 2003b; OME, 2009), where the more toxic, bioaccumulative form MeHg comprises over 90% of THg in fish (Bloom, 1992). The vast majority of fish MeHg burden is acquired from their ingestion of MeHg-laden organisms as opposed to directly from aqueous dissolved or particulate phases (Bodaly et al., 1997). Concentrations of Hg have continued to increase in fish, especially from oligotrophic forest lakes that have never been subjected to any direct discharge of Hg (Andersson et al., 1990).

Verta (1984) first noted that concentrations of THg in fish tissue from some brown water lakes was higher than models at that time predicted. Over the last two decades, wetlands, including peatlands, have been implicated as ideal methylation ecosystems, contributing to elevated Hg concentrations in fish tissues of pristine lakes (St. Louis et al., 1994; Rudd, 1995; Branfireun et al., 1998; Ullrich et al., 2001). The methylation of Hg by wetlands has now been reported so frequently that it is "nearly axiomatic" (Grigal, 2003).

Recent studies have focused on detailed Hg methylation factors and microbial and geochemical mechanisms specific to peatlands. These include a) the various roles of organic matter (Drexel et al., 2002; Haitzer et al., 2002; Gustafsson et al., 2003; Ravichandran, 2004), b) the implications of acid rain sulphate loading in ecosystem-scale studies (Jeremiason et al., 2006), c) an identification of MeHg hotspots in peatlands (Mitchell et al., 2008b) and d) the combined contributing roles of carbon and sulphate as methylating mechanisms in peatlands (Mitchell et al., 2008a). In the boreal region, peatlands represent a widespread and crucial link between terrestrial landscapes and aquatic food-webs,

so the elucidation of controls on MeHg production in these ecosystems with biogeochemical transformation potential was deemed critical (Branfireun et al., 2001). Although biotic methylation was presumed to be the dominant mechanism by which Hg becomes MeHg, abiotic methylation by organic matter may be relevant in organic ecosystems such as peatlands.

Bacterial Transformations

Unique microorganisms survive and grow in bogs at low pH under both aerobic and anaerobic conditions (Leduy, 1980). Biotic methylation of Hg may occur by either nonenzymatic or enzymatic means. The former methylation reaction was found to be mediated by methylcobalamin (Neujahr and Bertilsson, 1971), a form of vitamin B_{12}. Ehrlich and Newman (2009) found for the reaction

$$Hg^{2+} \xrightarrow{CH_3B_{12}} (CH_3)Hg^{+} \xrightarrow{CH_3B_{12}} (CH_3)_2Hg \tag{1.4}$$

the initial methylation of Hg^{2+} proceeds 6000 times as fast as the second one, although rates of each are dependent on the counter ion. Studies have shown Hg methylation by both aerobes, anaerobes and fungi and has been reviewed by Robinson and Tuovinen (1984) and Barkay and Wagner-Dobler (2005).

Peatlands contain high numbers of metabolically diverse heterotrophic microorganisms (10^6–10^7 mL^{-1} in interstitial water), and sulphate-reducing bacteria (SRB) from various Minnesota peatlands (most probable number) ranged from 10^3 to 10^5 microbes mL^{-1} (Williams, 1980). Enzymatic methylation of Hg in most aquatic environments appears to mainly resulting from metabolic activities of SRB such as *Desulfovibrio desulfuricans* (Compeau and Bartha, 1985; Benoit et al., 2001; Gilmour and Henry, 1991; King et al., 2000). Research suggests Hg^{2+} acts as a competing methyl acceptor in acetate synthesis from CO_2 by the acetyl-CoA pathway, with the methyl group originating from the methylcobalamin-protein complex and proceeding 600 times as fast as uncatalyzed transfer from methylcobalamin, at pH 7 (Ehrlich and Newman, 2009).

Recently, studies have confirmed the ability of Fe(III)-reducing bacteria (FeRB) to methylate Hg (Fleming et al., 2006; Kerin et al., 2006), and in some cases to a greater extent than SRB (Fleming et al., 2006). Slowey and Brown (2007) suggested that since SRB and FeRB methylate Hg, the reduced species of S and Fe (sulphide S(-II); ferrous iron Fe(II)) should be useful indicators of Hg methylation by microorganisms. Sulphur

and Fe cycling at redox boundaries in water columns and sediments, and any resulting species that interact strongly with Hg, will affect its reactivity, including its propensity to be methylated and participate in other processes dependent on its bioavailability (Water Science and Technology Board, 2003). That statement was confirmed under laboratory conditions by Slowey and Brown (2007), where investigations on how combined and constrained processes involving S and Fe were demonstrated to either reduce or enhance the reactivity of Hg.

Demethylation of MeHg may also be mediated by microbial activities, with cleavage of the Hg-C bond catalyzed by mercuric lyases. Further reduction of Hg(II) to volatile Hg(0) is catalyzed by the enzyme mercuric reductase. The later reductive demethylation would reduce the availability of MeHg for bioaccumulation, whereas the former oxidative demethylation would leave Hg(II) available to be re-methylated (Barkay and Wagner-Dobler, 2005). Again, the important role of redox chemistry in the Hg cycle is suggested.

As intricately explored by Jackson (1989), the nature, abundance and surface chemistry of humic matter colloids coupled with clay minerals and Fe and Mn oxides, has been shown to alter the biotic methylation and demethylation rates of Hg in aquatic sediments. He described the reactions as "variable, inconsistent and not altogether predictable". Such complex reactions are surely occurring in peatlands as well.

Abiotic Transformations

Organic matter may also play a role in Hg methylation and Hg reduction processes in peatlands. The thermodynamically possible reduction of Hg(II) to Hg(0) with subsequent volatilization represents a pathway by which Hg is removed from a food web. A first order rate constant with natural humic acid was first calculated by Alberts et al. (1974), being 0.009 hr^{-1}. Though pH was found to influence the total amount of Hg reduced, it was not a factor in the rate determining reaction. Later studies by Allard and Arsenie (1991) showed abiotic reduction of Hg by soluble humic substances as significant, and highest in oxygen free environments at pH 4.5 without chloride present and in the presence of light. Darkness, air and chloride decreased production of Hg(0). They hypothesized an intra-molecular process since a reduction in the number of complexing sites on fulvic acid also inhibited Hg(0) production. Fulvic acid, derived from soil, was shown to have a reduction potential of 500 mV, causing the reduction of Hg(II) and Fe(III) under conditions characteristic of natural waters, with reduction potential increasing as pH

decreased (Skogerboe and Wilson, 1981). Humic acid has a reduction potential of 700 mV (Thurman, 1985), thus is less of a reducing agent than fulvic acid.

Small amounts of MeHg may be produced by abiotic transmethylation from humic acids and nonenzymatic methylation of Hg^{2+} by methylcobalamin (Neujahr and Bertilsson, 1971). Nagase et al. (1982) found humic and fulvic acids from leaf mould and river sediments could methylate Hg in the dark and in the absence of bacteria. Weber et al. (1985) found methylation by soil derived fulvic acid was dependent on the speciation of Hg(II) in solution, with relative rates and yields ordered as $Hg(NO_3)_2$ (pH 4)>>$Hg(NO_3)_2$ (pH 6)>>$HgCl_2$ (pH 4 or 6). However, in salt marsh sediments, abiotic methylation was deemed of little importance with the production of 21 μg L^{-1} of MeHg, while biochemical methylation under similar conditions formed up to 288 μg L^{-1} (Berman and Bartha, 1986).

The catalytic effect of various metal ions on the methylation of Hg^{2+} in the presence of humic substances was reported by Lee et al. (1985) to be dependent on the Hg^{2+} concentration, fulvic acid concentration and the metal ions added. The optimum pH for methylation was observed to be pH 4 to 4.5 where the order of catalytic metals was $Fe^{2+}(Fe^{3+}) > Cu^{2+} \approx Mn^{2+} > Al^{3+}$. Catalysis by Fe had an optimum pH of 4.5. Their research suggested that methylation of Hg increases when fulvic acid is strongly coordinated to other metal ions, or in some way, when the complexation between fulvic acid and Hg becomes weaker. Recent work by Lee et al. (2009) found that binding of Hg(II) to muscovite minerals was influenced by its prior complexation to fulvic acid, with binding of Hg(II) to a pre-exisiting fulvic acid film after 5 h of reaction being weaker than binding of Hg(II) to dissolved fulvic acid prior to uptake on the muscovite surface.

Photodegredation of MeHg lake surface water has been reported and may be an important process in other aquatic systems and more dominant than microbial demethylation (Seller et al., 1996). Flux chambers and gas spectrophotometers are now deployed to terrestrial and aquatic ecosystems to quantitate Hg flux to the atmosphere (Siciliano et al., 2002; O'Driscoll et al., 2007, 2008). Organic matter may also play a role. A dissertation by Siciliano et al. (2005) found solar irradiation and DOM characteristics controlled the abiotic formation of MeHg, with smaller DOM fractions generating MeHg. Furthermore, water from lakes with logged watersheds were found to generate more MeHg when exposed to sunlight, whereas water from lakes with low levels of logging or undisturbed watersheds did not. It was concluded that although sunlight may promote evasion of Hg through reduction, thereby decreasing bioaccumulation potential, sunlight may also

promote methylation of Hg thus increasing bioaccumulation potential. Such mechanisms are certain to be ecosystem and perhaps site specific.

Miscellaneous Processes

Dimethylmercury is far more toxic than MeHg, and responsible for causing the death of a 48-year old chemistry professor nine months after several drops were spilled onto her gloved hand (Siegler et al., 1999). Dimethylmercury ($(CH_3)_2Hg$) was detected in Canadian high arctic seawaters where flux and subsequent deposition and oxidation were sufficient to likely result in elevated concentrations of MeHg observed in nearby snowpacks (Water Science and Technology Board, 2003). Conaway et al. (2009) recently detected increased dimethylmercury concentrations in water profiles that coincided with spring upwellings in Monterey Bay, California.

The detection of ethylmercury in sediments of four wetlands, but not in porewaters or the water column, indicated that ethylation of Hg may be a significant part of Hg cycling in eutrophic/mesotrophic reed and rush marshes (Mason et al., 2006). Alterations to marsh conditions that decrease E_h and oxygen levels, will see increased MeHg concentrations in sediment and porewater, with greater diffusion of MeHg to the water column (Mason et al., 2006).

1.7 Site Description

The study peatland for this research was located in the northwestern region of Ontario, Canada (Fig. 1.6), in an area described by Peat Resources Ltd. as the Upsala corridor, for which a land use permit was issued (Fig. 1.7). The Upsala corridor covers an extensive area of 186,500 ha, stretching 88 km along the TransCanada highway (DST, 2005). Based on classification by the National Wetlands Working Group, the corridor resides in a boundary region of boreal lower, humid mid-boreal and continental mid-boreal zones (NWWG, 1988). Total precipitation (sum of total rainfall and water equivalent of total snowfall) at the Upsala weather station (as reported by Environment Canada, some missing data) totaled 880.5 mm in 2007, 899.9 mm in 2008 and 769.4 mm in 2009.

Figure 1.6: Location of peatland study site (GG3) in Ontario Canada, with approximate coordinates. Google Map generated 17 August 2011.

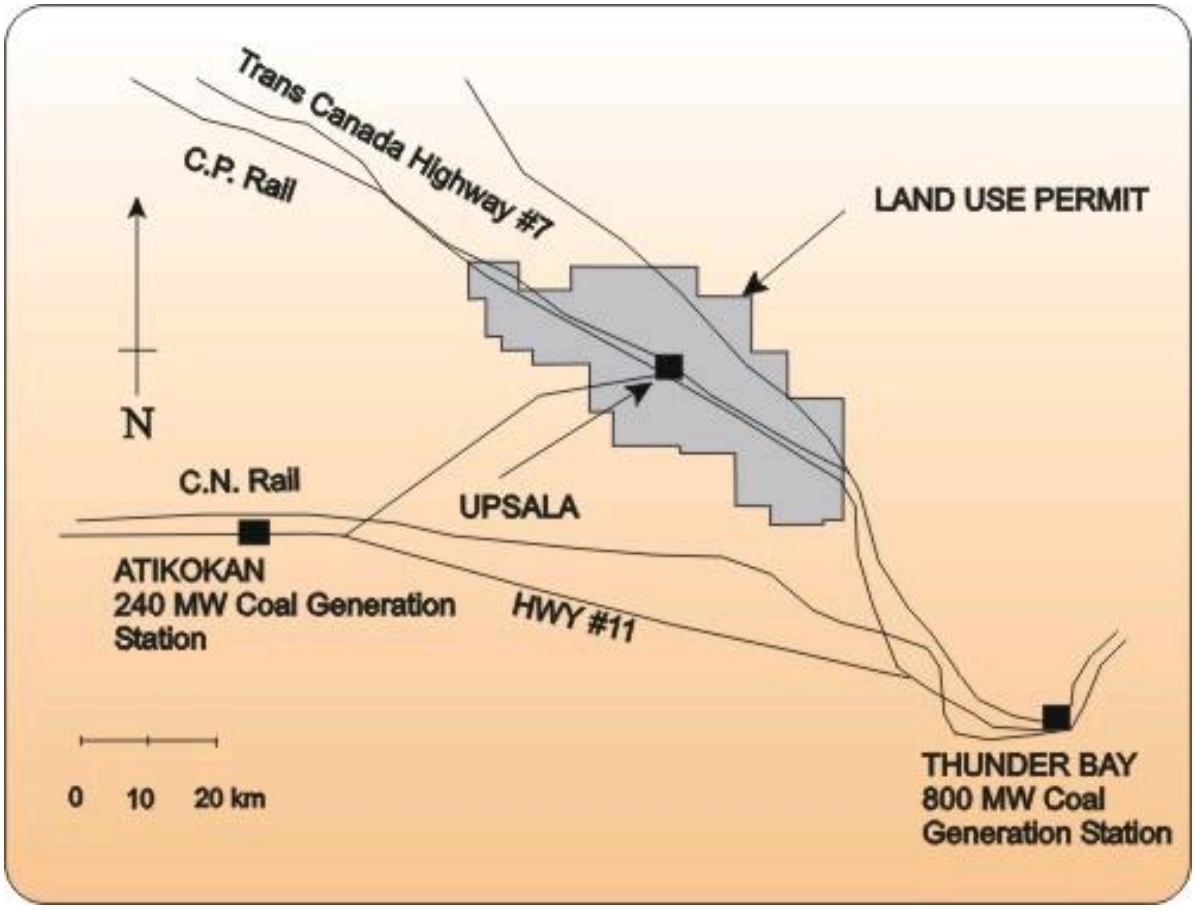


Figure 1.7: Land use permit area for Peat Resources Limited, an area termed the Upsala Corridor (Peat Resources Ltd, 2005). Note its proximity to coal generating stations in Atikokan and Thunder Bay with highway and rail access.

Formal federal and provincial wetland classifications at the study site have not been done, but consultant work stated peatlands within the Upsala corridor were low moor deposits, either as open or treed bogs (Watts, Griffis and McOuat Ltd., 2004). The corridor wetland areas have also been described as a series of water track poor fens and bogs (McLaughlin, pers. corr.). Fig. 1.2 in Section 1.3 showed satellite imagery of peatland patterning at the study site, quite typical for water track fens.

The entire Upsala corridor was extensively surveyed for energy reserves by DST Consulting Engineers in 2005, with each peatland being delineated, named and numbered based on its township location. The GG3 (Goodfellow/Gibbard) peatland, used for this research, was approximately 100 km northwest of Thunder Bay and 50 km southeast of Upsala, lying just north of Hwy 17. The specific study location within the GG3 peatland for this dissertation was within the surveyed area and nearest the natural outflow area (OME, 2006). An extensive light detection and ranging (LIDAR) survey showed the upfield area near Muskeg Lake to be at an elevation of 477 m, while the culvert at the outflow site was 471 m. Elevation within 1000 m of the outflow was 473 m, with a clear decreasing slope along the transect towards the study site outflow area (see Line 5 in Fig. 1.9). A simple topographic map of the area is shown in Fig. 1.8.

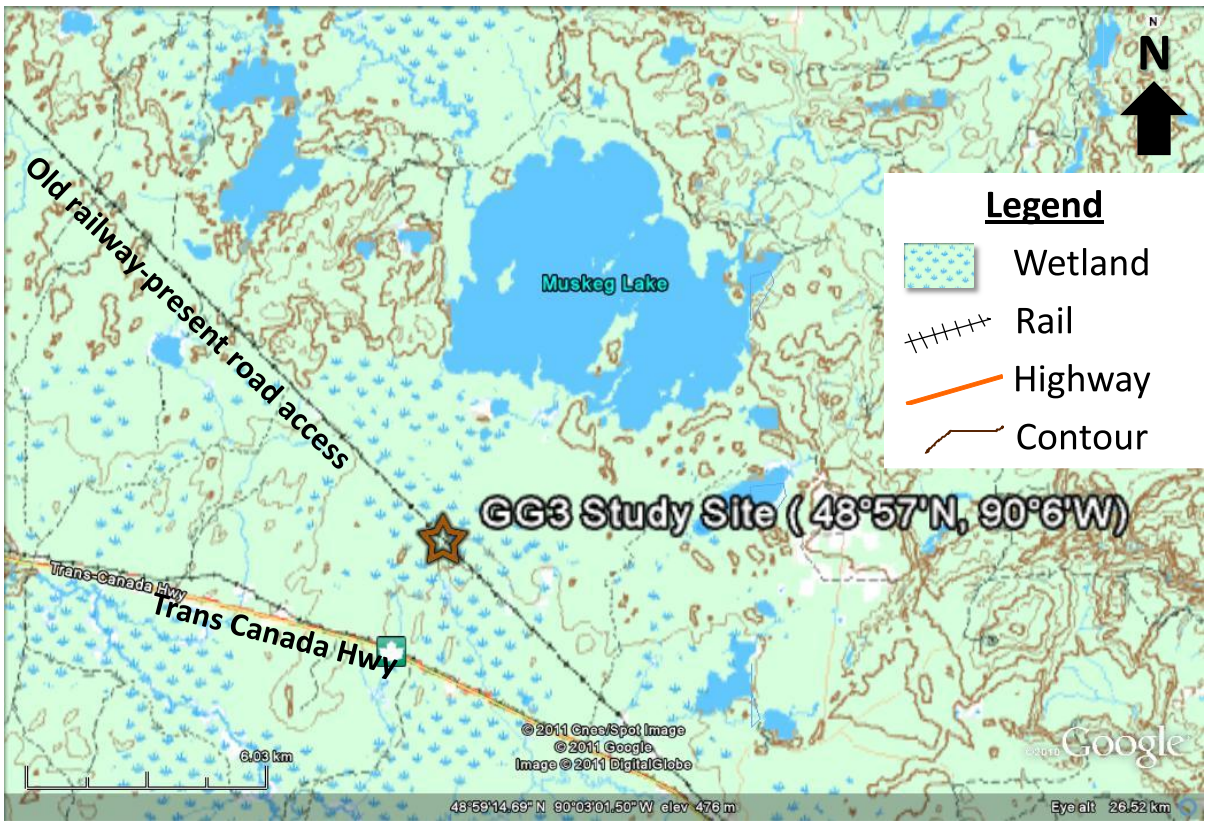


Figure 1.8: Physical features of GG3 study area from the Canadian topographic maps overlay for Google Earth (scale 1:50000). Contour intervals are at 15.24 m intervals.

The GG3 peatland had an area of 1080 ha, average peat thickness of 2.36 m and estimated mass of 5.336 million tonnes at 50% moisture (DST, 2005). Peat was mainly *Sphagnum* derived, with peat pH for H_4 to H_7 ranging from 3.7 to 5.7, and ash contents ranging from 5 to 15%. Data from DST summarized by (Mol, 2009), showed an increase in pH with decreasing depth, from a mean of 5.3 in the upper acrotelm layers to 5.8 in lower, humified layers. Core drilling by DST revealed clay substrate underlying peat deposits. Their report also stated, that based on historical testing of samples from the property, the peat in the Upsala corridor contained much less S and Hg than coal, although data and references were not provided.

Peat core samples from the DST energy survey made available by Peat Resources were further analyzed by Mol (2009). Locations of the GG3 bog boreholes are presented in Fig. 1.9. Briefly, cores as sectioned and identified by DST were dried at 38°C, sieved through 2 mm, homogenized and analyzed by Lakehead University Environmental Laboratory (LUEL) according to standard operating procedures. Some caution is warranted as cores were stored since 2005 under poor conditions, and degradation of organic matter may have occurred. Therefore, MeHg was not analyzed. It is unlikely clean handling procedures for Hg were undertaken, as this was not an objective of the original sampling plan. LUEL total extractable metals are presented in Table 1.4, where maximum values were associated with underlying clay substrate. It appeared cores were composite and relabeled, since provided cores provided did not necessarily match labels in the DST report. Nonetheless, cores nearest the study location showed typical chemical profiles and trends (e.g. Fig. 1.10), as described previously in Section 1.4.2.

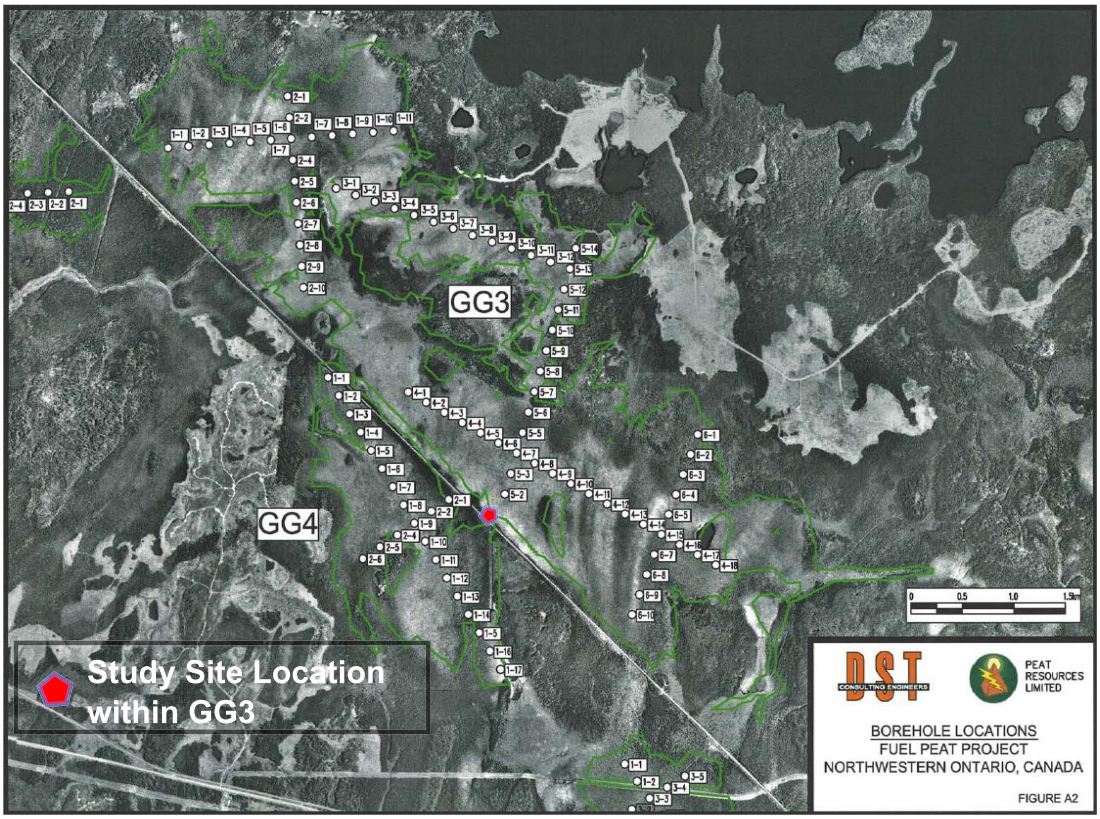


Figure 1.9: Line and borehole (core) locations from the DST peat energy survey conducted for Peat Resources Ltd by (DST, 2005).

Table 1.4: Total extractable metals (minimum, maximum, mean and standard deviation (SD)) for peat cores as sampled by DST (2005), provided by Peat Resources Ltd. and analyzed by Lakehead University Environmental Laboratory (LUEL).

Analyte (μg g^{-1} dw)	Min.	Max.	Mean	SD
Hg	0.03	2.84	0.34	0.40
Co	0.25	24.86	5.98	4.44
Cr	0.88	50.27	8.08	6.50
Pb	0.22	76	10.1	14.4
Ni	1.25	71.3	12.4	9.77
Cu	3.31	292	17.8	25.0
V	1.25	134	19.9	25.5
Zn	0.63	340	37.6	51.4
Sr	10.2	124	38.6	18.1
Ba	48.5	571	128	79.4
Ti	9.90	2584	163	328
Na	1.25	3156	201	373
Mn	10.6	3961	517	646
K	82.1	10475	547	1038
P	178	3182	864	528
Mg	412	21378	3309	2497
S	12.0	9940	3455	1871
Al	345	22777	4392	3228
Fe	2028	142074	21922	20246
Ca	2368	99072	25201	17137

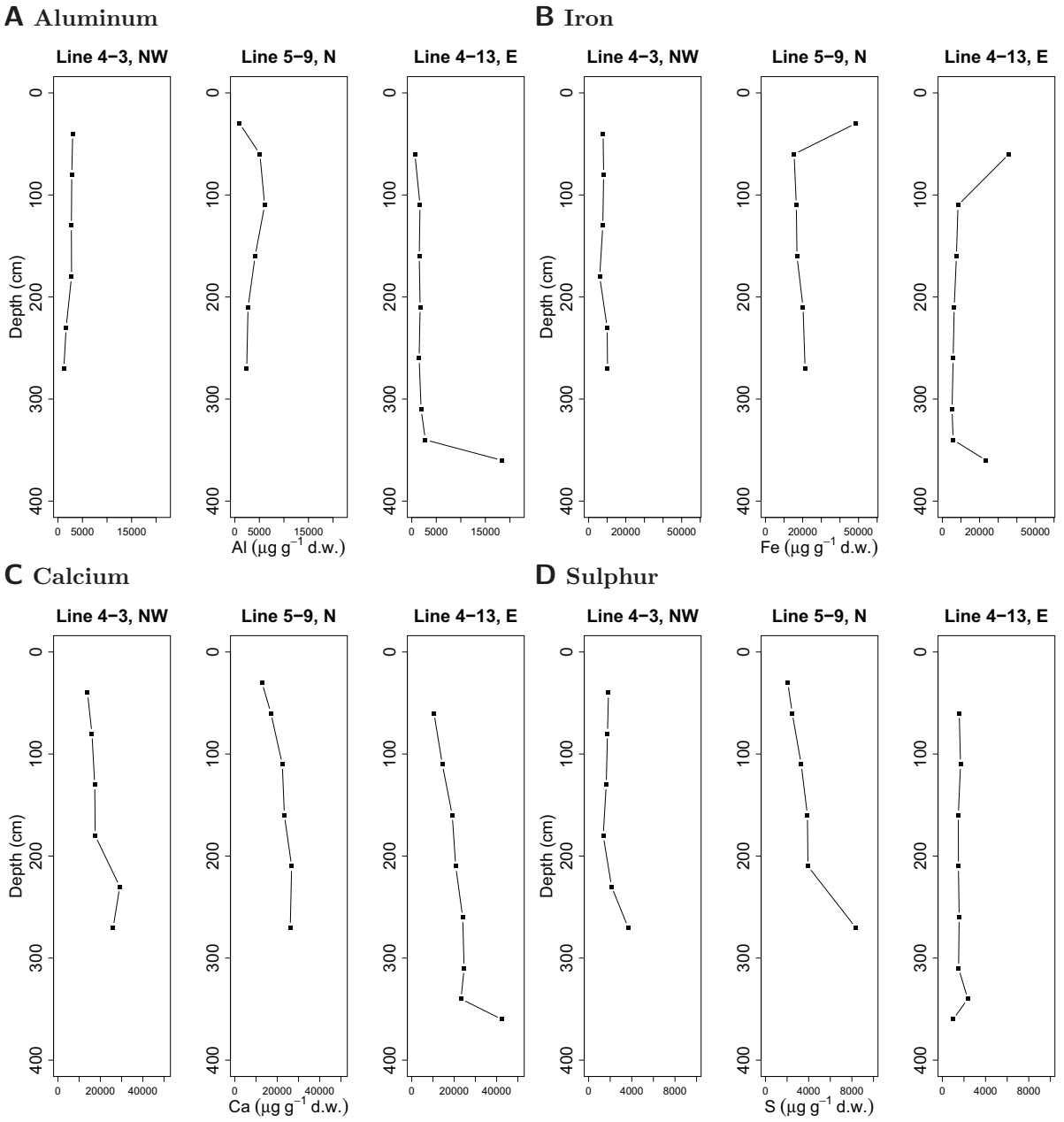


Figure 1.10: Typical chemistry profiles of peat cores (dw) from the GG3 peatland, as sampled by DST and processed and analyzed by LUEL. Direction of borehole was in relation to the study site outflow area (culvert). Aluminum (**A**), iron (**B**), calcium (**C**) and (**D**) profiles. Line 4-13 shows an indication mineral (clay) substrate at the base of the core sample. When corrected for bulk density, profiles were similar with concentrations expressed as μg cm^{-3} approximately 10-fold lower.

During this research, the GG3 peatland was observed as sparsely treed with dwarfed tamarack (*Larix laricina*) and bog birch (*Betula pumila*). Hummock-hollow topography was dominated by *Sphagnum* and *Carex* species, respectively. Ericaceous plants such as cotton grasses (*Eriophorum spp.*), cranberries (*Vaccinium spp.*), bog laurels (*Kalmia spp.*) and horsetails (*Equisetum spp.*) were present. Carnivorous plants including pitcher plants (*Sarracenia purpurea*) and sundews (*Drosera spp.*) were also present. Moose had traversed the study site on occasion, and an abundance of wasps and biting flies were frequently encountered. Based on vegetation, hydrology and water chemistry, the study site was considered a typical oligotrophic, soligenous poor fen (P.F. Lee, Waddington, Turetsky, pers. corr.).

The peatlands of northwestern Ontario, including the GG3 site, were likely formed in depressions left after the last ice age, once occupied by the great glacial Lake Agassiz (Watts, Griffis and McOuat Ltd., 2004). A map is shown in Fig. 1.11.

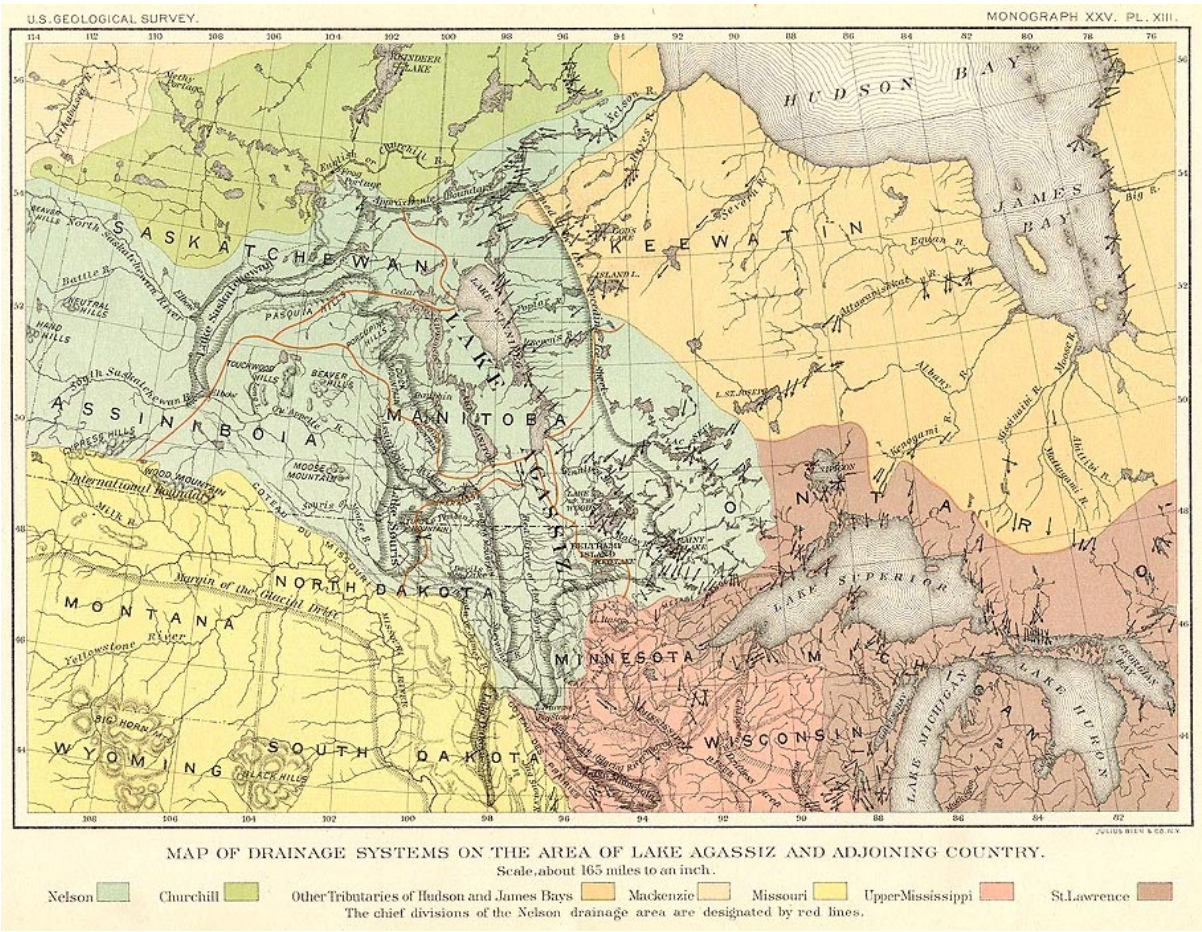


Figure 1.11: Lake Agassiz (13,000 years BP), an immense glacial lake once fed by glacial runoff from the last glacial period that influenced climate, hydrology and likely peat formation within the Upsala corridor and GG3 study site. Map from (Upham, 1895).

1.8 Research Questions and Associated Hypotheses

Little research for wet peat mining and restoration exist whereas a multitude of studies have been published for dry peat harvesting. As reviewed, the complex and dynamic nature of peatlands coupled with a different peat extraction and restoration method makes an extrapolation of environmental impacts from dry harvested sites to wet mined sites difficult and somewhat speculative.

This research is meant to provide sound scientific evidence to advance the understanding of environmental impacts associated with wet peat mining. An understanding of wet mining impacts will allow environmentalists, regulatory bodies and industry to better manage our peatland resources. This understanding is required before the peatlands of northwestern Ontario are wet mined for energy.

The main research question was: How would wet mining a peatland impact its adjacent ecosystem with respect to water quality and the bioaccumulation potential of Hg species? The specific key questions addressed in three research chapters were:

1. What impact would wet peat mining and acrotelm transplant restoration have on the water quality of peat porewater and downfield surface waters?

2. As a result of wet peat mining, would "peat-type" sediments have THg and MeHg that was bioavailable to benthic organisms?

3. How would the quality of peat mining process water (PMPW) produced from Upsala corridor peat compare with previous studies and does PMPW meet Canadian Water Quality Guidelines (CWQG)? Are peatlands suitable as primary treatment systems for that wastewater?

Each question is further discussed and hypotheses put forth.

1.8.1 Chapter 2: "Porewater and outflow water quality after peat mining and rehabilitation"

Differences in water chemistry between peatlands that were being actively ditched compared to peatlands that had been dessicated for some time were noted by Shotyk (1986b) and more recently by Aström et al. (2001). Gleeson et al. (2006), in their preliminary literature review for peat as a fuel source in Ontario found "knowledge of and experience

with wet mining extraction is minimal...uncertainty exists about the environmental impacts and potential restoration approaches for wet mining". Some of the Gleeson et al. (2006) hypotheses with regards to changes in aquatic water chemistry are herein challenged. Specifically, the assumptions that peat mining in Ontario would lead to increases in suspended solids, organics, TN, TP, trace metals (including Hg) and acidity in adjacent water bodies are tested. Similar impacts were predicted to occur from peat mining operations in the United States (Winkler and DeWitt, 1985). It was hypothesized that peat particulates and their associated analytes (nutrients, metals and organics) would be released to downstream ecosystems by wet peat mining in the Upsala corridor. However, since wet peat mining more closely resembles the ditching phases of dry harvesting, increases in acidity would not be evident.

A Before-After-Control-Impact (BACI) experimental design was used to detect whether significant changes in general peatland porewater and surface water chemistry (pH, alkalinity, conductivity, anions, redox potential, TSS, colour, DOC, nutrients (TN, TP), cations and metals (including Hg and MeHg) occurred when an experimental plot was mined and restored by acrotelm replacement as compared to a control plot in the same fen. The precautionary principal to environmental management was applied, using a statistical significance value of $p \leq 0.10$ for the analysis of variance (ANOVA) and Tukey pairwise comparison tests.

1.8.2 Chapter 3: "Bioaccumulation potential of mercury species from peatlands of interest for peat mining"

The potential for Hg release and bioaccumulation is difficult to predict given the myriad of processes occurring in natural peatland systems (Fig. 1.5). Two separate studies concluded that the bioaccumulation of Hg released from dry harvested peatlands was not an issue in downstream environments (Surette et al., 2002; DiGiulio and Ryan, 1987). Binding constants between Hg and organic matter at environmentally relevant concentrations are extremely high (Ravichandran, 2004) and inverse relationships between Hg uptake by benthic invertebrates and sediment organic matter have been noted (Breteler et al., 1981; Langston, 1982; Nuutinen and Kukkonen, 1998; Mason and Lawrence, 1999; Lawrence and Mason, 2001). Peat, by its definition, is highly organic with organic matter content from the experimentally mined peatland in the Upsala corridor exceeding 90% (DST, 2005). This value was much higher than the above studies. Therefore, it

was hypothesized that THg and MeHg in sediments from this experimentally wet mined peatland would not bioaccumulate in benthic organisms feeding on that sediment.

The bioaccumulation potential was determined using a Biota-Sediment Bioaccumulation Factor (BSAF) as a measure, defined as the concentration of a contaminant in tissue divided by the concentration of a contaminant in sediment. Site-specific BSAFs for THg and MeHg from the experimentally wet mined peatland were determined in three laboratory bioaccumulation trials and a kinetic trial. The test organism was *Lumbriculus variegatus* (Ingersoll et al., 1995; EPA, 2000c). Results were compared to indigenous benthic invertebrates and literature data. A lack of BSAF values for MeHg from highly organic sediments is lacking in the literature, hindering our ability to predict the movement of Hg species in peatland ecosystems. This study addresses that knowledge gap and directly comments on the bioaccumulation potential of THg and MeHg from a wet mined peatland in the Upsala corridor.

Bioaccumulation methods suggested by EPA (2000c) were necessarily refined between trials. The major refinement (sugar solution flotation) is presented in Chapter 5. The findings would validate the necessary refinement for the laboratory BSAF values determined.

1.8.3 Chapter 4: "Treatment of peat mining process waters with acrotelm hummock peat: an initial assessment"

One environmental concern of wet peat mining was the fate of PMPW generated from squeezing and pelletizing of wet peat (ORF, 1984). The proposed treatment of PMPW put forth by Peat Resources Ltd. was to distribute PMPW onto adjacent peatlands. This treatment appeared plausible since numerous studies have highlighted the ability of peat to remove contaminants from wastewaters (Viraraghavan, 1991; Couillard, 1991, 1994; Bhatnagar and Minocha, 2006). However, since PMPW contains elevated concentrations of solids and organics known to bind analytes of concern (ORF, 1984), the success of peatland filtration to remove contaminants was hypothesized to depend on the efficiency of acrotelm peat to remove high concentrations of particulate matter from PMPW.

Once the chemistry of PMPW produced from the experimentally wet mined site within the Upsala corridor was determined, an initial assessment the proposed treatment process was conducted using hummock peat mesocosms. Diluted and 100% PMPW would be applied to mesocosms. The efficiency of mesocosms to remove analytes of concern

and the suitability of mesocosm leachate for release to waterbodies would be assessed. These studies will provide guidance for industry, environmental regulators and future researchers concerning the feasibility of using peatlands as primary filtration systems for PMPW.

Chapter 2

Change in Porewater and Surface Water Quality After Wet Peat Mining and Restoration

2.1 Introduction

Canada possesses vast peatland complexes estimated to contain 507 billion tonnes of peat covering 11.1% of its land area in mostly northern regions (Tibbetts, 1986; Tarnocai et al., 2000). Although Canada uses 15% of its peatland area for agricultural production (IPS, 2008), less than 1% by area is extracted for horticultural products and none for biofuels (Daigle and Gautreau-Daigle, 2001). Globally, about 50% of extracted peat is used for energy (Asplund, 1996).

In northwestern Ontario, remote First Nation reserves are currently reliant on fuel oils that must be transported by plane or ice roads. Peat fuels offer local energy solutions for small generating plants (Obernberger, 1998) and large generating stations (OME, 2006). In northwestern Ontario, large quantities of high quality energy peat were identified that could be wet mined for energy (DST, 2005). Furthermore, a significant removal of wet peat seems necessary before the "Ring of Fire" chromite mine operation in northwestern Ontario can proceed.

Wet peat mining advantages include a longer production season (9-10 months) and extraction in areas where drainage is impossible due to climatic (too wet) and/or physical (woody debris) impediments. Though similar practices occurred in the former USSR for

some 40 years (Monenco, 1981a; Tibbetts, 1986), more efficient technology has since been developed. Such technology involves pumping the peat as a slurry with transport through pipes to a mobile processing plant that presses the biomass into pellets with low moisture content (pers. corr. Peat Resources Ltd). Mobile technology potentially decreases transportation costs and CO_2 emissions associated with moving and burning other energy fuels.

The major processes of recharge, evaporation, storage and discharge of water determine vegetation types and decomposition factors of peatlands. Over the long term, hydrology dictates peat chemistry and peat interstitial water (porewater) chemistry. Eventually, the water chemistry of surrounding ecosystems may be affected (Boelter and Verry, 1977; Gorham et al., 1985; Daigle and Gautreau-Daigle, 2001). Peat removal may alter flows and concentrations of metals, nutrients and organic constituents in peatland outflow waters (Brooks and Predmore, 1978; Winkler and DeWitt, 1985; Monenco, 1986; Gleeson et al., 2006). Environmental impacts associated with dry harvesting are well studied, but much uncertainty exists about the environmental impacts and potential restoration approaches for wet mining (Gleeson et al., 2006).

Gleeson et al. (2006) suggested that peat mining in Ontario would result in an increase in suspended solids, organics, nitrogen, phosphorous, trace metals and acidity to adjacent ecosystems, which was consistent with conclusions by Winkler and DeWitt (1985) for peat mining in the United States. The potential of eutrophication due to peat mining was also stated by (Shotyk, 1986b; Surette et al., 2002). However, Shotyk (1986b) and Aström et al. (2001) noted the release of basal porewaters from peatland ditching leads to increases in pH and cations and decreases in organics. Since wet peat mining is resemblant of peatland ditching, it was hypothesized that increases in acidity would not be evident, though analytes associated with particulate matter would be released.

The major objective of this targeted study was to determine the impact wet peat mining would have on water quality in peat porewater and adjoining surface waters. A Before-After-Control-Impact (BACI) experimental design was used to detect significant changes in porewater and surface water chemistry (pH, alkalinity, conductivity, anions, redox potential, total suspended solids (TSS), colour, dissolved organic carbon (DOC), nutrients, cations and metals (including Hg and methylmercury (MeHg)) when a fen was experimentally mined and restored by acrotelm replacement.

2.2 Methods

2.2.1 Study Site

The study site was a 1080 ha soligenous open poor fen located near Raith, Ontario, Canada (40°57′33″N, 90°6′20″S). The climate is continental, with mean July and January temperatures of 19°C and -17°C, respectively.

The fen's average peat thickness was 2.36 m with an estimated mass of 5.3 million tonnes of peat at 50% moisture (excludes blonde layer) (DST, 2005). Typical hollow-hummock microtopgraphy was present (Fig. 1.1). Hummocks 1 to 2 m in diameter were raised some 30 to 50 cm above the water table and consisted of mainly *Sphagnum* mosses interspersed with ericaceous plants. Hollows were estimated as a metre in diameter and consisted of mainly sedge species. Core samples from this fen were described by Mol (2009). Humification (von Post and Granlund, 1926) ranged from H2 (poorly decomposed) in upper peat to H8 (highly decomposed) in the lowest peat. Peat at 1.5 to 3.0 m depths and nearest the site tended to H7. Less humified peat at 0.2-0.6 m deep had lower extractable Ca and higher extractable P, K, Mg, Cu, Fe, Mn and Zn compared to peat with H7. Mean bulk density and mean pH (1:1 soil:water) increased when humification increased from H2 to H7 (0.073 to 0.145 g cm^{-3}, 5.14 to 5.61, respectively).

A reference plot (RP) and experimental plot (EP) (12.5×25.0 m) were located nearest a natural drainage area (OME, 2006). Each plot had similar morphological characteristics (slope continuity, homogeneity of plant species and surface microtopography). Peat depth at the site was estimated as 3 to 4 m (DST, 2005). The RP was located approximately 110 m upslope (NW) of EP, and not impacted during peat mining (Fig. 2.1). Boardwalks minimized site disturbance.

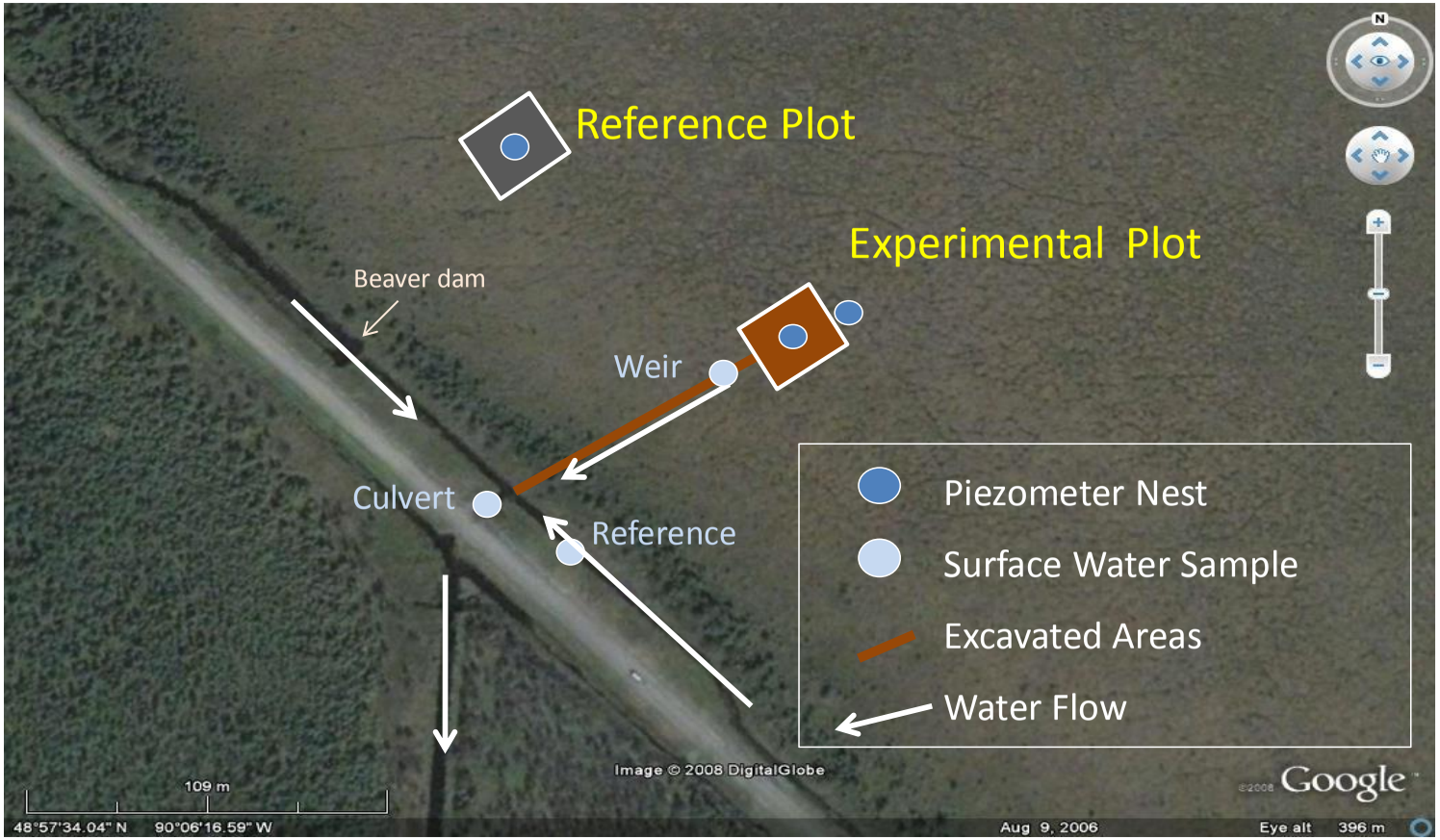


Figure 2.1: Generalized layout of experimental plot (EP) and reference plot (RP) at the research peatland, including excavated areas and locations of porewater (piezometer nest) and surface water sampling sites. Figure may not be to exact scale.

At the centre of each plot within a hollow, a nested set of piezometers was installed (Fig. 2.2). An additional nest, back of experimental plot (BEP), was installed about 2 m from the back edge of EP after mining to monitor inflow water quality to EP. Each piezometer was a PVC pipe ($\approx$ 5 cm diameter) with a 10 cm perforated slot length wrapped in 500 μm Nitex mesh. Each nest had piezometers with inlets situated at 25 cm, 50 cm, 100 cm, 150 cm and 300 cm below the peat surface (Fig. 2.2). Hydraulic head was determined each sampling visit and indicated horizontal flow without upwelling from mineral substrate. Monitoring wells (PVC pipe with 1 m inlets covered with 500 μm Nitex mesh just below the peat surface) were installed throughout the site to determine depth to water table (DWT).

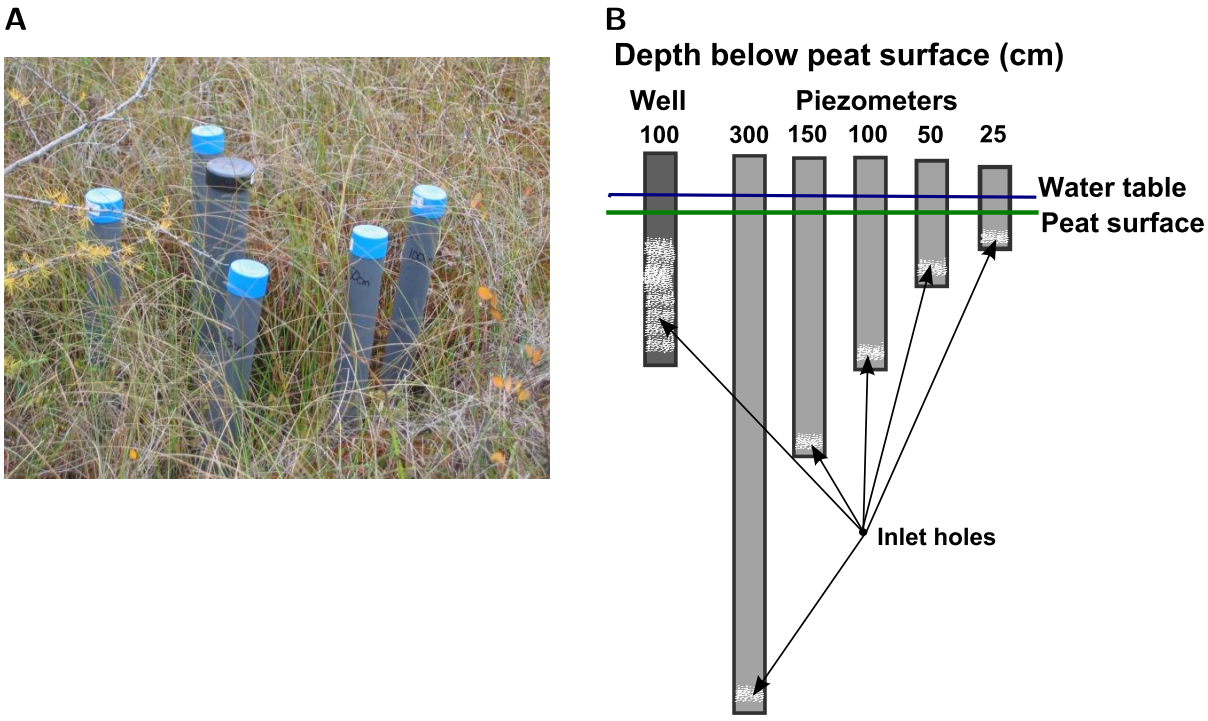


Figure 2.2: Nested set of piezometers (blue caps) encircle a hydrology well (black cap) (A). Schematic representation of piezometers and well (B). Nests were located in hollows capturing porewater at 25 cm, 50 cm, 100 cm, 150 cm, and 300 cm depths.

Surface water sampling sites were located at *a*) a **culvert**, which received outflow for the entire peatland area via drainage ditches (circa 1940) that ran parallel to road access (old railway bed), with water sampled before entering the culvert; *b*) a **reference site**, upstream of the culvert and extraction area, nearest a bridge crossing to facilitate sampling and away from a beaver dam; and *c*) a **weir**, installed at the discharge site of EP after mining (Fig. 2.1). Water depth was measured on each sampling date. Low water in 2008 required a second depth measurement location be established, as denoted by A and B in Fig. 2.14. Flow (volume/time) over the weir was also measured.

2.2.2 Wet Peat Extraction and Restoration

Peat mining coincided with spring thaw (2008), with ice observed in acrotelm layers and snow in hollows (Fig.2.3A). A backhoe supported by wood mats was used to prepare the site. A single drainage ditch, 1 to 2 m in depth, was sloped from EP ($\approx$ 110 m long) towards the pre-existing drainage ditch at the culvert (Fig. 2.1).

Peat extraction was initiated in EP by removing the acrotelm layer ($\approx$ 0.5 m, Fig. 2.3B), which was placed aside for later use. One meter of catotelm was mined over two weeks, leaving an open pit (Fig. 2.3C). The final excavated plot measured 12.5$\times$12.5 m. Water level in EP visually decreased after extraction, then stabilized. The 300 cm piezometer remained fixed during extraction and the 150 cm and 100 cm piezometers were replaced to their original depths after restoration. Therefore, the 100 cm piezometer was just at the new peat surface, the 150 cm piezometer was 50 cm below the new peat surface and the 300 cm piezometer was 200 cm below the new peat surface. The 25 and 50 cm piezometers could not be replaced.

Restoration was based on methods used for dry harvested drainage ditches (Cagampan and Waddington, 2008b,a). Restoration was accomplished in one day about two weeks after mining ceased and EP water level stabilized. Pieces of reserved acrotelm were cut by handsaw to manageable sizes before manual placement in EP. Pieces were placed tightly together, with space along the sides and middle of EP open to facilitate water flow to the weir. The restored EP resembled a floating mat peatland (Fig. 2.3D). *Sphagnum*, sedges and other ericaceous plants survived, though *Larix sp.* died later the first season.

Some transplanted acrotelm pieces were lost to the drainage ditch during 2008, likely during high rainfall events. During the summer of 2008, algae grew in the drainage ditch and in EP (Fig. 2.3E). An oily blue sheen appeared on surface water in EP (Fig. 2.3F),

though this was noted in hollows in 2007 of both EP and RP and assumed the result of the oxidation of ferrous carbonate to ferric hydroxide (Shotyk, 1986b). An orange floc also appeared in EP (Fig. 2.3G). When the site was visited in the summers of 2010 and 2011, transplanted acrotelm was intact with viable *Sphagnum sp.*, sedges and ericaceous (including carnivorous) plants present.

Acrotelm peat surrounding EP and the drainage ditch became dessicated. The DWT in hollows about 2 m from the drainage ditch decreased about a metre by the end of 2008, and remained at that level in 2009. Peat in these hollows subsided 30 to 50 cm (Fig. 2.3H). Hollows within RP maintained a water table above or just below the peat surface, remaining moist. Hummocks along the drainage ditch became dry and cracked, with visual bleaching of *Sphagnum*. Less dessication occurred at BEP due to constant lateral water flow from upfield. In 2010-2011, dessicated and drier areas showed evidence of a changing plant community, with goldenrod observed along the drainage ditch and around EP.

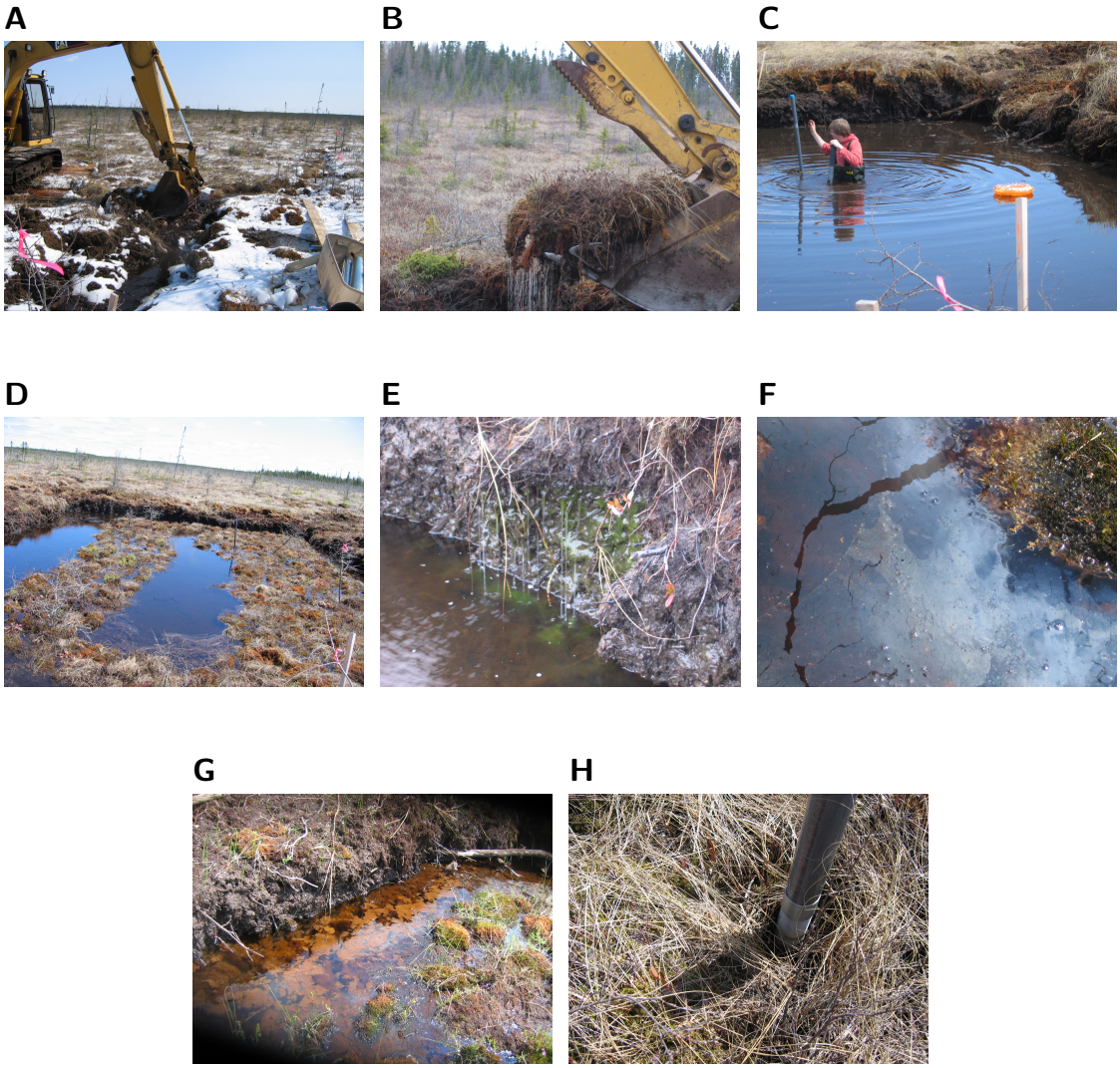


Figure 2.3: **A** Start of experimental peat mining in northwestern Ontario, spring thaw (23 April 2008). **B** The acrotelm layer was first removed. **C** One metre of catotelm (energy peat) was mined, leaving a pit. **D** To restore peatland function, preserved acrotelm was replaced forming a floating mat peatland system. **E** Algal growth was observed in pit and drainage ditch. **F** Oily blue sheen was observed on surface water of pit and hollows. **G** Orange floc in pit. **H** Dessication and peat subsidence along the drainage ditch; peat surface of this hollow was at the top of duct tape before mining.

2.2.3 Sampling Methods

Water sampling during ice free periods was initiated fall 2007 and concluded fall 2009. Samples for all analyses were held on ice during transport and not filtered unless specified in analytical procedures. Samples for metal analysis were preserved immediately upon lab reception (pH<2, HCl Fisher TraceMetal).

Porewater samples were drawn from purged and recharged piezometers (2 min, 30 min respectively) using a peristaltic pump. Surface water samples were grab samples from about 10 cm below the surface. Some surface samples were drawn during peat extraction from the drainage ditch before the installation of the weir and pooled with weir data. For Hg and MeHg, trace metal procedures were followed (EPA, 1996, 2002), including the use of a Teflon tubing and Teflon collection bottle, with field transfer of samples to Hg clean amber bottles and lab preservation (pH<2, HCl Fisher OmniTrace).

Rainfall for general chemistry and metals (preserved aliquot) was collected in only 2009 in four litre plastic containers equipped with plastic funnels and located on a hummock near both RP and EP. Analyte concentrations were compromised by insects and pollen. Rainwater for Hg and MeHg were collected in similar locations, but in elevated one litre amber glass Hg clean bottles containing 2.5 mL of conc. HCl (Fisher OmniTrace) equipped with Hg clean glass funnels (Ahmed et al., 1987). Pollen contamination was evident. Since rainfall was not filtered, values reflect both aqueous and particulate atmospheric contributions of analytes to surface peat.

Snow samples were collected April 2009 with a Teflon core sampler from locations near RP, BEP and the weir. Cores per location were composite and stored without preservation in plastic jars. Aliquots for metal analysis were removed and preserved (pH<2, HCl Fisher TraceMetal) after melting. Snow samples for Hg and MeHg were distributed directly from the sampler to Hg clean amber glass jars and preserved when melted (pH<2, HCl Fisher OmniTrace). Known core volumes of snow were sampled in triplicate to calculate snow density, assuming 1 mL of snow water was equivalent to 1 g.

2.2.4 Chemical Analysis

Quantification of analytes (pH, alkalinity, conductivity, anions, redox potential, TSS, colour, DOC, nutrients, cations and metals (including Hg and MeHg) was conducted at the Lakehead University Environmental Laboratory (LUEL), which demonstrated proficiency (anions, cations, metals) and held accreditation (total nitrogen (TN), total

phosphorus (TP), pH, alkalinity, conductivity, TSS) through the Canadian Association of Laboratory Accreditation. Additional quality was assured via participation in round-robin studies through the National Water Research Institute (all above plus Hg, DOC and colour) during the study period. Analyses followed LUEL standard operating procedures, which included the use of blanks, quality control samples, duplicates and spikes. An exception were select 2007 samples for MeHg, which were sent to a private laboratory (ALS Canada Ltd.).

Metals (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sr, Ti, V, Zn) were measured after digestion and concentration via microwave irradiation after the addition of concentrated HNO_3. Digestates were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Both Hg and MeHg were determined using instrumentation from Brooks Rand Laboratories (Model III) following United States Environmental Protection Agency (USEPA) methods 1631 (EPA, 2002) and 1630 (EPA, 2001b), respectively. All Hg in a 100 mL aliquot was oxidized to Hg(II) with BrCl. After oxidation, the sample was sequentially reduced with $NH_2OH{\cdot}HCl$ to destroy free halogens, then reduced with $SnCl_2$ to convert Hg(II) to volatile Hg(0). The Hg(0) was separated from solution by purging with nitrogen gas and collected onto a gold trap. The Hg was thermally desorbed from the trap into an argon gas stream that carried the Hg into the quartz cell of the cold-vapor atomic fluorescence spectrometer (253.7 nm). For MeHg, 45 mL of sample was treated with 200 μL of 1% ammonium pyrrolidine dithiocarbamate solution distilled at 125$^{(}\circ$) under nitrogen flow. Distillate was buffered to pH 4.9 with an acetate buffer before 50 μL of 1% $NaBEt_4$ was added to convert all CH_3Hg to volatile methylethyl mercury, which was traped on a Carbotrap via nitrogen gas purging. The trapped methylethyl mercury was thermally desorbed into an argon gas stream and separated on a gas chromatography column then pyrolytically decomposed to convert organo mercury forms to Hg(0) for detection as for total Hg above.

The remaining analyses were conducted on unpreserved samples. The TSS were determined gravimetrically on the solids portion from 250 mL of sample as retained on pre-weighed 0.45 μm glass fiber filters (FisherScientific), dried at 105°. Redox potential (Accumet platinum indicating half-cell), conductivity (Accumet two-cell glass) and pH (Mettler Ag/AgCl) were determined by calibrated electrodes, with temperature correction only. Alkalinity was determined by titration of a 50 mL sample to pH 4.5 with 0.02 N H_2SO_4 (Mettler). Colour was determined on filtered samples (0.45 μm syringe type) using a Cary 50 spectrophotometer at 456 nm calibrated with platinum-cobalt standards,

thus, reported as true colour units (TCU). Chloride (Cl^-), nitrate (NO_3^- as N), nitrite (NO_2^{-2} as N) and sulphate (as SO_4^{2+}) ions were determined on filtered samples (0.45 μm syringe type) by ion chromatography (Dionex DX-120; AG14 guard column with AS14 analytical column; ion suppression).

Segmented flow colourimetry (Skalar Sans $^{++}$, Netherlands) was used for the following analytes on unpreserved sample aliquots: DOC was determined after online filtration and acidification, releasing CO_2 gas that passes through a membrane into weakly buffered alkaline solution with phenolphthalein indicator for detection and quantification; TP was determined via phosphomolybdate method after fuming acid digestion with a sulphuric acid/potassium sulphate/ mercuric oxide solution (prior to instrument failure in February 2009, the Skalar module for online UV radiation after treatment with potassium peroxodisulphate and disodium tetraborate solution was utilized as the initial digestion step for TP); TN was determined via by online digestion with potassium peroxodisulfate/sodium hydroxide solution and heating, UV radiation with a borax buffer and subsequent nitrate quantification with the Griess reaction after reduction by a cadmium copper reductant.

2.2.5 Experimental Design and Statistics

A BACI design (Green, 1979) was used to detect changes in water quality associated with peat mining and restoration. The statistical analysis proceeded in steps. First, porewater and surface water samples were coded by the time period sampled: *a*) **Before** (before peat mining in 2007 and 2008), *b*) **Impact** (while peat was mined and acrotelm replaced, 2008), *c*) **After 2008** (2008 immediately following restoration), and *d*) **After 2009** (one season after impact, 2009). Second, the difference in concentration between a paired reference site and experimental site was calculated for each sampling date (Experimental site - Reference site). Third, an analysis of variance (ANOVA) was performed to determine whether a significant difference existed among the means of the differences in concentrations (MDCs) calculated for each time period. A significance value of $\alpha \leq 0.10$ was selected *a priori* to minimize Type II errors (Buhl-Mortensen, 1996; Underwood and Chapman, 2003; Manly, 2009). Post-hoc analysis was Tukey HSD multiple comparison test. Welch's t-test was used to compare the MDC for After 2008 and After 2009 BEP data. No correction was done for the number tests performed, conceding false negatives as environmentally protective.

Parameters censored by LUEL as below detection limit (DL) were set equal to DL/2

prior to analyses (EPA, 2000b). When an analyte had greater than 75% of the data reported as DL in an unbiased fashion across all sampling locations, depths or time periods, the analyte was removed. To describe relationships between analytes, Pearson's product-moment correlations (r) were determined. For brevity, they were stated in text as significant when $p \leq 0.001$. Mean±standard deviation (SD) are presented unless otherwise stated. Statistical analysis was conducted with the statistical program R (R Development Core Team, 2010).

2.3 Results

2.3.1 Porewater

The appendices contain summarized porewater data (Tables A.1 to Table A.5) and statistics (Table A.6 to Table A.8). Porewater pH, alkalinity and conductivity clearly increased over time in EP compared to RP with significant MDCs among all time periods at depths measured (Figs. 2.4, 2.5 and Appendix A.6). Pairwise comparisons were also significant between all time periods ($p \leq 0.007$). Alkalinity and conductivity in BEP showed a decreasing trend after mining (Fig. 2.4, 2.5), whereas pH was less definitive (Fig. 2.4). For combined porewater data, a significant correlation between alkalinity and conductivity ($r > 0.99$) and between pH and alkalinity ($r = 0.84$) and conductivity ($r = 0.84$) were found. Cations that contribute to conductivity (Ca, Mg, K, Na) followed similar increasing trends in EP and decreasing trends in BEP (Fig. 2.6, 2.7). Correlations of cations with conductivity were significant (Ca, Mg $r = 0.99$; Na $r = 0.95$; K $r = 0.87$).

Concentrations of TN in porewater appeared seasonal (Fig. 2.5). Higher mean TN in 100 cm porewater occurred after mining (Before 0.92±0.17 mg L^{-1}, After 2008 1.34± 0.30 mg L^{-1}, After 2009 1.97±0.43 mg L^{-1}), with significant pairwise differences between Before and After 2009 and between After 2008 and After 2009 ($p < 0.001$). An increase in mean TN also occurred at 150 cm (Before 0.88±0.30 mg L^{-1}, After 2008 1.84±0.34 mg L^{-1}, After 2009 2.23±0.51 mg L^{-1}), with significant pairwise MDC for all time periods ($p \leq 0.004$). The difference for 300 cm was between Before and After 2009 ($p = 0.084$), with lower TN at EP than RP Before mining (2.12±0.53, 3.14±0.97 mg L^{-1}, respectively) and more similar in 2009 (2.16±0.47, 2.19±0.52 mg L^{-1}, respectively). Concentrations in BEP were lower than RP, though similar to EP before mining at comparable depths (Fig. 2.5).

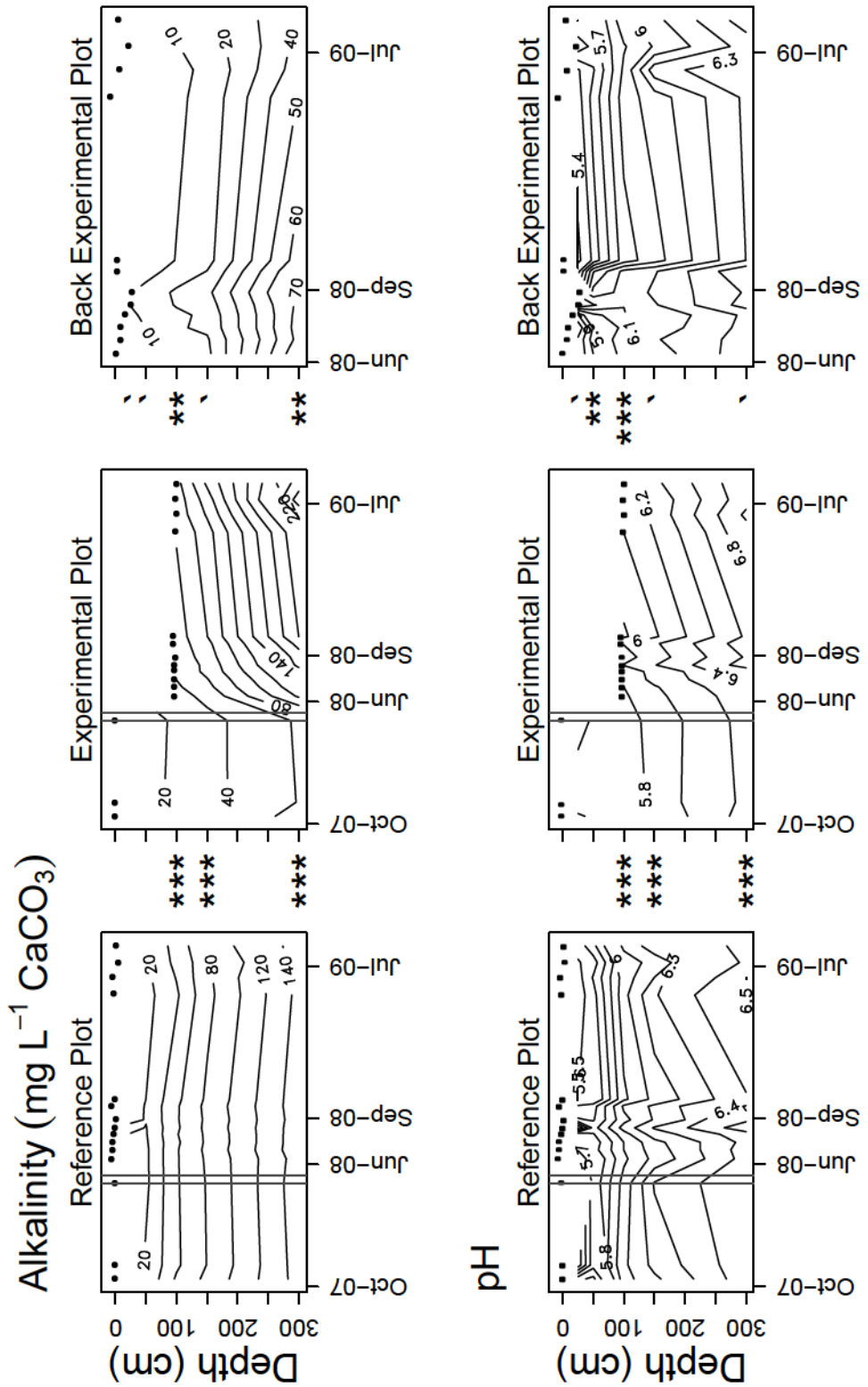


Figure 2.4: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

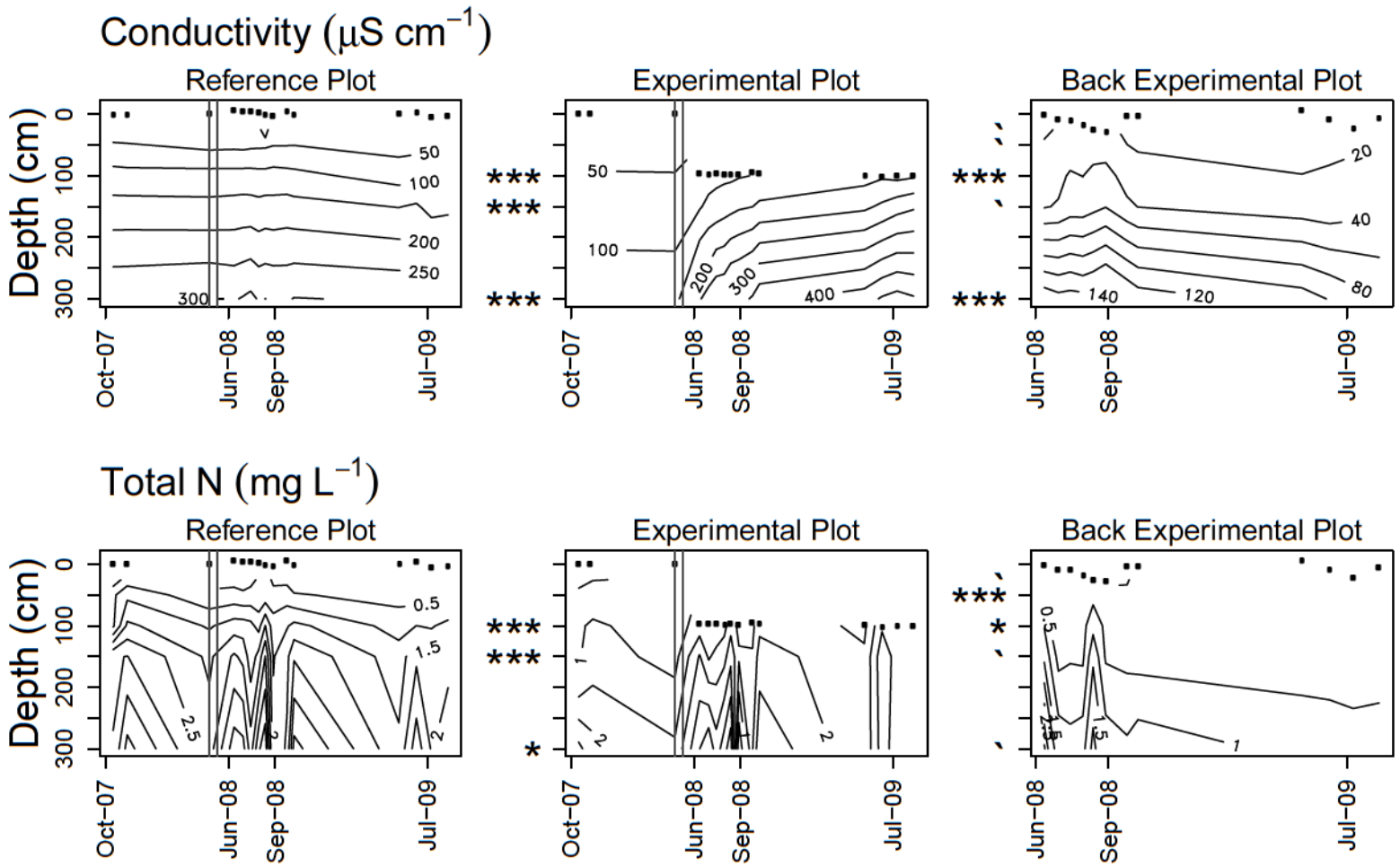


Figure 2.5: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, $p^* \leq 0.10$ and tick mark was not significant.

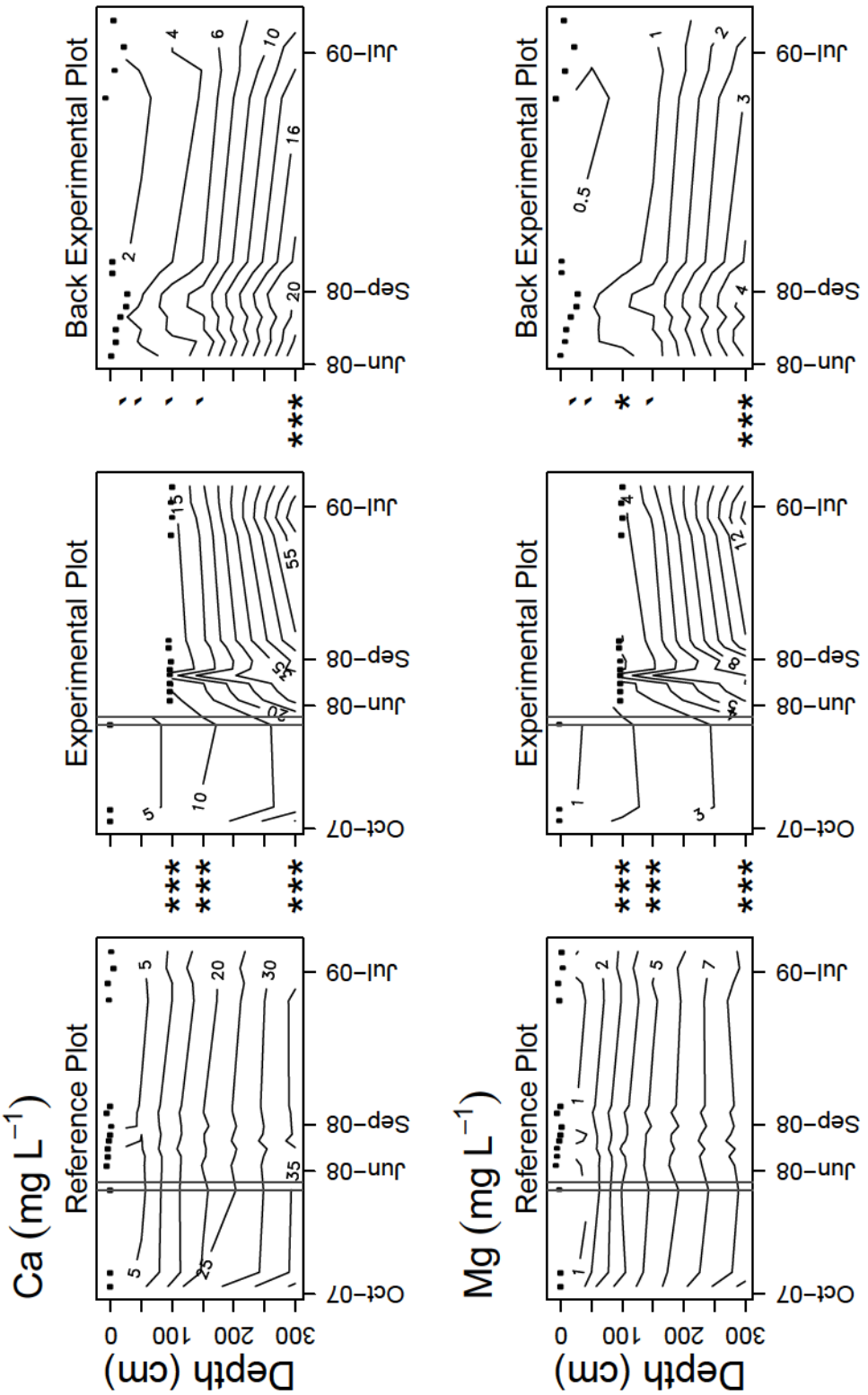


Figure 2.6: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

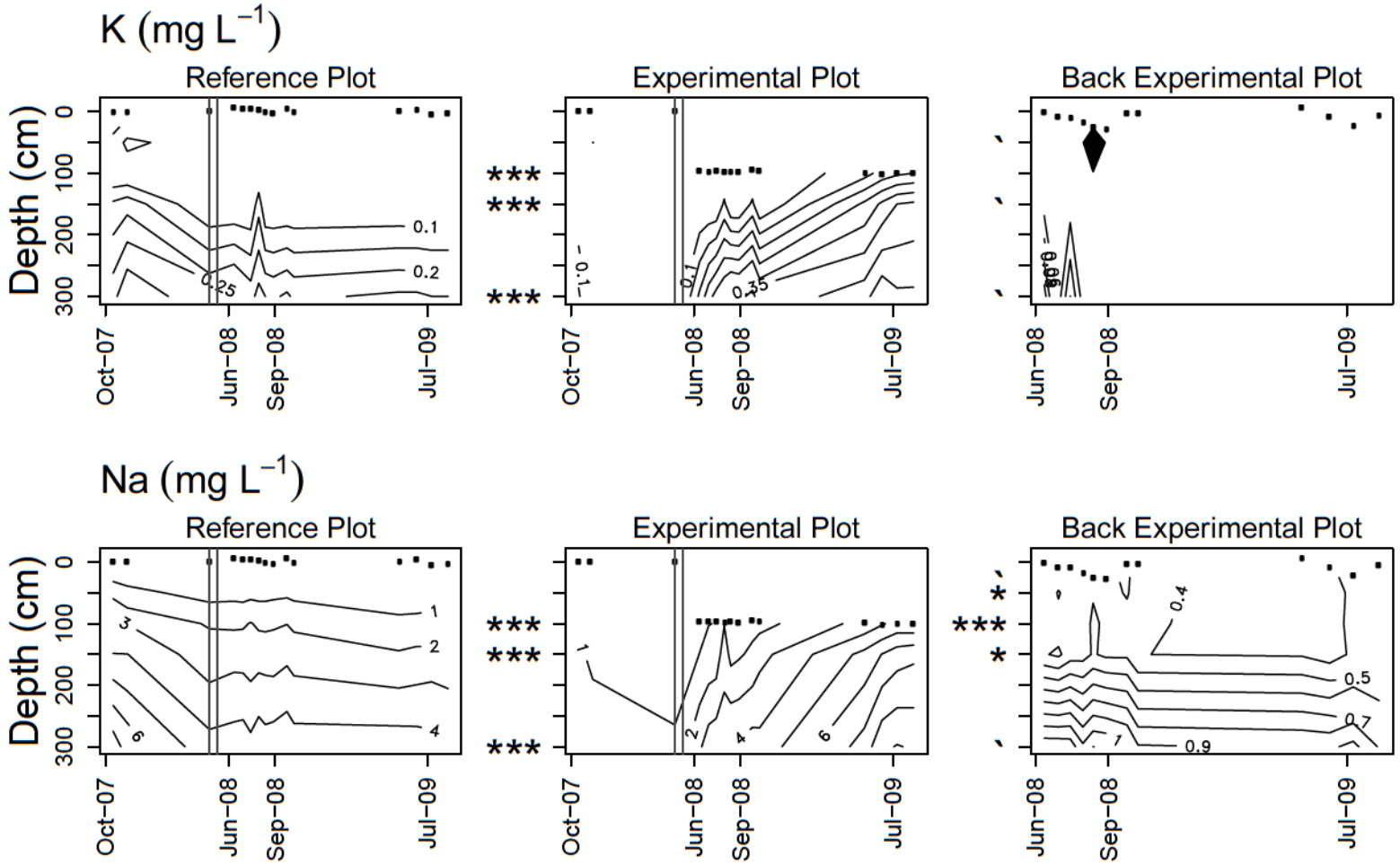


Figure 2.7: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, $p^* \leq 0.10$ and tick mark was not significant.

Porewater trace metals Sr, Ba, Mn, Fe had significant MDC, increasing in EP and decreasing in BEP, similar to conductivity (Fig. 2.8, 2.9). Both Sr and Ba were significantly correlated (r=0.98), as were Mn and Fe (r=0.86). Concentrations of Sr and Ba also significantly correlated with conductivity (r=0.99, r=0.98, respectively), as were Mn and Fe with conductivity (r=0.65, r=0.79, respectively).

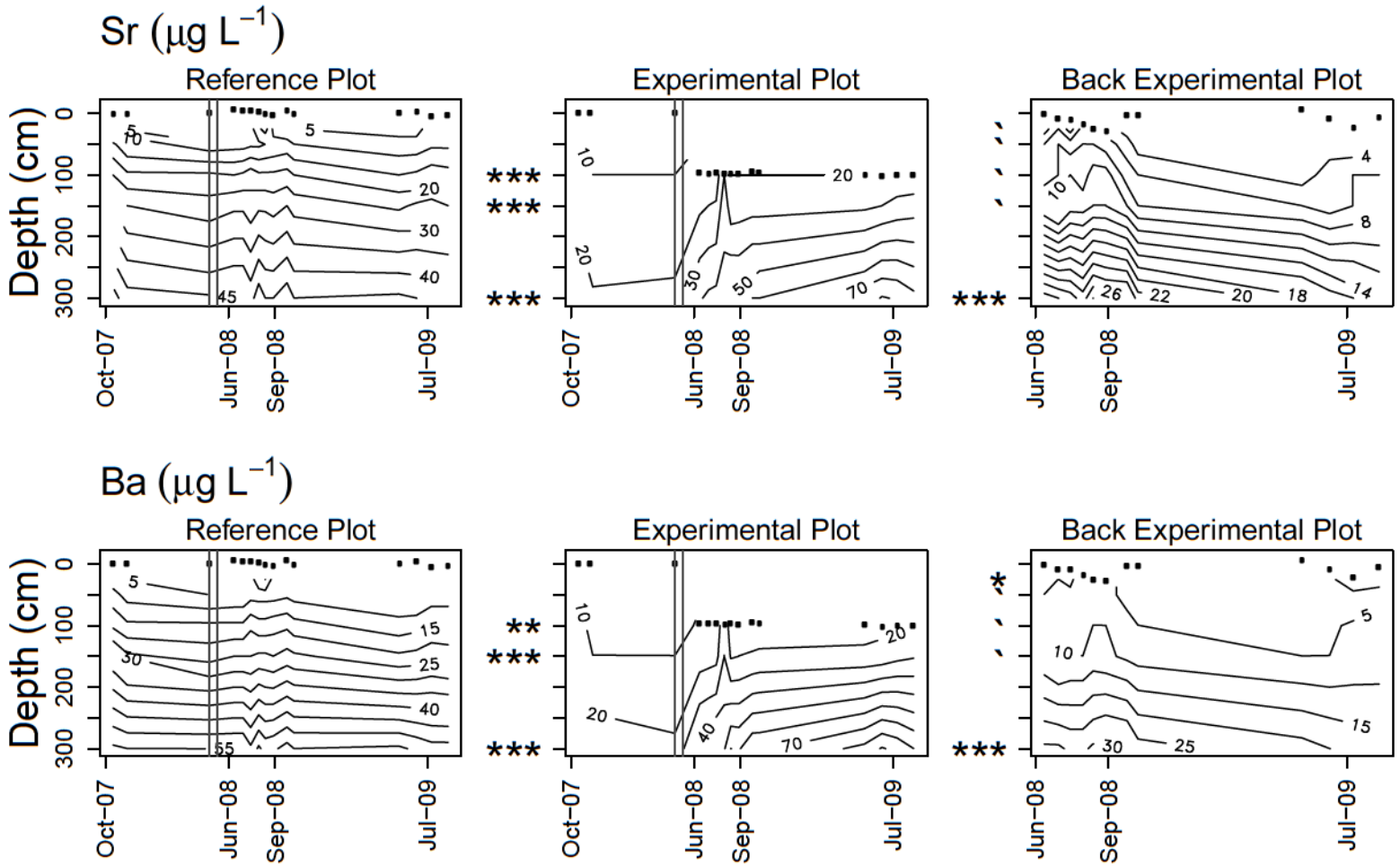


Figure 2.8: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

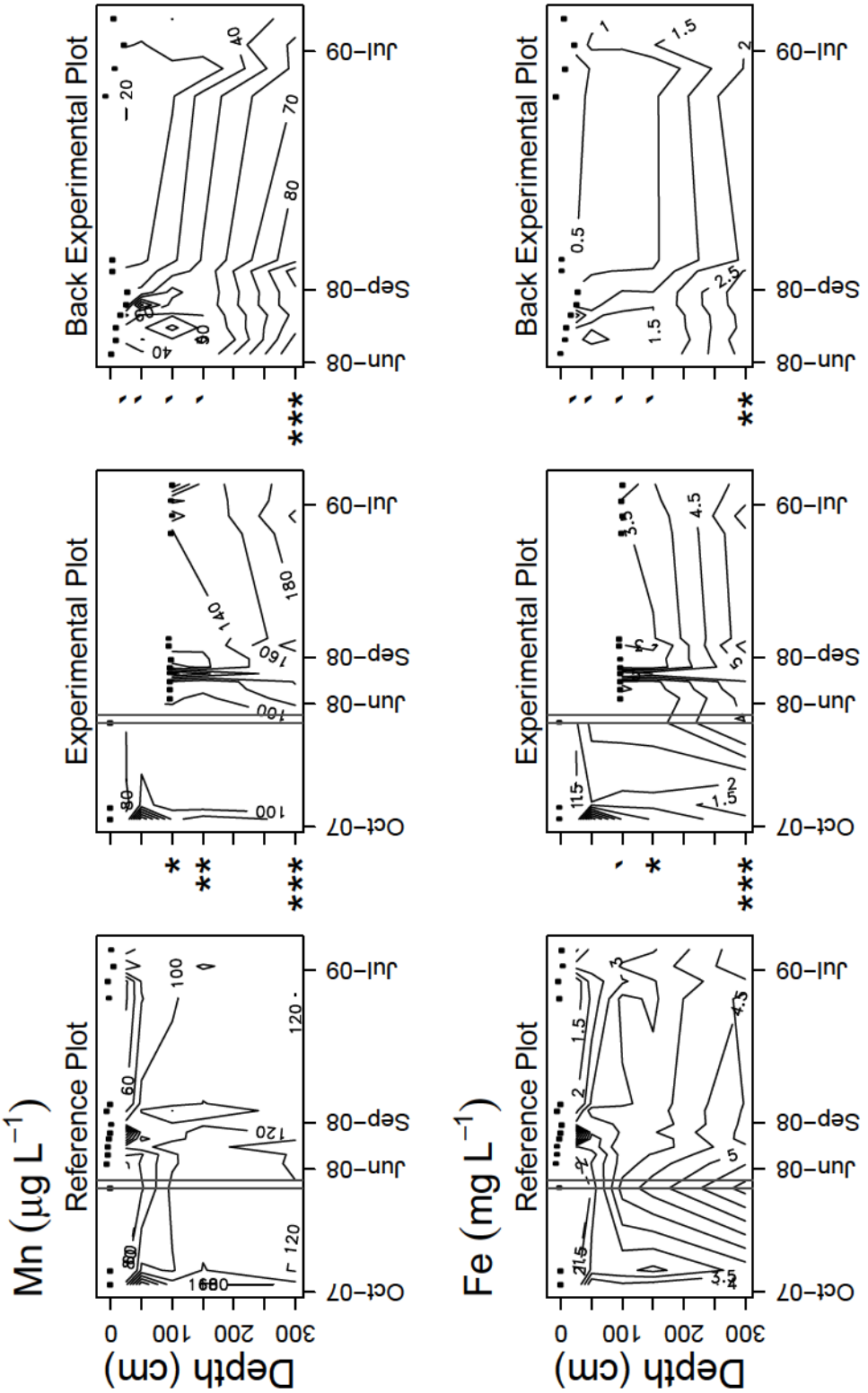


Figure 2.9: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

Porewater colour showed some significant change associated with wet mining in EP and BEP compared to RP, though values at EP and BEP were generally lower than RP at comparable depths (Fig. 2.10). For EP at 100 cm, Before and After 2008 MDC differed (p=0.006) as did Before and After 2009 (p=0.076), with similar colour over time at RP (Before 98.0±14.4 TCU, After 2008 109±11.3 TCU, After 2009 103.9±7.4 TCU) and decreasing colour at EP (Before 98.3±22.3 TCU, After 2008 81.7±7.9 TCU, After 2009 83.9±3.4 TCU) and BEP (After 2008 126±23.8 TCU, After 2009 93.6±13.7 TCU). Highest colour occurred during the summer of 2008 at 25 cm in RP during a drier period, ranging from 59.8 to 298 TCU in 2008. Porewater colour was significantly correlated with DOC (r=0.43).

Porewater redox potentials at the three sites were seasonal, being lower in late summer than spring, and in deeper porewater than shallower (Fig. 2.10). Porewater was generally oxidizing (redox>0 mV), with a few negative values recorded at 300 cm in EP (min. -17 mV).

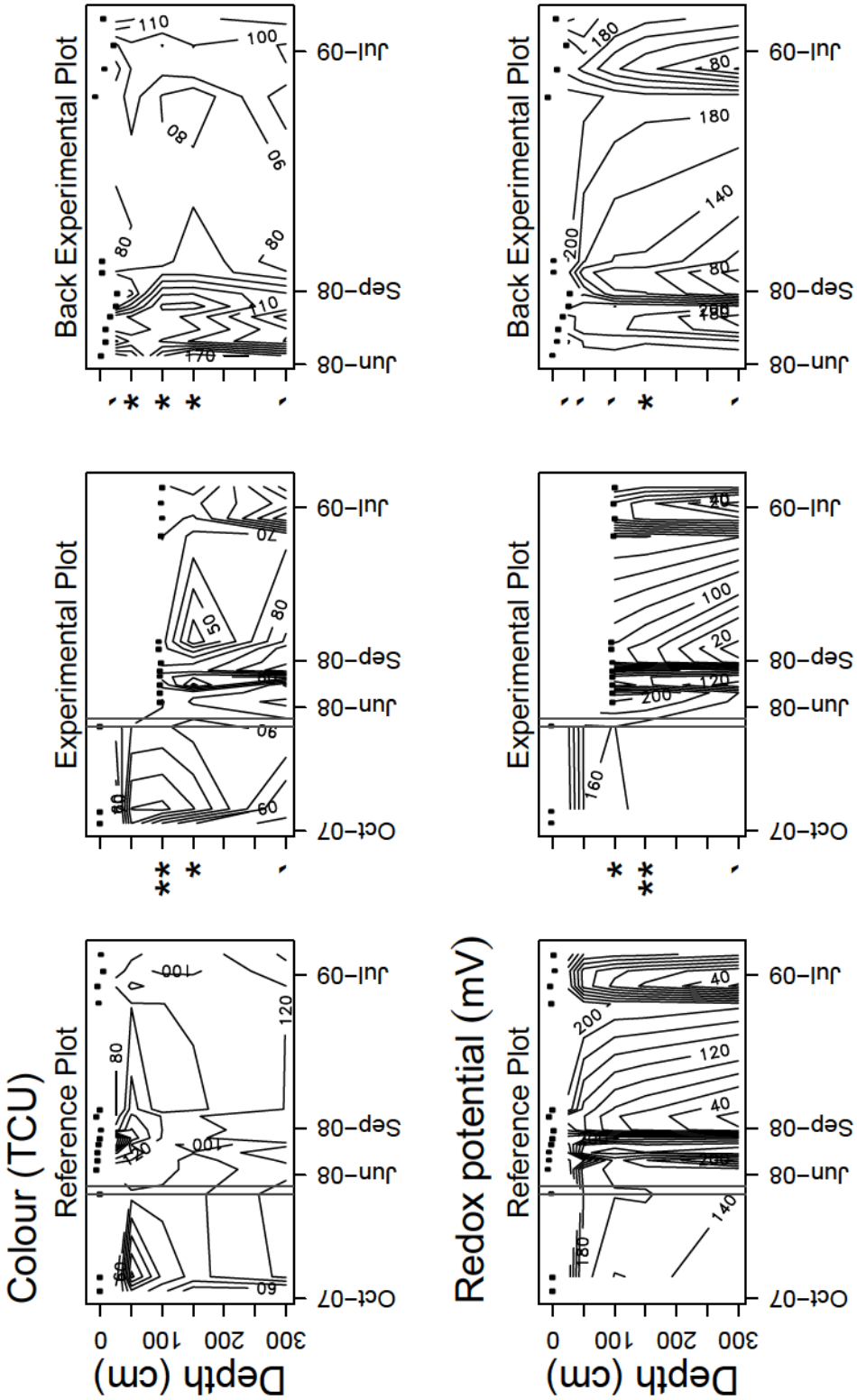


Figure 2.10: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

Porewater MeHg concentrations at RP and EP were less than 0.080 ng L^{-1} after restoration at 100, 150 and 300 cm. The highest concentrations of MeHg were found at 25 cm in RP, which ranged from 0.03 (DL) to 0.423 ng L^{-1} over the study period (Fig. 2.11).

Porewater TSS concentrations from RP, EP and BEP were generally less than 10 mg L^{-1} (Fig. 2.11). High TSS was noted after mining in EP (max. 52.8 mg L^{-1} at 100 cm) and BEP (max. 125 mg L^{-1} at 300 cm), which later stabilized. One high datum was recorded at RP (Before at 150 cm 57.2 mg L^{-1}). The only significant MDC result was for 150 cm (Before and After 2008 p=0.035) with one elevated datum after mining in EP (30.3 mg L^{-1}) recorded at that depth. Porewater TSS correlations were significant for Al (r=0.65), Hg (r=0.32) and TP (r=0.24).

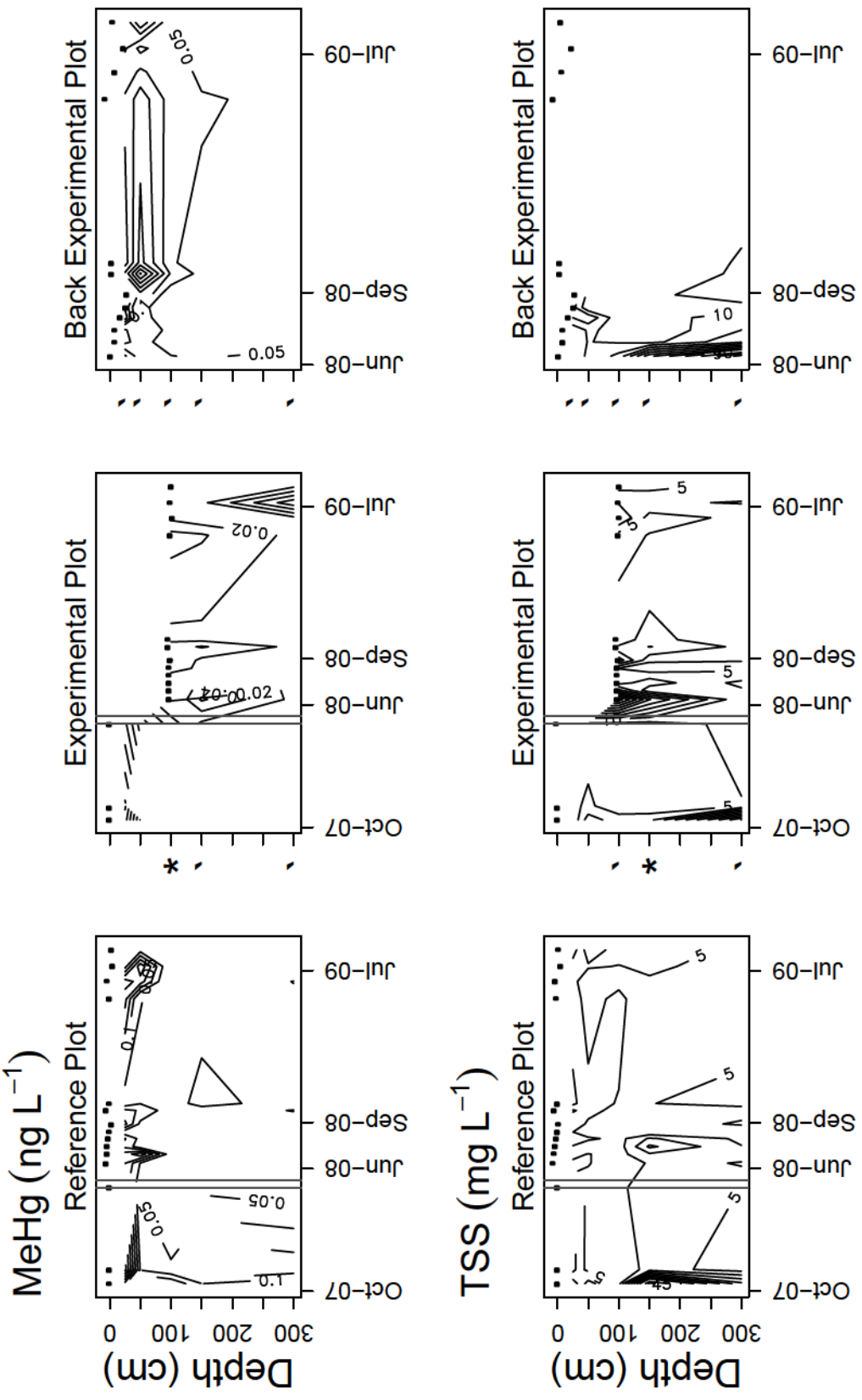


Figure 2.11: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

Porewater DOC concentrations from EP and BEP appeared similar to RP after mining for all depths (Fig 2.12). Significant MDC for BEP at lower depths were found, though concentrations were within the range measured for RP at 25 cm (6.0–24.6 mg L^{-1}). The highest significant correlation for DOC after colour was Al (r=0.31).

Porewater TP concentrations were erratic at all depths in all plots, with concentrations rarely exceeding 100 μg L^{-1} (Fig 2.13). Mean TP for all piezometers was 16.8±18.5 μg L^{-1} (median 11.0 μg L^{-1}, n=184). The highest significant correlation for TP was with TN (r=0.55).

Porewater Hg concentrations showed no discernible trend or significant MDC (Fig 2.13). After mining, a maximum concentration of 5.68 ng L^{-1} was measured at 150 cm, and generally below 2 ng L^{-1} in 2008 and 2009. The strongest significant relationship of Hg was with MeHg (r=0.65). When only RP data was considered, this relationship increased (r=0.82).

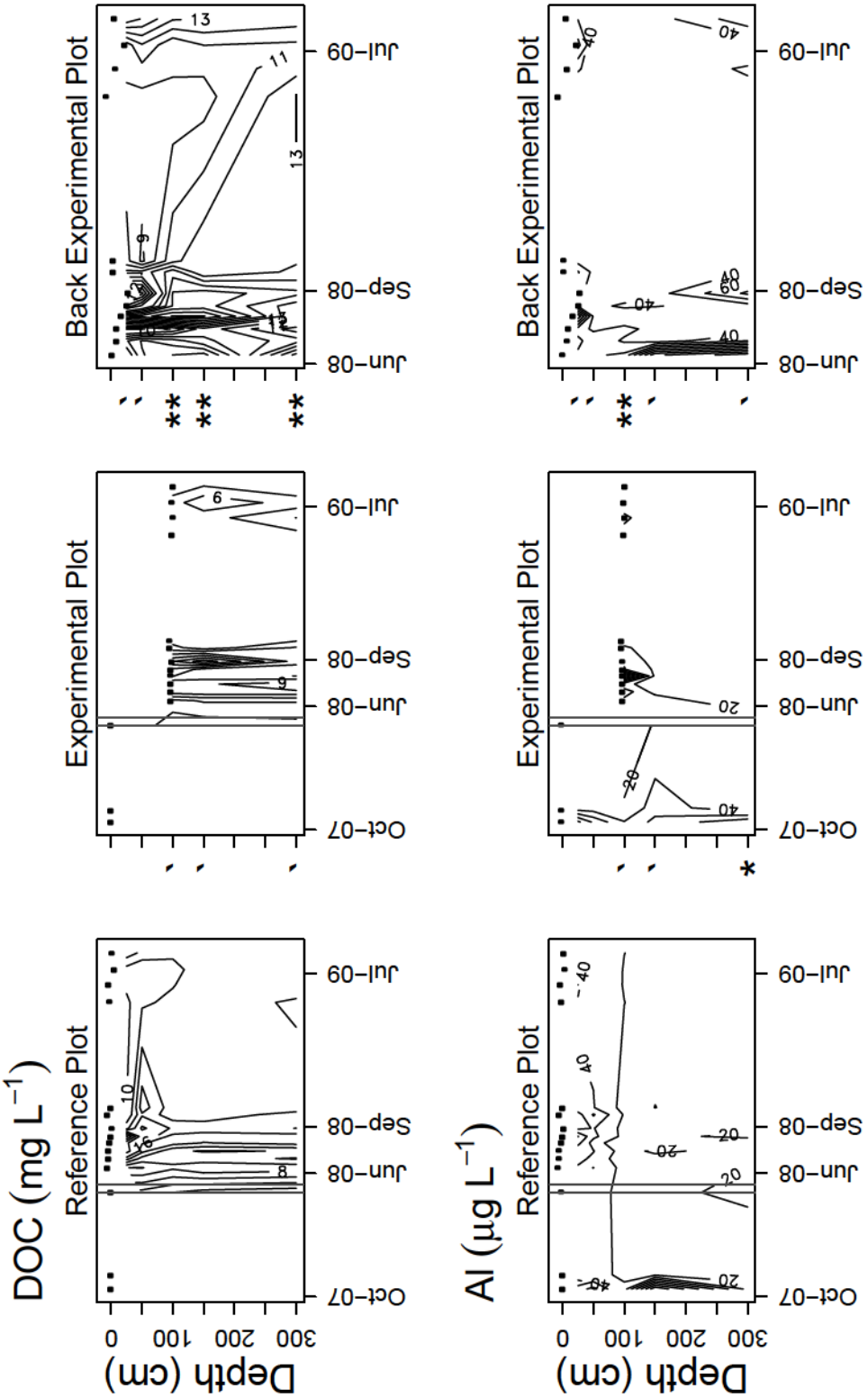


Figure 2.12: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and tick mark was not significant.

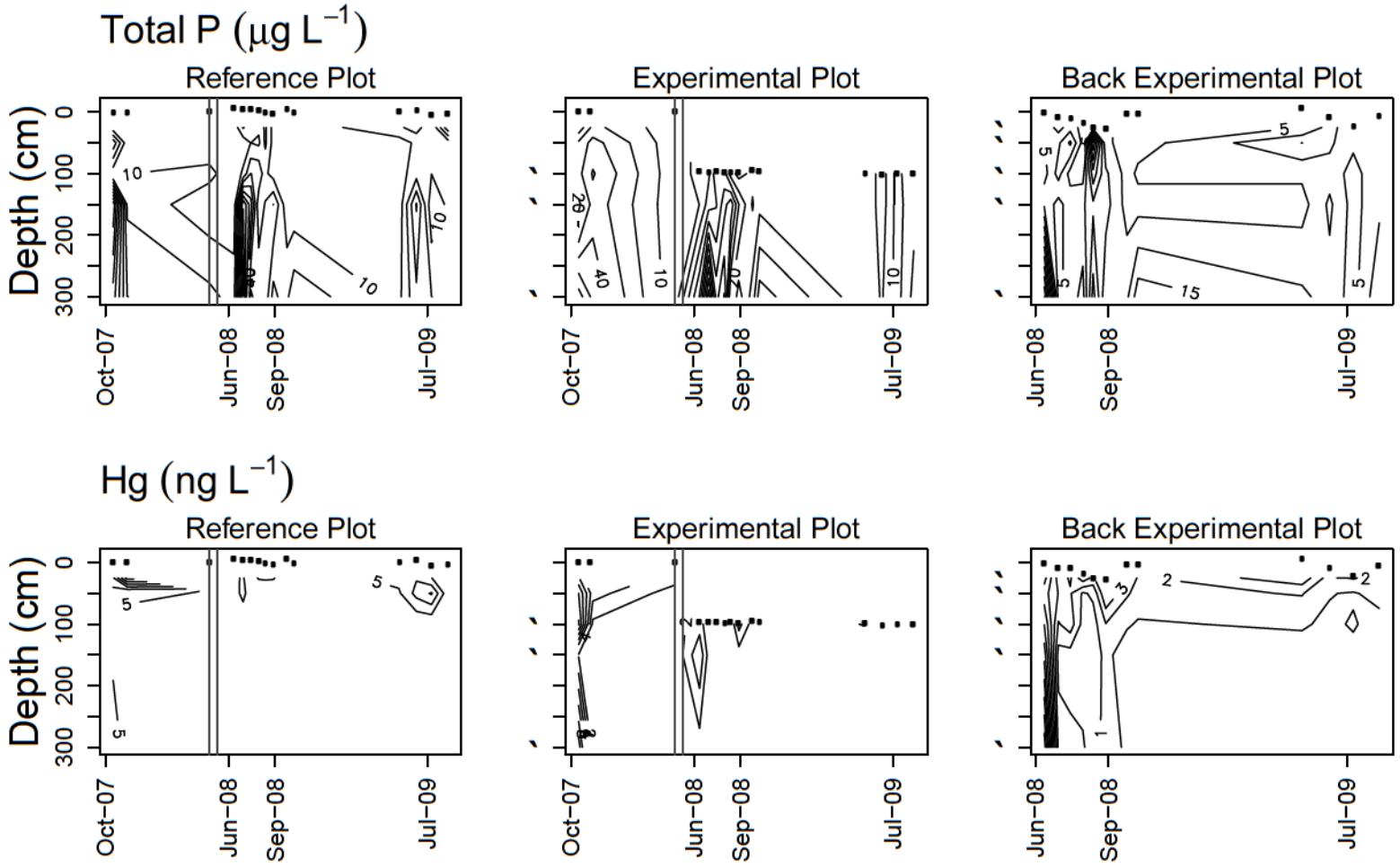


Figure 2.13: Isopleth lines depicting porewater concentration over depth and time. Vertical lines show start of mining and end of restoration, respectively, thus delineating Before, Impact and After time periods. Circles show position of water table relative to peat surface. Significant means of the differences in concentration (MDC) between reference plot (RP) and experimental plot (EP) among time periods (ANOVA) and between RP and back of experimental plot (BEP) (t-test) for depths with measured concentrations are provided in the appropriate y-axis where ***$p \leq 0.001$, **$p \leq 0.01$, $p^* \leq 0.10$ and tick mark was not significant.

Percent increases in concentration between RP and EP were calculated for analytes showing significant change (Table 2.1). Although Al had a significant MDC for 300 cm (Fig. 2.12), variability in Before data was noted (see also Table A.5) and a decrease of 80% calculated. There were significant yet weak correlations of Al to conductivity and TSS (r=-0.37, r=0.65).

Table 2.1: Percent change of analytes in experimental plot (EP) porewater after wet peat mining. Calculated as ((Mean After-Mean Before)/Mean Before)*100, where After was either After 2008 or After 2009. NS indicates Tukey pairwise comparisons were not significant.

	100 cm Piezometer		**150 cm Piezometer**		**300 cm Piezometer**	
Parameter	**Before to After 2008**	**Before to After 2009**	**Before to After 2008**	**Before to After 2009**	**Before to After 2008**	**Before to After 2009**
H^+	−33.6	−56.9	−34.2	−59.7	−43.4	−79.8
Alkalinity	90.3	202	99.7	233	147	281
Conductivity	74.3	168	87.4	212	141	250
Ca	77.4	115	85.8	141	99.6	206
Mg	59.0	98.6	70.0	127	131	262
K	0.0	245	30.0	540	291	431
Na	98.0	481	118	631	161	477
Sr	65.9	97.7	75.9	125	108	223
Ba	86.0	107.0	81.8	134	145	276
Mn	NS	65.2	19.3	42.1	60.8	101
Fe	NS	NS	NS	60.7	109	131
TN	NS	115	180	152	NS	1.74
Colour	−16.9	−14.6	−18.4	NS	NS	NS
MeHg	−56.6	−54.9	NS	NS	NS	NS
TSS	NS	NS	190	NS	NS	NS

2.3.2 Surface Water

Surface water concentrations showed seasonal trends with some exceptions. Total Hg, Fe, DOC and TSS are provided as examples (Fig. 2.14) since Gleeson et al. (2006) suggested these would increase in receiving waters as a result of peat mining in Ontario. Weir flow, precipitation and water depths are also presented since seasonality appears in the analyte concentrations (Fig. 2.14). Peak concentrations occurred during the summer, coinciding

with lower flows and lower water depths. Lower concentrations occurred during spring runoff and after rainfall events. Summaries of surface water chemistry with indicated significant MDC among time periods are presented in Table 2.2 and Table 2.3. Graphs for all analytes are presented in Appendix A.1.

Weir flow ranged from 15.2 to 162 L min^{-1} in 2008 and from 17.4 to 299 L min^{-1} in 2009 (Fig. 2.14E). Weir alkalinity (r=-0.76), colour (r=-0.61), conductivity (r=0.82), Ba (r=-0.85), Ca (r=-0.83), Fe (r=-0.72), Mg (r=-0.83), Mn (r=0.63), Na (r=0.82), Sr (r-0.83), pH (r=-0.72) and TN (r=-0.63) were significantly and inversely correlated with flow rate over the weir. Culvert Ca (r=-0.44), Mg (r=-0.44), Zn (r=-0.51) and pH (r=-0.61) were significantly and inversely related to water depth whereas sulphate (r=0.62) had a significant positive relationship.

The maximum Hg value in surface water was measured at the weir during mining (17.2 ng L^{-1}), with pairwise significant MDCs (p<0.001) between Impact and After 2008 and between Impact and After 2009, with no significance between After 2008 and After 2009. Weir Hg correlated significantly with TSS (r=0.92), Al (r=0.87) and colour (r=0.72). Culvert Hg correlated significantly with only Al (r=0.85). Reference site Hg had no highly significant (p<0.001) correlations. Higher culvert than reference Hg concentrations were measured during mining (culvert max= 9.19 ng L^{-1}; reference max= 2.96 ng L^{-1}), being more similar after (Table 2.2). A limited Before data set showed significant MDC results for MeHg. Concentrations of MeHg from all sites were low (Table 2.3).

Maximum concentrations of Al (121 μg L^{-1}), colour (336 TCU), TSS (156 mg L^{-1}) and TN (1.50 mg L^{-1}) were measured at the weir the day the plot was restored. There were pairwise differences in MDC between Impact and After 2008 and between Impact and After 2009 for Al (p<0.001, p=0.002), colour (p=0.016, p=0.003), TSS (p=0.009, p=0.024), DOC (p<0.001, p=0.004) and sulphate (p=0.005, p=0.032). For TN, differences were between Impact and After 2009 (p=0.003) and between After 2008 and After 2009 (p=0.017). For detailed statistics see Table A.9 and A.10.

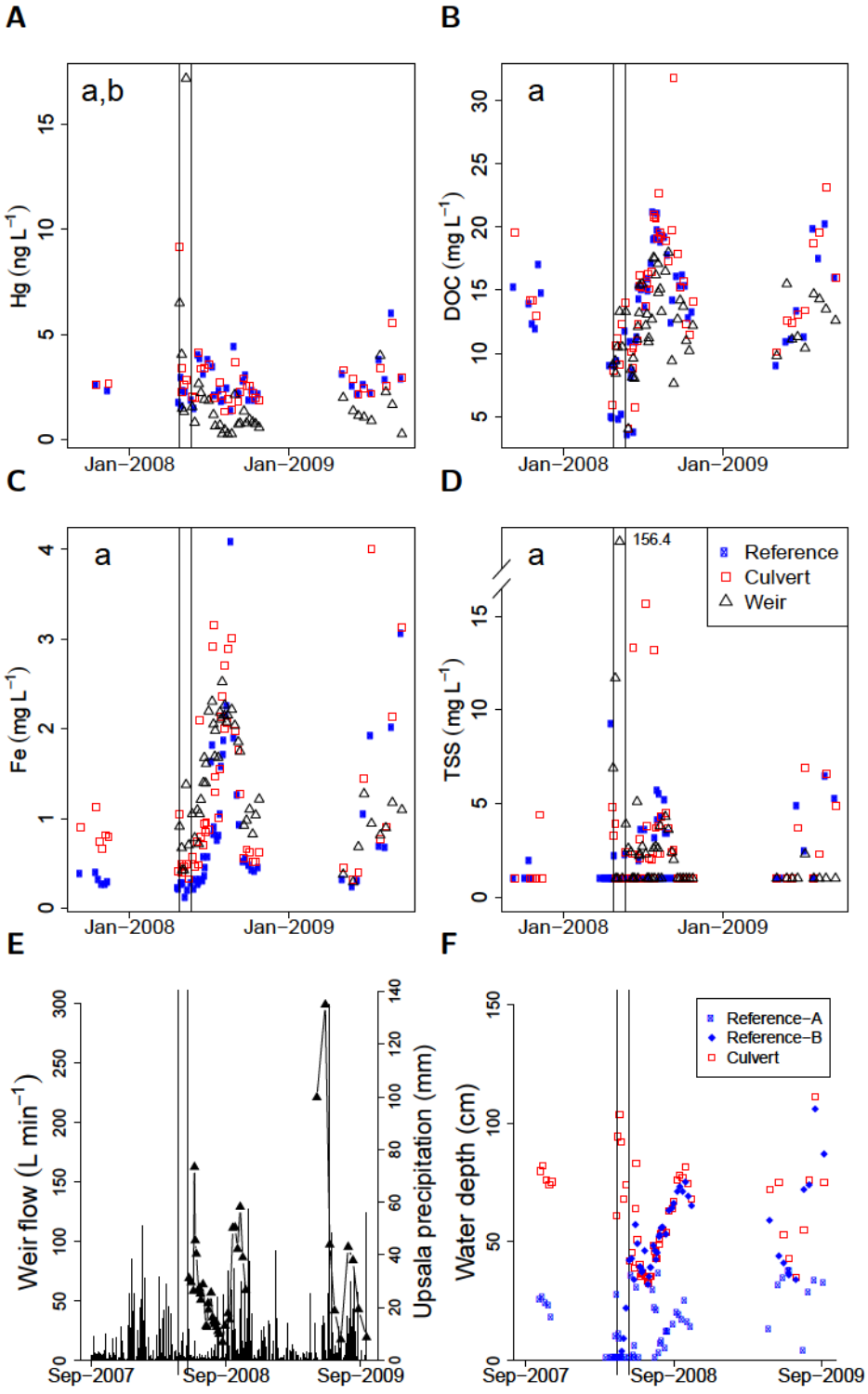


Figure 2.14: Typical chemistry of surface water (**A**–**D**). Lowercase letters indicate significant means of the differences in concentration (MDC) between weir (**a**) or culvert (**b**) and reference site. Peak concentrations of Hg (**A**) and TSS (**D**) occurred during mining. Concentrations of DOC (**B**) and Fe (**C**) showed seasonal trends coincident with weir flow (**E** triangles), precipitation (**E** bars) and water depth at the actual sampling sites (**F**). Horizontal lines show start of mining, end of restoration, respectively.

Table 2.2: Chemistry of surface water. DL was analytical detection limit, SD was standard deviation, NA was not applicable and — was not analysed. Significant means of the differences in concentration (MDC) between reference water and weir or culvert among time periods (ANOVA) are provided (MDC Sig.) where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and NS was not significant.

	Sampling	MDC		**Before 2007-2008**			**Impact 2008**			**After 2008**			**After 2009**		
Analyte	**Site**	Sig.	DL	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
Hg (ng L^{-1})	**Culvert**	**	0.50	2.62	0.07	2	4.05	2.90	5	2.43	0.77	22	3.03	1.05	9
Hg (ng L^{-1})	**Reference**		0.50	2.49	0.21	2	2.17	0.54	5	2.56	0.88	22	3.14	1.20	9
Hg (ng L^{-1})	**Weir**	***	0.50	—	—	—	6.10	6.56	5	1.06	0.69	22	1.61	1.07	9
Al (μg L^{-1})	**Culvert**	NS	5	54	21	7	91	133	6	81	117	33	62	25	9
Al (μg L^{-1})	**Reference**		5	44	18	7	21	5	6	55	16	33	56	25	9
Al (μg L^{-1})	**Weir**	***	5	—	—	—	39	41	6	29	7	33	33	8	9
K (mg L^{-1})	**Culvert**	NS	0.10	0.20	0.09	7	0.26	0.10	6	0.10	0.09	33	0.17	0.18	9
K (mg L^{-1})	**Reference**		0.10	0.20	0.10	7	0.23	0.11	6	0.10	0.10	33	0.18	0.19	9
K (mg L^{-1})	**Weir**	***	0.10	—	—	—	0.16	0.09	6	0.16	0.03	33	0.08	0.07	9
DOC (mg L^{-1})	**Culvert**	NS	0.5	13.4	4.9	5	10.4	1.4	6	15.7	5.2	33	15.5	4.2	9
DOC (mg L^{-1})	**Reference**		0.5	12.9	3.9	7	7.1	2.3	6	14.6	4.4	33	14.4	4.2	9
DOC (mg L^{-1})	**Weir**	***	0.5	—	—	—	10.2	1.7	6	12.6	3.3	33	12.6	2.0	9
Fe (mg L^{-1})	**Culvert**	NS	0.002	0.778	0.219	7	0.536	0.257	6	1.41	0.87	33	1.51	1.32	9
Fe (mg L^{-1})	**Reference**		0.002	0.312	0.064	7	0.229	0.063	6	0.983	0.837	33	1.14	0.98	9
Fe (mg L^{-1})	**Weir**	***	0.002	—	—	—	0.750	0.358	6	1.61	0.54	33	0.839	0.340	9
pH	**Culvert**	***	NA	5.82	0.21	7	5.49	0.25	6	6.12	0.29	33	6.07	0.33	9
pH	**Reference**		NA	5.95	0.16	7	5.61	0.12	6	6.13	0.27	33	6.09	0.31	9
pH	**Weir**	NS	NA	—	—	—	5.60	0.16	6	6.10	0.15	33	6.09	0.20	9
TN (mg L^{-1})	**Culvert**	NS	0.015	0.504	0.199	7	0.378	0.071	6	0.518	0.248	33	0.413	0.162	9
TN (mg L^{-1})	**Reference**		0.015	0.407	0.204	7	0.351	0.046	6	0.479	0.181	33	0.388	0.147	9
TN (mg L^{-1})	**Weir**	**	0.015	—	—	—	0.854	0.597	6	0.781	0.201	33	0.411	0.171	9
Mn (μg L^{-1})	**Culvert**	NS	1	25	13	7	24	16	6	57	47	33	54	65	9
Mn (μg L^{-1})	**Reference**		1	8	5	7	9	5	6	42	52	33	42	48	9
Mn (mg L^{-1})	**Weir**	**	1	—	—	—	41	18	6	98	32	33	39	16	9
Colour (TCU)	**Culvert**	*	1.0	99.7	23.6	7	94.0	11.6	6	141	34.0	33	134.7	38.3	9
Colour (TCU)	**Reference**		1.0	82.2	16.4	7	71.3	4.4	6	129	36.3	33	131.2	42.6	9
Colour (TCU)	**Weir**	**	1.0	—	—	—	122	106	6	122	22.6	33	99.6	18.2	9
Sulphate (mg L^{-1})	**Culvert**	NS	0.05	0.22	0.17	4	0.23	0.07	6	0.08	0.06	33	0.10	0.08	9
Sulphate (mg L^{-1})	**Reference**		0.05	0.24	0.19	4	0.26	0.13	6	0.08	0.06	33	0.09	0.07	9
Sulphate (mg L^{-1})	**Weir**	**	0.05	—	—	—	0.19	0.05	6	0.08	0.07	33	0.09	0.09	9
Conductivity (μS cm^{-1})	**Culvert**	NS	1.5	19.8	2.0	7	12.7	0.9	6	36.2	18.2	33	34.9	20.6	9
Conductivity (μS cm^{-1})	**Reference**		1.5	19.1	1.3	7	12.1	1.0	6	34.5	18.7	33	33.8	20.9	9
Conductivity (μS cm^{-1})	**Weir**	**	1.5	—	—	—	17.9	8.3	6	47.2	11.0	33	32.9	11.9	9

Table 2.3: Chemistry of surface water. DL was analytical detection limit, SD was standard deviation, NA was not applicable and — was not analysed. Significant means of the differences in concentration (MDC) between reference water and weir or culvert among time periods (ANOVA) are provided (MDC Sig.) where ***$p \leq 0.001$, **$p \leq 0.01$, *$p \leq 0.10$ and NS was not significant.

		Sampling	MDC		Before 2007-2008			Impact 2008			After 2008			After 2009		
Analyte	Site	Sig.		DL	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n
Sr (μg L^{-1})		**Culvert**	NS	5	<DL	NA	7	<DL	NA	6	9	4	33	9	6	9
Sr (μg L^{-1})		**Reference**		5	<DL	NA	7	<DL	NA	6	8	5	33	8	5	9
Sr (μg L^{-1})		**Weir**	**	5	—	—	—	<DL	NA	6	10	2	33	7	3	9
TSS (mg L^{-1})		**Culvert**	NS	2.0	2.0	1.8	7	1.9	1.4	6	3.2	3.7	33	3.2	2.5	9
TSS (mg L^{-1})		**Reference**		2.0	2.3	3.1	7	1.2	0.5	6	2.0	1.6	33	2.7	2.2	9
TSS (mg L^{-1})		**Weir**	**	2.0	—	—	—	29.7	62.2	6	2.0	1.2	33	1.1	0.4	9
MeHg (ng L^{-1})		**Culvert**	*	0.030	0.196	NA	1	0.071	0.007	5	0.087	0.039	22	0.094	0.047	9
MeHg (ng L^{-1})		**Reference**		0.030	0.128	NA	1	0.050	0.021	5	0.090	0.034	22	0.094	0.047	9
MeHg (ng L^{-1})		**Weir**	*	0.030	—	—	—	0.083	0.038	4	0.079	0.033	22	0.066	0.024	9
Ba(μg L^{-1})		**Culvert**	NS	3	3	1	7	3	2	6	7	3	33	7	4	9
Ba (μg L^{-1})		**Reference**		3	4	1	7	<DL	NA	6	6	4	33	7	4	9
Ba (μg L^{-1})		**Weir**	*	3	—	—	—	4	2	2	8	2	33	6	3	9
Ca(mg L^{-1})		**Culvert**	NS	0.005	2.33	0.32	7	1.28	0.14	6	4.72	2.42	33	4.66	3.12	9
Ca (mg L^{-1})		**Reference**		0.005	2.23	0.31	7	1.09	0.24	6	4.57	2.68	33	4.41	2.84	9
Ca (mg L^{-1})		**Weir**	*	0.005	—	—	—	2.04	1.06	6	6.14	1.54	33	4.34	1.76	9
Chloride (mg L^{-1})		**Culvert**	NS	0.05	0.22	0.06	3	0.06	0.02	6	0.26	0.24	33	0.59	0.47	9
Chloride (mg L^{-1})		**Reference**		0.05	0.24	0.08	3	0.11	0.02	6	0.25	0.22	33	0.47	0.48	9
Chloride (mg L^{-1})		**Weir**	*	0.05	—	—	—	<DL	NA	6	0.12	0.17	33	0.13	0.11	9
Mg(mg L^{-1})		**Culvert**	NS	0.01	0.96	0.16	7	0.53	0.05	6	1.59	0.73	33	1.55	0.91	9
Mg (mg L^{-1})		**Reference**		0.01	0.90	0.13	7	0.42	0.09	6	1.54	0.83	33	1.50	0.90	9
Mg (mg L^{-1})		**Weir**	NS	0.01	—	—	—	0.65	0.25	6	1.66	0.34	33	1.18	0.37	9
Na (mg L^{-1})		**Culvert**	*	0.01	0.64	0.18	7	0.34	0.03	6	0.72	0.23	33	0.72	0.4	9
Na (mg L^{-1})		**Reference**		0.01	0.69	0.18	7	0.31	0.07	6	0.66	0.22	33	0.64	0.31	9
Na (mg L^{-1})		**Weir**	NS	0.01	—	—	—	0.39	0.08	6	0.70	0.09	33	0.59	0.17	9
Alkalinity (mg L^{-1} as $CaCO_3$)		**Culvert**	NS	1.0	6.2	0.6	4	3.6	0.5	6	15.1	9.8	33	12.8	8.8	9
Alkalinity (mg L^{-1} as $CaCO_3$)		**Reference**		1.0	6.3	0.6	4	3.5	0.6	6	14.4	10.1	33	12.2	7.8	9
Alkalinity (mg L^{-1} as $CaCO_3$)		**Weir**	NS	1.0	—	—	—	6.6	4.2	6	21.0	5.8	33	15.5	10.4	9
Redox (mV)		**Culvert**	NS	NA	288	NA	1	291	25	5	214	38	22	184	23	7
Redox (mV)		**Reference**		NA	277	NA	1	287	26	5	212	36	22	184	18	7
Redox (mV)		**Weir**	NS	NA	—	—	—	302	20	5	205	47	22	186	29	7
TP (μg L^{-1})		**Culvert**	NS	5	10	8	7	<DL	NA	6	11	10	33	12	14	9
TP (μg L^{-1})		**Reference**		5	6	4	7	<DL	NA	6	10	10	33	9	4	9
TP (μg L^{-1})		**Weir**	NS	5	—	—	—	8	1	6	17	17	33	5	2	9

Mining produced runoff waters that were visually high in suspended solids (Fig. 2.15). Larger peat pieces and woody debris, common at one metre depths, were also released downstream. Drainage waters appeared clearer within an hour of active peat mining. Significant correlations of TSS for each sample site are presented in Table 2.4.

Table 2.4: Correlations (Pearson's r, $p \leq 0.001$) of surface water analytes with total suspended solids (TSS). NS indicates not highly significant (i.e. $p > 0.001$). For sampling sites, see Fig. 2.1.

	Surface water sampling site		
Analyte	Weir	Culvert	Reference
Hg	0.92	NS	NS
Al	0.88	0.53	NS
Colour	0.79	0.44	0.47
reduced Fe	0.70	0.77	0.74
Fe	NS	0.60	0.64
Mn	NS	0.59	0.62
Ba	NS	0.56	0.62
Sr	NS	0.47	0.61
Ca	NS	0.45	0.58
Mg	NS	0.44	0.58
Alkalinity	NS	NS	0.62
Conductivity	NS	NS	0.58
Na	NS	NS	0.51
S	NS	NS	0.50
pH	NS	NS	0.49

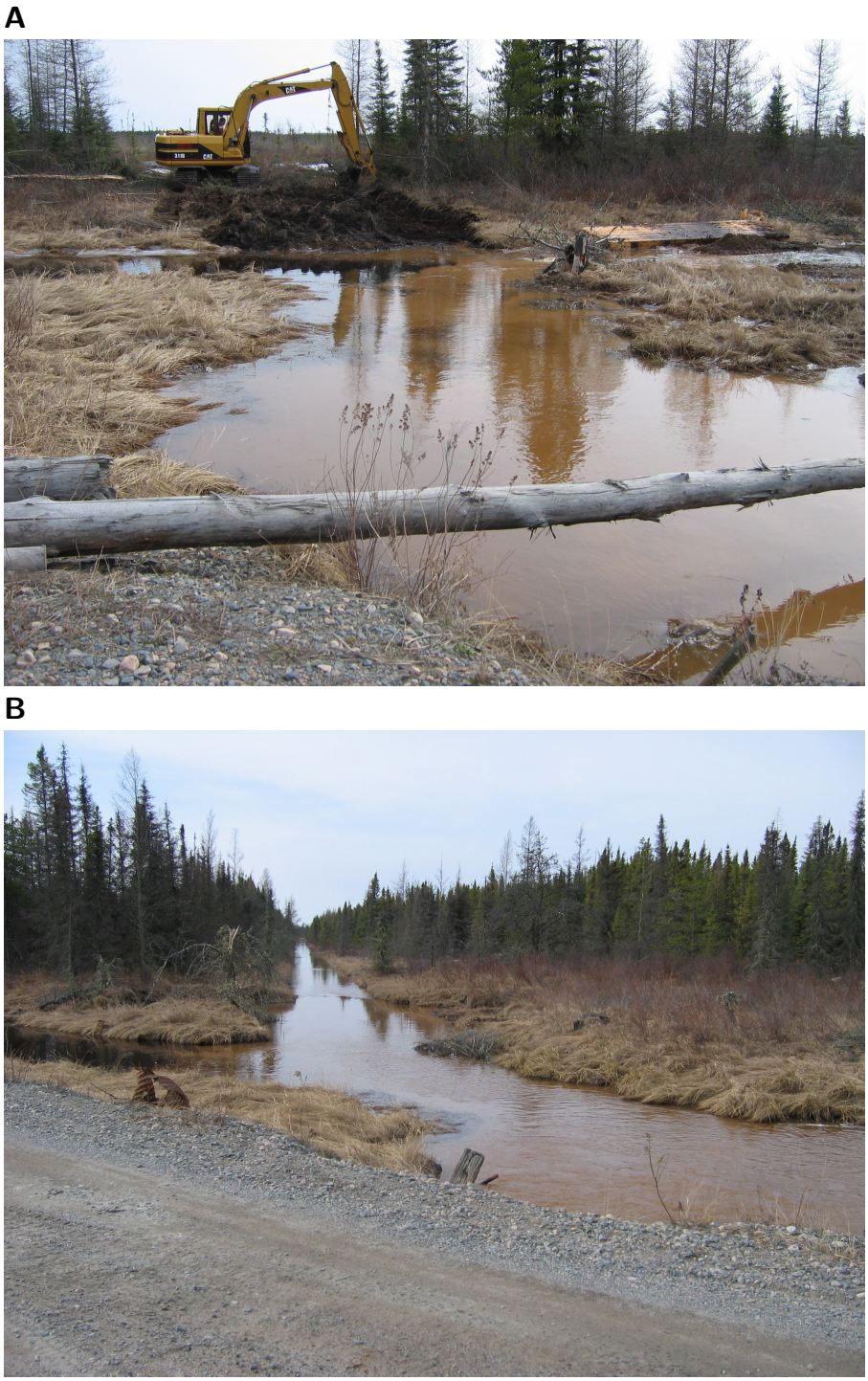


Figure 2.15: Observational evidence of solids discharged during active wet peat mining. Photo **A** was observed from the road atop the culvert location, looking upfield towards the experimental wet mining study site. Photo **B** was observed from the same location, looking downstream towards the receiving water ecosystem that consisted of pre-existing drainage ditches (circa. 1940's). See Fig. 2.1 for schematic representation.

2.3.3 Water Temperatures

Water temperatures in 2009 were seasonal for porewater and surface water (Fig. 2.16).

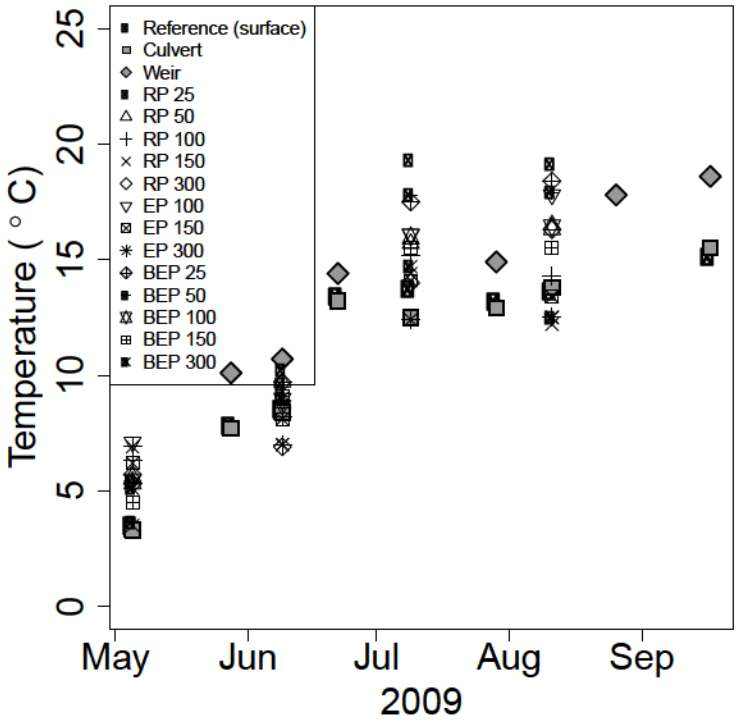


Figure 2.16: Temperatures of surface and porewater during 2009 sampling season. Piezometers coded: reference plot (RP), experimental plot (EP), back of experimental plot (BEP); numbers represent porewater depth in cm before peat extraction.

2.3.4 Bulk Precipitation

Rainfall and snowfall analytes likely to influence upper porewater (25 cm) and surface water quality are presented in Table 2.5.

Table 2.5: Chemistry of rainfall (unfiltered) collected near the experimental plot (EP) and EP of the study peatland from 31 July to 17 September 2009 (n=6), of porewater from RP at 25 cm below the peat surface (2009, n=4) and of snow composite samples collected in April 2009 from three areas in the study site (near EP, back of experimental plot (BEP) and the weir).

	Rainfall			25 cm Porewater		Snow	
Parameter	**Range**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
pH	5.44–6.13	5.76	0.31	5.58	0.04	5.32	0.14
Colour (TCU)	4.6–42.5	19.8	13.3	112	21.9	3.6	5.4
DOC (mg L^{-1})	1.70–10.3	3.91	3.31	11.6	2.4	0.62	0.32
Alkalinity (mg L^{-1} as $CaCO_3$)	1.50–4.35	2.93	1.13	8.08	3.88	1.63	0.21
Conductivity (μS cm^{-1})	4.30–15.6	8.22	4.14	21.6	6.8	5.57	0.65
TSS (mg L^{-1})	3.70–44.8	16.0	14.8	8.5	2.7	5.5	2.0
TN (mg L^{-1})	0.386–1.87	1.00	0.595	0.264	0.061	0.345	0.054
TP (μg L^{-1})	22–227	133	82	25	16	<5	NA
Ca (mg L^{-1})	0.134–0.592	0.347	0.168	2.66	1.06	0.199	0.063
Mg (mg L^{-1})	0.035–0.200	0.092	0.064	0.910	0.323	0.043	0.023
K (mg L^{-1})	0.18–1.36	0.50	0.44	<0.10	NA	<0.10	NA
Na (mg L^{-1})	0.03–0.49	0.13	0.18	0.41	0.05	0.103	0.021
Sr (μg L^{-1})	<5	<5	NA	5	2	<5	NA
Ba (μg L^{-1})	<3	<3	NA	6	<3	<3	NA
Fe (mg L^{-1})	0.006–0.034	0.016	0.010	1.75	0.73	0.057	0.027
Al (μg L^{-1})	<5	<5	NA	45	13	61	35
Mn (μg L^{-1})	4–19	8	5	65	38	4	3
Zn (μg L^{-1})	9–52	35	16	33	12	23	2
Hg (ng L^{-1})	6.05–24.3	14.2	6.99	5.98	2.88	2.11	1.37
MeHg (ng L^{-1})	<0.030–0.283	0.163	0.085	0.162	0.101	0.087	0.058

2.4 Discussion

Changes in porewater and surface water quality associated with wet peat mining and acrotelm transplant restoration were attributed to porewater quality of exposed peat layers, decomposition of transplanted acrotelm and natural seasonal fluctuations.

2.4.1 Porewater Changes

The increased pH, alkalinity, conductivity and cations in EP porewater (Table 2.1) were in agreement with trends in bog drainage waters summarized by Shotyk (1986b), who concluded such increases occur because more alkaline basal porewaters are released during peatland ditching. Similarly, Wind-Mulder et al. (1996) concluded that dry-harvesting upper bog peat, that coincidently exposed lower fen peat, resulted in peatlands with fen-type porewater (higher Na, K, Ca, Mg, sulphate and chloride) when compared to adjacent undisturbed sites. These findings would cause contrary impacts to downstream water courses than those surmised by Gleeson et al. (2006) and Winkler and DeWitt (1985), who suggested peat mining would result in acidification of adjacent waterbodies. Such discrepancies in the literature were noted by Aström et al. (2001), who likewise reported an increase in pH, alkalinity, conductivity, Mn, Ca and Mg in drainage waters after re-ditching forested boreal peat areas in Finland. Alkalinity, conductivity and cations showed evidence a decrease may be occurring at the more dessicated BEP site (Figs. 2.4, 2.5, 2.6, 2.7), suggesting changes in porewater chemistry are linked to the water regime of the exposed peat layers.

Once restoration was complete, a shift from a low bicarbonate concentration buffered pH to higher bicarbonate concentration buffered pH was evident. Though partly a consequence of basal porewaters, decomposition of peat under more aerobic conditions may also contribute to increased alkalinity. Organic matter decomposition was the dominant contributer to bicarbonate in shallow layers of a calcareous, intermediate fen (McLaughlin and Webster, 2010). Only an extended sampling of porewater beyond this study can determine whether one peatland function, that of increasing porewater acidity by providing additional weak acid sites, was restored because the acrotelm was returned to the mined plot.

Some specific metals (Ba, Sr, Fe, Mn) are expected to mobilize in porewater after peat mining and restoration as conducted here (Table 2.1). However, low concentrations, even if significantly changed from the reference site, do not appear to pose an environmen-

tal risk. Porewater concentrations of Ba and Sr (Fig. 2.8) were well below any aquatic or terrestrial toxicological impacts reviewed by Choudhury and Cary (2001) and Watts and Howe (2010), respectively. Porewater Fe concentrations (Fig. 2.9) did exceed the 0.300 mg L^{-1} Canadian Water Quality Guidelines (CWQG) for the protection of aquatic life (CCME, 2007), though this was also exceeded at the surface water reference site (Table 2.3). Porewater Mn concentrations (Fig. 2.9) were below 25% inhibition concentrations (IC25 4.67 mg L^{-1}) for brown trout (Stubblefield et al., 1997). Previous research on peatland geochemistry has focused on the release of metals due to peat acidification (Tipping et al., 2003). Model simulations for increases in pH, alkalinity and conductivity are required to predict peatland geochemistry associated with wet mining.

Porewater Hg concentrations were similar to surface waters, except during the active mining phase (Table 2.3). Porewater Hg was below the current CWQG of 26 ng L^{-1} (CCME, 2003) and an Ontario guideline of 100 ng L^{-1} (MOE, 1994) before and after wet mining, and did not differ significantly among time periods (Fig. 2.13). Concentrations of Hg in upper porewater were within rainfall and snowfall ranges (Table 2.5), suggesting the major anthropogenic source was likely limited to atmospheric deposition. Runoff from a Minnesota bog (Grigal et al., 2000) had higher Hg concentrations (12.9±2.2 ng L^{-1}), although watershed rain (9.9±1.2 ng L^{-1}) and bog snow (9.4± 1.4 ng L^{-1}) were comparable. Peatlands can be significant Hg sinks and are known production sites for MeHg (St. Louis et al., 1994; Ullrich et al., 2001; Grigal, 2002, 2003). However, sustained Hg associated porewater quality impacts due to wet peat mining appear negligible.

Surface porewater MeHg concentrations were variable (Fig. 2.11). A limited Before dataset made interpreting change here difficult. However, MeHg concentrations throughout this study were similar to pristine peat porewaters of the Experimental Lakes Area (ELA) (Heyes et al., 2000; Grigal, 2003; Branfireun, 2004; St. Louis et al., 2004), with less than detectable concentrations (<0.03 ng L^{-1}) measured in deeper porewater. This was similar to Grigal (2003), who noted MeHg in soil solutions was typically higher nearer the surface and in peatland discharge zones, and suggested a major source of MeHg to receiving water was due to surficial processes. Branfireun (2004) likewise found highly variable MeHg concentrations in poor fen porewater, noting higher values in shallow hollows than hummocks. Elevated concentrations of MeHg as a result of wet peat mining, acrotelm decomposition or peat dessication at this site were not evident (Fig. 2.11).

Porewater TP concentrations were similar to surface water (Fig. 2.13 and Table 2.3),

with no evidence of increased TP in porewater after peat mining. The potential of eutrophication due to peat mining was stated in several reviews (Winkler and DeWitt, 1985; Shotyk, 1986b; Surette et al., 2002; Gleeson et al., 2006). However, atmospheric contributions of TP (Table 2.5), plant movement of TP (Brown and Bates, 1990) and seasonal water trends (Figs. 2.14, A.1), were likely the major influences on porewater TP concentrations. Eutrophication due to released phosphorous may only be a mining concern at peatlands impacted by an anthropogenic source (e.g. agriculture, forestry). The low and naturally variable TP concentrations at this site makes eutrophication due to released phosphorous seem unlikely. It is hypothesized that increased nitrogen concentrations caused the observed algae within the plot (Fig. 2.3E).

Increased concentrations of TN in EP appeared after mining and restoration (Table 2.1), with water from BEP apparantly not a contributing factor (Fig. 2.13). Therefore, TN was likely released from transplanted acrotelm peat and basal peat porewaters. Koerselman et al. (1993) had found 95% of the TN released in *Sphagnum* laboratory mineralization assays was ammonia, with *Sphagnum* soils releasing significantly more ammonium than *Carex* soils. Wind-Mulder et al. (1996) found higher ammonium-nitrogen in wetter peatland sites that had been dry harvested and suggested increased aeration and higher pH allowed more aerobic and nitrifying bacteria to grow and more organic nitrogen to be mineralized. Higher redox and pH were measured in EP porewater (Figs. 2.10, 2.4, respectively). Kane et al. (2010) found the effects of water table manipulation on the various forms of dissolved nitrogen (ammonia, nitrate, organic N) to be variable. A detailed nitrogen study for wet mined and restored peatlands seems required.

Decreases in EP porewater colour and non-significant change in DOC (Table 2.1) were similar to Aström et al. (2001), who reported a decrease in total organic carbon concentrations in ditched peatland outflow compared to control site outflow. Decreased concentrations were attributed to decreased resident time of water in the ditched site, which likely occurred here. Kane et al. (2010) also found consistently higher DOC in lowered water table treatments than control and raised water table treatments. Leaching and export of DOC was common at drained peatland sites undergoing various rehabilitation strategies (Bourbonniere, 2009). Therefore, maintenance of a high water table after wet mining, which prevents peat dessication and/or porewater concentration of organic species, may mitigate elevated colour and DOC in mined plot outflow waters.

The porewater chemistry of this fen over a 3 m profile was quite typical for peatlands in general (Figs. 2.4 to 2.10). Porewater possessed low concentrations of metals, ions

and nutrients, with measurable alkalinity, colour and DOC. Water flow through the peatland prevented a substantial accumulation of organic components (e.g. colour, DOC) in porewater, as typically would occur in bogs (Gorham et al., 1985). As per Siegel et al. (1995), lack of an inflection point in conductivity profiles before mining (Fig. 2.5) suggests underlying clay substrate had little influence on measured water quality. When not impacted by mining, the stratified porewater profiles for most analytes were attributed to the greater decomposition of peat with increased depth, as described elsewhere (Gorham, 1949; Siegel and Glaser, 1987; Komor, 1994; Reeve et al., 1996; McLaughlin and Webster, 2010).

Before wet mining, gross intra-peatland differences in porewater between RP and EP (e.g. alkalinity Fig. 2.4; conductivity Fig. 2.5) have previously been noted in other peatlands (Summerfield, 1974), and were not unusual. Intra-RP porewater differences were especially noted in surface peat for nutrients (TN, TP), some metals (Al, Fe, Hg, Mn, S) and organics (colour, DOC). Variable meteoric water chemistry (Table 2.5), changes in DWT (Ingram, 1983; Devito and Hill, 1999), translocation of metals and nutrients by vegetation (Brown and Bates, 1990; Tyler, 1990), influences of wet and dry deposition (pollen, dustfall) and potential contamination by birds, small animals and insects, were all identified as contributing factors. However, the majority of factors would similarly influence all measured porewaters and be negated by the BACI experimental design. The design minimizes spatial and temporal confounding at a site (Green, 1979), and was suggested as "ideal" for determining water quality changes associated with peat extraction (Shotyk, 1986b).

2.4.2 Surface Water Changes

Obvious changes in porewater chemistry (Section 2.4.1) did not translate to similar changes at weir or culvert surface water sites. In general, all surface waters (Table 2.2, 2.3) were of similar water quality as upper layer acrotelm peat porewater from RP and BEP (Table A.1, A.2). Interpreting scattered MDC results (Table 2.3) was difficult for several reasons. First, seasonal variation in analyte concentrations was observed, though not consistent (Fig. 2.14, Appendix A.1). Second, when compared to waters from the relatively small mined and restored plot, there were large volumes of upland peatland water entering the surface water sites at this natural outflow location (OME, 2006). Third, analytes from catotelm peat below EP were likely released to porewater to an unknown

extent (Shotyk, 1986b) and influenced weir chemistry. Fourth, the far field location of the culvert site (≈110 m) facilitated adsorption/desorption and biogeochemical reactions to occur in water as it passed along the drainage ditch, in addition to receiving water inputs from the adjoining, pre-existing drainage network (Fig. 2.1). Fifth, additional waters would enter the drainage ditch from peat along the ditch sides, which had dessicated more so (Fig. 2.3H) than the BEP piezometer nest. Ideally, future research should be conducted on a larger scale with increased replication.

Significant increases in surface water Hg during the impact phase of wet peat mining (Table 2.2, Table A.9) suggest Hg concerns raised by others (Winkler and DeWitt, 1985; Gleeson et al., 2006) cannot be discounted here. Concentrations measured during this study were similar to runoff from an unimpacted central Swedish bog (range 1.20-13.39 ng L^{-1}), assumed to be less polluted by industrialization (Westling, 1991). Results for weir Hg here, as strongly associated with TSS (Table 2.4) and colour (Section 2.3.2), were comparable with impacted (filtered) and natural bog (unfiltered) drainage waters near a commercial peat operation in New Brunswick (Surette et al., 2002), who found up to 97% of Hg in drainage water associated with suspended solids. Both TSS and organic analytes are accepted transport mechanisms for Hg in aquatic systems (EPA, 1997a). Further investigations into whether particulate bound Hg species were bioavailable to benthic invertebrates is presented in Chapter 3.

Elevated solids were qualitatively (Fig. 2.15) and quantitatively (Table 2.3) released during active wet mining. Pavey et al. (2007) found suspended solids greater than 1.2 μm from active dry harvested bogs (New Brunswick), on average, exceeded the 25 mg L^{-1} discharge limit 72% of the time. The admittedly short impact period and small sampling size used for this northwestern Ontario study may have failed to identify environmental issues associated with released solids. Sallantaus and Pätilä (1985) reported TSS reached several thousand parts per million during peat ditching in Finland. Suspended solids released from peatland drainage may decrease light penetration and interfere with respiration and filter feeding in fish and invertebrates (Winkler and DeWitt, 1985). Peat solids were likely responsible for the deterioration of stream riffle beds (Laine and Heikkinen, 2000) and the reduced habitat quality for estuarine macrofauna (Ouellette et al., 2006). Since the release of solids also appears coupled to a release of metals (Table 2.4), the major pulse impact associated with peatland ditching and extraction likely requires some control by industry. (Kløve, 1997) offered suggestions.

This research showed elevated TSS concentrations in weir and culvert surface water

recovered after wet mining, being similar to that of reference site surface water (Table 2.3). Concentrations below 10 mg L^{-1} in 2009 are comparable to the 10.74 mg L^{-1} mean at control sites presented by Pavey et al. (2007), and within ranges for unimpacted sites in Minnesota (Clausen, 1980; Clausen and Brooks, 1983). In contrast, Aström et al. (2001) found drainage waters over two years from their ditched sites had, on average, three times the suspended material (>0.45 μm) than a control site. They attributed the difference to soil erosion. Elevated solids release from BEP during this study appeared limited to the first year after mining (Fig. 2.11). Continuous water flow through a wet mined peatland may mitigate a loss of peat material through erosion due to peat dessication.

2.5 Conclusions

Significant changes in water quality associated with wet peat mining a northwestern Ontario poor fen containing large quantities of energy peat were determined with a BACI experimental design. Porewater in the wet mined and restored experimental plot showed significant increases in pH, alkalinity, conductivity, some metals (Ca, Mg, Na, K, Sr, Ba, Mn, Fe) and TN when compared with reference plot porewater. Significant changes in porewater quality did not clearly translate to similar significant changes in surface water quality. Surface water results were difficult to interpret due to seasonality with the data. Since surface water TSS was positively correlated to Hg, initial findings suggest that solids released during the active phases of wet mining (ditching, extraction) remain a legitimate concern. However, concentrations of TSS and Hg in surface water from the mined and restored plot were found to recover to reference site concentrations within the same sampling season.

Chapter 3

Bioaccumulation Potential of Mercury Species from Peatlands of Interest for Peat Mining

3.1 Introduction

Mercury (Hg) and methylmercury (MeHg) are commonly accepted as detrimental to ecological and human health (WHO, 1989, 1990). Sediments are not only sinks for Hg, but are sites where the conversion of inorganic mercury (iHg) to the neurotoxic and bioaccumulative organic form MeHg occurs (Jensen and Jernelov, 1969; Ullrich et al., 2001). Mercury and notably MeHg will biomagnify in aquatic food webs. An initial bioaccumulation of Hg and MeHg by sediment dwelling benthic organisms may, through trophic transfer, result in MeHg concentrations in fish tissue toxic to fish predators (EPA, 1997b). Humans are principally exposed to MeHg through fish consumption (Clarkson and Magos, 2006).

This dissertation examines some environmental impacts associated with wet peat extraction (peat mining) in an open poor fen near Raith, Ontario, Canada (40°57′33″N, 90°6′20″S). Wetlands, including peatlands, methylate Hg and are large contributors of Hg and MeHg to adjoining water bodies (Grigal, 2003; St. Louis et al., 1994). Environmental impacts associated with wet peat mining were previously speculative and included the mobilization of metals such as Hg through suspended solids (Winkler and DeWitt, 1985; Gleeson et al., 2006). It has been determined that during the impact phase of wet peat

mining, a release of suspended solids and associated metals does (Chapter 2) or may (Chapter 4) occur. Such solids are apt to deposit in pre-existing (circa 1940's) drainage ditches that run alongside the research peatland. Furthermore, the experimental peat extraction and rehabilitation technique created a new "pond" and watercourse. Catotelm peat layers became "bottom" sediments. Such new aquatic habitats were identified here as a potential entry point of Hg and MeHg to pelagic systems.

Binding constants between Hg and organic matter at environmentally relevant concentrations are extremely high (Ravichandran, 2004) and inverse relationships between Hg uptake by benthic invertebrates and sediment organic matter have been reported (Breteler et al., 1981; Langston, 1982; Nuutinen and Kukkonen, 1998; Mason and Lawrence, 1999; Lawrence and Mason, 2001). Peat, by its definition, is highly organic. Organic matter content from the research peatland exceeded 90% (DST, 2005), much higher than previous studies. Furthermore, previous conclusions from ecosystems receiving particulate runoff from dry harvested peatlands suggested Hg was not an issue (DiGiulio and Ryan, 1987; Surette et al., 2002). Therefore, total mercury (THg) and MeHg in sediments from an experimentally wet mined peat site were hypothesized not to bioaccumulate in benthic organisms feeding on that sediment.

To test the hypothesis, laboratory and field Biota-Sediment Bioaccumulation Factors (BSAFs) for THg and MeHg from the impacted site were determined. A BSAF is the ratio of a given toxin in the tissue of an organism to that found in its sediment habitat (EPA, 1995). The BSAFs for THg reported for lower trophic level aquatic organisms in a variety of ecosystems ranged from <1 to over 100 (Greichus et al., 1978; Chapman et al., 1979; Hildebrand et al., 1980; Wren and MacCrimmon, 1986; Lindqvist et al., 1991; Beauvais et al., 1995; Thomann et al., 1995; Tremblay et al., 1995, 1996; Department of Energy, 1996; Cardoso et al., 2009), where the highest values were associated with low organic matter (sand) type sediments. Fewer data were available for MeHg, with MeHg BSAFs generally an order of magnitude higher than THg BSAFs (Saouter et al., 1993; Tremblay et al., 1996; Nuutinen and Kukkonen, 1998; Mason and Lawrence, 1999; Lawrence and Mason, 2001). DeForest et al. (2007) suggested that within a given aqueous ecosystem, MeHg BSAFs would exceed those of THg BSAFs. Reviews of water-only bioaccumulation potentials for metals and MeHg demonstrated that bioconcentration and bioaccumulation factors are variable and inversely related to exposure concentration, suggesting the use of such general values in site-specific environmental evaluations may not be in the best interest of protecting ecological and human health (McGeer et al., 2003; DeForest et al.,

2007).

The objective of this research was to determine site-specific BSAFs for THg and MeHg from a northwestern Ontario peatland experimentally wet mined and comment directly on the bioaccumulation potential of THg and MeHg from the impacted area. Three laboratory bioaccumulation trials and a kinetic trial using *Lumbriculus variegatus* (Ingersoll et al., 1995; EPA, 2000c) were conducted and results compared to indigenous benthic invertebrates and literature data. Bioaccumulation methods were necessarily refined between trials due to some difficulties in assessing very organic (>90%) and ambient Hg concentration (THg<81 ng g^{-1} dw) sediment. To date, experimentally derived BSAF for peatlands are limited, hindering our ability to predict food chain movements of Hg associated with ecosystem peturbations such as wet peat mining.

3.2 Methods

3.2.1 Bioaccumulation and Kinetic Trials

Bioaccumulation and kinetic trials were based on methodology by EPA (2000c), with noted modifications. The freshwater benthic worm *Lumbriculus variegatus* (Oligochaeta) was used, being tolerable to a wide range of sediment physicochemical characteristics (Ankley et al., 1994), including polluted sediments (Phipps et al., 1993). Worms were exposed to organic "peat-type" sediments from the wet mined peatland (Fig. 3.1) for 28 days prior to determining concentrations of THg and MeHg in tissue. To confirm achievement of tissue steady state and determine if methylation of iHg occurred in sediments under laboratory conditions, an additional kinetic trial was conducted using sediment spiked with iHg.

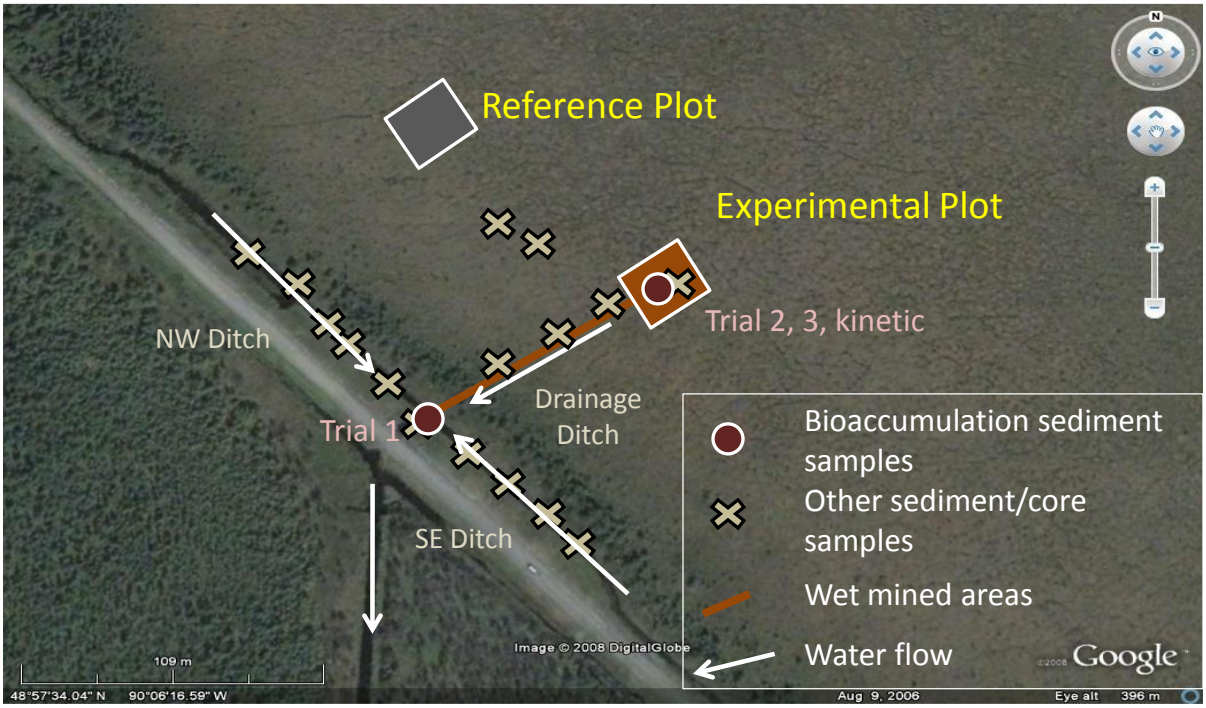


Figure 3.1: Sites sampled for general physico-chemical analysis, bioaccumulation and kinetic trials. Figure not to exact scale. Symbols for location only and do not represent an exact number of replicates.

Test Organism

Cultures of *L. variegatus* were initiated at Lakehead University from organisms obtained from the United States Environmental Protection Agency (USEPA) laboratory in Duluth, MN. Worms were housed in flow through aquaria (23±3°C, 16:8 hr light:dark cycle). Culture water was municipal water (L. Superior), dechlorinated and continuously aerated (Table 3.1). Worm substrate was unbleached paper towel and food was trout chow (2-3× per week). Trout chow pellets were analyzed once and found to contain 82 ng g^{-1} of THg (dw). Worms analyzed directly from culture (unexposed) had 9.78 ± 3.82 ng g^{-1} (ww, n=25) THg and 4.64 ± 0.75 ng g^{-1} (ww, n=11) MeHg in tissue (Fig. 3.3). Worm tissue moisture factor (ww/dw) averaged 8.14±0.65 (n=44).

Table 3.1: Culture water/renewal water quality (dechlorinated municipal, L. Superior) sampled from bottom tank of water renewal system (Fig. 3.2A) on Days 0, 7, 14, 21 and 27 of the bioaccumulation trials; n=15.

Analyte	**Mean ± SD**
Alkalinity (mg L^{-1} as $CaCO_3$)	46.7±9.4
Conductivity (μS cm^{-1})	113±6
Hardness (mg L^{-1} as $CaCO_3$)	45.6±1.1
Total ammonia (mg L^{-1} as N)	< 0.03
pH	7.25±0.18

Test Equipment and Conditions

A modified Zumwalt system (EPA, 2000c; Zumwalt et al., 1994), custom built (Environmental Consulting and Testing Inc., Superior, WI), provided automated overlying water renewal to each exposure vessel (Fig. 3.2 A). Renewal water was culture water (Table 3.1). The system was housed in a laboratory on a 16:8 hr light:dark cycle. At least 30% of the overlying water in a test vessel was renewed every 30 min during a trial, with temperature maintained at (23±3°C). The *L. variegatus* were not fed during trials (EPA, 2000c).

During the recommended 4-day screening test (EPA, 2000c), *L. variegatus* showed no obvious aversions to preliminary ditch site sediment samples (Fig. 3.1), nor to commer-

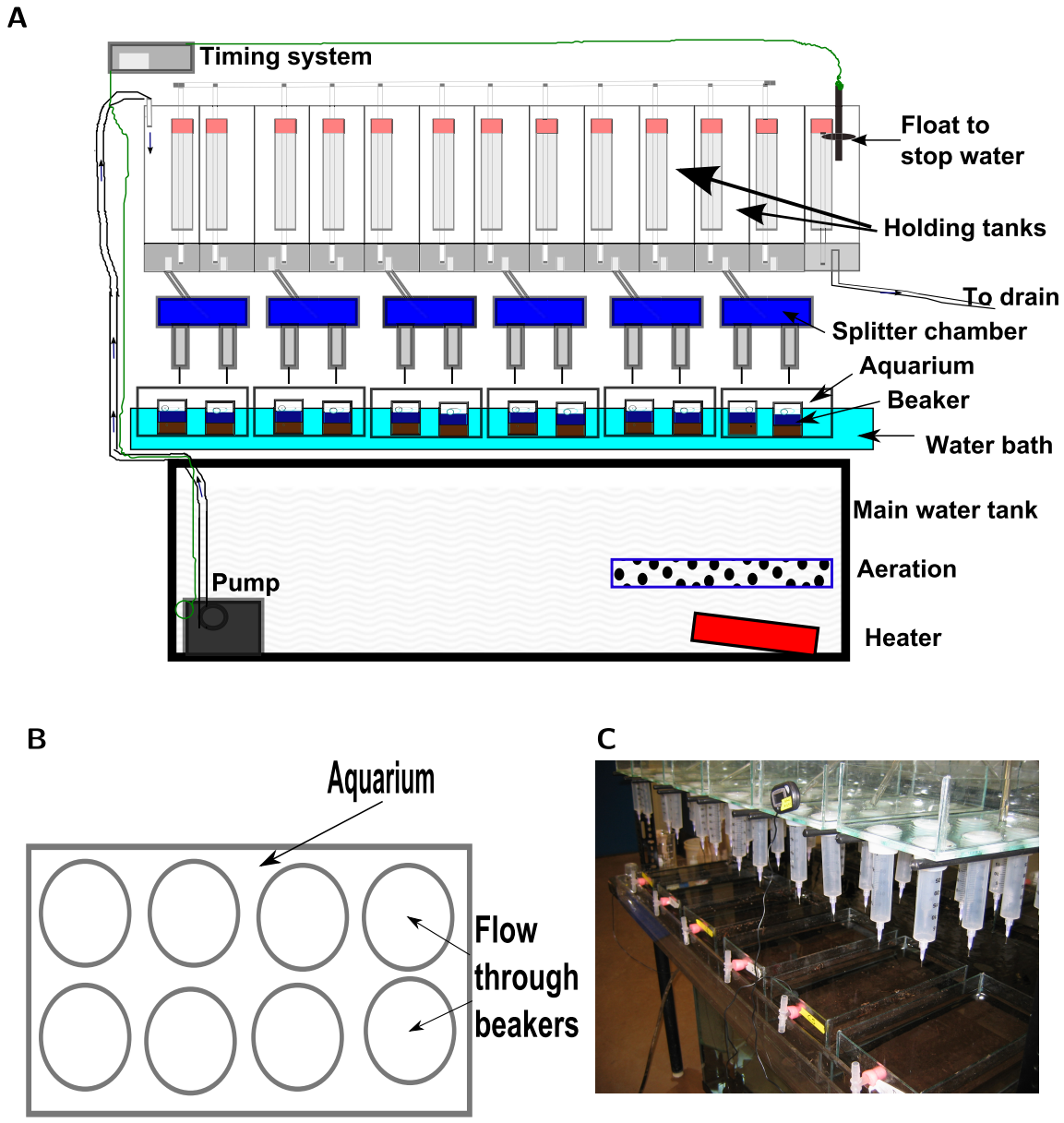


Figure 3.2: Schematic of the modified Zumwalt renewal system used here, as described in Appendix A of EPA (2000c). **A** shows a side view schematic of the overall renewal system. Water is pumped at set intervals from the main water tank (bottom) to the first in a series of holding tanks (top left). Each holding tank fills, before overflowing to fill its adjacent tank. When the final tank in the series is full (top right), a float sensor shuts off the pump. Draining of the final tank creates suction, that releases stoppers of each holding tank simultaneously, draining 1 L of renewal water into splitter chambers where eight 50 mL syringes distribute water to eight independent 300 mL beakers of sediment containing *L. variegatus*. **B** shows a top view layout of the eight individual flow through beakers in the 3 L aquarium. Photo **C** was Bioaccumulation Trial 1.

cially available pre-packaged cattle manure (composted) used as control sediment (pH 7.22-7.51, loss on ignition (LOI) 33-37%, bulk density 0.23-0.32 g cm^{-1}, total organic carbon 14-16%). Packaged manure was chosen because of its high organic content and as recommended in EPA (2000c) Worms embedded their anterior in upper centimeters of sediment while posteriors in overlying water displayed characteristic undulatations for gas exchange. Worms became darker in colour throughout an exposure, an indication sediment organic matter was being ingested. These observations were common to subsequent bioaccumulation and kinetic trials, with no mortality noted. After 28 day exposures, worms appeared to have worked upper layers of sediment, qualitatively of finer consistency than lower sediment. Worms did not qualitatively show any adverse behaviour (mortality, lack of feeding, lack of burrowing, lack of gas exchange) to Hg concentrations in spiked sediment kinetic trials.

Bioaccumulation Trial Experimental Approach

A bioaccumulation trial consisted of *L. variegatus* exposed for 28 days to randomized replicated experimental treatments consisting of experimental ("peat-type", Fig. 3.1) or control (manure) sediments. Control sediment did not show evidence of external contamination from the system (Appendix B). Parameters altered between bioaccumulation trials are summarized in Table 3.2.

At the conclusion of a trial, worms were removed from the sediment. It was difficult to separate *L. variegatus* from both experimental and control sediments. Therefore, different exposure vessels and tissue composites were used for each trial (Table 3.2). For Trial 1, more than one hour per replicate was required to manually remove *L. variegatus* from sediments. Insufficient tissue mass was collected and only THg determined. Method refinement was deemed essential. Smaller aliquots of sediment in smaller vessels were used in Trial 2 (Table 3.2). Separation times for one control and one experimental replicate were still lengthy (>1 h). Therefore, on Day 29, a sugar flotation method reported by Anderson (1959) was employed for the remaining five replicates of each sediment type. Neither THg nor MeHg tissue concentration were significantly affected by sugar flotation (Chapter 5). Sugar floation was used for Trial 3 and Kinetic Trial.

After separation from sediment, organisms were rinsed thrice with renewal water and allowed to purge their guts overnight (>6 h) in separate beakers of flowing, aerated culture water (Mount et al., 1999). Worms were then rinsed thrice with Type I water

Table 3.2: Summary of conditions altered between Bioaccumulation and Kinetic Trials. Alterations were necessary to facilitate timely separation of *L. variegatus* from organic sediment and recover sufficient biomass for both THg and MeHg analysis.

	Bioaccumulation			Kinetic
Parameter	**Trial 1**	**Trial 2**	**Trial 3**	**Trial**
Sample date	13-Aug-08	26-Aug-09	7-Jun-10	7-Jun-10
Day 0	15-Aug-08	28-Aug-09	8-Jun-10	9-Jun-10
Exposure vessel size	3000 mL	300 mL	300 mL	300 mL
Sediment aliquot size per vessel	1000 mL	100 mL	100 mL	100 mL
Experimental sediment spiked with iHg	no	no	no	yes
Number vessels for tissue composite (Control)	1	8	1	Trial 3
Number vessels for tissue composite (Experimental)	1	8	6	2
Control tissue n	6	6	6	Trial 3
Experimental tissue n	6	6	6	3
Initial mass of *L. variegatus* per vessel	6-10 g	3-5 g	3-5 g	≈2 g
Sugar flotation for separation of *L. variegatus*	no	yes (n=5)	yes	yes
Tissue THg determined	yes	yes	yes	yes
Tissue MeHg determined	no	yes	yes	yes

before being accurately wet weighed to Hg clean and pre-weighed glass vials for freeze drying (Labconco Freezone 12), re-weighing, digestion and analysis. Aliquots of sample sediments post-trial and not exposed to sugar solution were sieved (#60, 250 μm) to remove overlying water, composite and frozen for analysis.

Bioaccumulation and kinetic trial quality control (QC) included weekly sampling of overlying water for pH, alkalinity, conductivity, dissolved oxygen and ammonia (Table 3.3), as per EPA (2000c). Temperature in random exposure vessels was monitored nearly daily and was within 3°C of the recommended 23°C.

Table 3.3: Water quality (ranges) for control and experimental sediment overlying water measured during the bioaccumulation and kinetic trials

Analyte	**Control**	**Experimental bioaccumulation trials**	**Experimental kinetic trial**
Alkalinity (mg L^{-1} as $CaCO_3$)	44.6-78.8	35.5-113	44.0-45.4
Conductivity (μS cm^{-1})	107-139	91.8-119	112-118
Hardness (mg L^{-1} as $CaCO_3$)	44.7-52.4	23.0-52.2	44.2-45.6
Ammonia (mg L^{-1} as N)	<0.03-0.14	<0.03-0.27	<0.03-0.13
pH	6.97-7.57	6.64-7.50	7.18-7.48
Temperature (°C)	21.6-24.6	21.3-24.8	21.4-22.9
Dissolved oxygen (%)	68-101	67.6-101	70.9-88.0

Kinetic Trial Experimental Approach

A kinetic trial was performed using the same sediment as Trial 3 (Table 3.2). The kinetic trial was performed by spiking iHg into site sediment at a concentration 3 orders of magnitude greater than the nominal sediment concentration. Such an elevated Hg concentration would produce a MeHg concentration significantly above nominal values if methylation was occurring under experimental conditions. The *L. variegatus* BSAF would be calculated over time (Day 1, Day 3, Day 7, Day 14, Day 28).

On the day the sediment was sampled (Day -2), experimental sediment was spiked. Sediment (50 mL) was placed in 40 flow-through beakers (300 mL) to which 200 μL of 1000 mg L^{-1} inorganic Hg (in 10% HNO_3, Fisher Scientific) and 100.0 mL of Type I water was added. Sediments were mixed and left to equilibrate on the counter overnight

(≈12 hrs) at room temperature (≈21°C). Therefore, the estimated sediment concentration was 57.1 μg g^{-1} (dw), assuming a bulk density of 70 μg cm^{-3} (Table 3.8, Experimental plot, 2009). On Day -1, eight beakers each were set in five 3 L aquaria of the Zumwalt system (Fig. 3.2B,C) and water renewal initiated (Fig. 3.2A). Test worms were isolated from culture on Day -1.

On Day 0, each of the five aquarium was randomly assigned an end day as Day 1, Day 3, Day 7, Day 14 and Day 28. About 2 g of isolated *L. variegatus* were added to six of the eight beakers per aquarium on Day 0. The two remaining beakers were used for THg and MeHg sediment analysis. There was an assumption that no effect due to the physical segregation of aquaria (i.e. pseudoreplication) occurred with this experimental design (ASTM, 2010). On specified end days, worms were separated from sediment by sugar flotation as in Trial 3 and composite (Table 3.2), while sediment in beakers without worms was sieved (#60, 250 μm), composite and frozen for analysis.

Calculation of Biota Sediment Accumulation Factors

The BSAF is formally defined as "the ratio of a substances lipid-normalized concentration in tissue of an aquatic organism to the organic carbon-normalized concentration in surface sediment, in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of the average surface sediment in the vicinity of the organism" (EPA, 1995). Lipid and carbon normalization is not recommended for metals or MeHg (EPA, 2000a), thus BSAF was calculated as

$$BSAF = \frac{C_t}{C_s} \tag{3.1}$$

where C_t was the mean concentration of THg or MeHg in worm tissue on the end day of a trial (Fig. 3.3) and C_s was the mean concentration of THg or MeHg in sediment (Table 3.4), both expressed as ng g^{-1} dry weight (dw). For this research, both the tissue and sediment moisture factors were similar (≈10), so dry weight BSAFs approximate wet weight BSAFs.

It became evident that sediment MeHg concentration may vary over the 28 days (Table 3.4), influencing BSAF. Higher sediment concentrations result in a lower estimate of BSAF (Eq. 3.1), thus ranges were calculated where possible. For Trial 1, THg C_s was determined on sediments frozen on Day -1. For Trial 2, Day 28 sediment for THg and Day -1 sediment for MeHg were inadvertently discarded and not preserved for analysis.

Table 3.4: Concentrations of THg and MeHg (mean±SD (n)) in sediment used for bioaccumulation trials and to calculate Biota-Sediment Bioaccumulation Factors (BSAFs). An exception was the asterisk result, which were results for sediments collected from the same site one month previous to actual sampling for Trial 2. NA was not analyzed.

	Experimental Sediment		Control Sediment	
	THg (ng g^{-1} dw)	MeHg (ng g^{-1} dw)	THg (ng g^{-1} dw)	MeHg (ng g^{-1} dw)
Trial 1: Day -1	33.2±1.9 (6)	0.080±0.008 (6)	28.7±1.3 (6)	0.064±0.013 (6)
Trial 1: Day 28	NA	NA	NA	NA
Trial 2: Day -1	39.5±6.7 (2)	0.253±0.164 (6)*	43.0±2.2 (2)	0.442 (1)
Trial 2: Day 28	NA	1.32 (1)	40.8±2.5 (2)	1.24 (1)
Trial 3: Day -1	80.5±6.9 (3)	0.559±0.192 (2)	59.1±4.0 (3)	0.527±0.089 (2)
Trial 3: Day 28	73.5±4.0 (2)	1.60±0.014 (2)	42.6±3.9 (2)	0.344±0.001 (2)

Since methylation occurred in experimental sediment of Trial 3, data for the sediment collected one month previous to Trial 2 was used to calculate a range of MeHg BSAFs.

For the kinetic trial, a mean experimental BSAF was calculated for each day that both a tissue and sediment concentration were measured (excluding Day 0; Table 3.6 and 3.7, Kinetic Trial, data, 2010). In addition, theoretical BSAFs from models were calculated (Table 3.6 and 3.7, Kinetic Trial, 2010, model). For THg, BSAF was calculated from the ratio of estimated steady state tissue concentration to the nominal sediment concentration (Fig. 3.4). For MeHg, BSAF was calculated from the ratio of slopes for linear models describing the production of MeHg in sediment and the uptake of MeHg in worms (Fig. 3.5).

For benthic invertebrates, mean whole body tissue concentration (excluding shells or casings; Fig 3.3 converted to dw) and 2008 mean sediment concentration (Table 3.8) were used to calculate a BSAF. To compare values here to literature values, BSAFs were estimated from studies that provided both sediment and tissue concentrations. In some instances, ww to dw tissue conversion factors were used, being median values reported by Ricciardi and Bourget (1998) (bivalvia, 8.6; oligochaeta, 18.0; polychaeta, 18.7) or 10 for mayflies as reported by Beauvais et al. (1995). A value of 10 was used for invertebrates here and for studies with undisclosed or composite species tissue.

3.2.2 Invertebrate Sampling

Hester-Dendy samplers were deployed 29 August 2008 for one month, located in similar areas sampled for sediment (Fig. 3.1). Samplers and storage jars were acid washed, rinsed with Type I distilled deionized water and stored clean prior to deployment. Upon collection, samplers were placed in storage jars with site water for transport to the lab where invertebrates were immediately sorted from debris, separated from shells or cases, placed in Hg clean glass vials and frozen until digestion and analysis. Rigorous identification was not undertaken. Samplers were not highly effective at capturing large samples of invertebrates. Species common to the samplers were caddisflies, mayflies, craneflies, midges, true bugs and snails. There was insufficient tissue mass to analyze both THg and MeHg for each organism. Therefore, randomly chosen individual organisms were analyzed for THg or MeHg and reported simply as invertebrates with a range of concentrations presented.

3.2.3 Sediment Sampling

Sediment for bioaccumulation testing and additional chemistry were collected from the mined site and from shallow (1-2 m), pre-existing drainage ditches (circa 1940) in both southeast and northwest directions (Fig. 3.1). Bioaccumulation experimental sediment were composites from an impacted area of interest and collected with a 1 L ponar dredge. About 10 L of sediment collected, homogenized and held in a walk-in cooler (2-6°C) until Day -1. Sediments were re-homogenized immediately before use.

For 2008-2009 general physico-chemical testing of ditch samples (Fig. 3.1), the top 30 to 50 cm layers of sediment were collected via a PVC pipe core device and held in zip-lock bags. In 2010, cores (50 cm length) were taken with a Russian side-core peat sampler from the peatland itself (shallow=0.75 m below peat surface; deep=2.0 m below peat surface) and from the experimental plot drainage ditch (0.50 m). These samples were analyzed fresh for redox potential then immediately frozen until analysis.

Experimental sediments were best described as “peaty” in nature, with muskeg type consistency. They were highly fibrous, dark in colour and very organic. In some cases, plant material was visible. An early analysis on one confluence ditch sample found 47% total organic carbon and less than 5% mineral content (LOI=95%). Control manure was 15% total organic carbon.

3.2.4 Statistical Methods

Data are presented as mean ± SD unless stated. Statistical analysis were conducted using R (R Development Core Team, 2010). Results for QC samples (sediments, peat and tissue) are based on dry weight (dw). Rules for error propagation were followed when calculating SDs for means of means (Bevington and Robinson, 2002). Kinetic data (tissue concentration over time) for MeHg fit a linear regression model, while THg was fit to a Michaelis-Menton equation (Lopez et al., 2000):

$$C = \frac{C_m \cdot t}{K_m + t} \tag{3.2}$$

where C_m was the maximum tissue concentration, K_m was 50% maximum concentration and t was time (in days). Uptake of measured Hg species were net accumulation, without differentiating between uptake and depuration rates. Steady state was operationally observed when three consecutive and statistically indistinguishable (p adjusted Holm comparison) time point concentrations occurred (ASTM, 2010; Kennedy et al., 2010). A valid bioaccumulation trial should reach 80% steady state (EPA, 2000c).

3.2.5 Analytical Methods

Several reference standards were chosen to assure the quality of data. Certified peat was generously provided by Dr. John G. Farmer (Edinburgh, Scotland). This reference material (NIMT/UOE/FM/001) was collected from an ombrotrophic peat bog at Flanders Moss, Scotland in 2001 and air dried to 10% moisture content, milled, sieved and homogenized. The certification was a co-operation between the School of GeoSciences, University of Edinburgh, a further 13 participant laboratories and the National Institute of Metrology (Thailand) by means of an inter-laboratory comparison exercise. A certificate of measurement was provided. A house peat QC was prepared by Lakehead University Environmental Laboratory (LUEL) from peat collected the research site in 2007, air dried, milled, sieved and homogenized. Quality control charts (warning limit 2×SD, control limit 3×SD) were established after 30 data points were available. The DORM-2 dogfish muscle certified reference material for trace metals was purchased from the National Research Council of Canada as prepared by the Canadian Institute for Fisheries Technology, Technical Uniersity of Nova Scotia, Halifax.

Sediment bulk density (BD) was determined by difference on known volumes of wet sediment dried at 103°C. Data were also used to calculate moisture factors (ww/dw) for

wet weight to dry weight conversions. Sediment pH and conductivity were determined by calibrated electrode on the overlying water after a 1:1 sediment:water mixture was mixed for 30 min and allowed to settle for an additional 30 min. Redox was measured by electrode with an accuracy verified with Zobell's solution. Total organic matter was estimated by LOI, determined after ashing known dry weights of a sample at 550°C. Total organic carbon content for Trial 1 sediment was determined on dried acidified sediments by thermal decomposition, amalgamation and atomic absorption spectroscopy (LECO CNS-2000). A site consistent ratio of organic carbon to LOI was assumed for sediments.

The THg in wet sediment and freeze dried tissue was determined as per USEPA Method 1631 (EPA, 2002, 2001a). Digestion and reflux with heated strong acids was followed by oxidation with BrCl before analysis via an atomic fluorescence spectrophotometer after purge and trap techniques (Brooks Rand Model III). Quality control included analysis of blanks, duplicates, spikes and quality control samples. Certified peat, house peat QC and DORM-2 were analyzed with each batch of samples. Recovery of THg in certified peat (Table 3.8 samples) was 83.5±10.6% (n=4). Increased recovery was noted when peat was digested with HNO_3/H_2SO_4 acids rather than HCl/HNO_3. The $HCl:HNO_3$ was used for sediment only in 2008 to expidite analysis by providing digestate aliquots for THg and total extractable metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES). In 2009 and 2010, separate sediment digestions were performed.

The MeHg in wet sediment was extracted with dilute H_2SO_4 overnight as per Branfireun and Roulet (2002). Sample preparation and analysis followed USEPA Method 1630 (EPA, 2001b), which included distillation, ethylation, purge and trap, gas chromatography and atomic fluorescence spectroscopy. Analysis of house peat QC by Dr. Hintelmann at Trent University was 1.71 ng g^{-1} (dw; n=3, relative SD=2%). Dr. Hintelmann further measured 1.68 pg of MeHg formed for every 15.5 ng of ^{200}Hg spiked to house peat QC (n=3), equating to 0.011% methylation. Simultaneously, Bloom et al. (1997) and Hintelmann et al. (1997) reported the distillation process was prone to artifact formation of MeHg, the later finding an overestimation of MeHg in organic sediments (especially peat) up to 80%. Based on QC results here (Table 3.5) being consistant with external analysis, artifact MeHg did not appear to be an issue.

The MeHg in freeze dried worm and invertebrate tissue was leached as per Hintelmann and Nguyen (2005) via an overnight extraction in heated 4N HNO_3, followed by analysis

after ethylation and chromatography as above. Certified tissue QC was DORM-2. No more than 100 μL of leachate could be ethylated without observing low MeHg recoveries.

Table 3.5 provides Hg QC data. For sediment, recoveries of analytes in certified QC peat for Al, Fe, Mn, P and Zn were 85.7±26.1%, 95.2±11.2, 102±32.3%, 94.7±4.5% and 106±16.3% respectively (n=4). There was no certifed value for MeHg (see or Table 3.5) or S (4134±375 μg g^{-1}).

Table 3.5: Quality control data for sediment and tissue analysis of total mercury (THg) and methylmercury (MeHg), expressed as mean percent recovery (% Rec.), mean percent relative deviation (% RD) or mean concentration. NA was not analyzed, n in parentheses.

	DORM-2		**House Peat**	
	THg (% Rec.)	MeHg (% Rec.)	THg (% Rec.)	MeHg (ng g^{-1})
Trial 1	94.5 (2)	NA	NA	NA
Trial 2	97.6 (3)	79.1 (3)	NA	1.65 (1)
Trial 3	88.7 (2)	90.1 (3)	NA	1.44 (2)
	Certified Peat		**Tissue**	
	THg (% Rec.)	MeHg (ng g^{-1})	THg (% RD)	MeHg (% RD)
Trial 1	60.1 (1)	4.29 (1)	NA	NA
Trial 2	92.4 (2)	3.48 (2)	5.7 (2)	3.7 (2)
Trial 3	95.7 (3)	NA	2.5 (1)	9.7 (1)

3.3 Results

3.3.1 Biota-Sediment Bioaccumulation Factors (BSAFs)

Laboratory derived THg and MeHg BSAFs (dw) for *L. variegatus* after 28 day exposures to sediments from an experimental wet peat mining site were similar between trials and comparable to field data and prior studies that involved sediments with some, but relatively low, concentrations of organic matter (Table 3.6 and Table 3.7, respectively).

Table 3.6: Laboratory (*) and field THg Biota-Sediment Bioaccumulation Factors (BSAFs) (dw unless stated).

Reference	**Organism**	**THg BSAF**	**Organic matter**	**Study location**
Trial 1, 2008	*L. variegatus*	1.39	>90% (peat)	Fen, Northwestern ON*
Trial 2, 2009	*L. variegatus*	1.59	>90% (peat)	Fen, Northwestern ON*
Trial 3, 2010	*L. variegatus*	0.91-1.00	>90% (peat)	Fen, Northwestern ON*
Kinetic Trial, 2010, data	*L. variegatus*	2.21±0.37	>90% (peat)	Fen, Northwestern ON*
Kinetic Trial, 2010, model	*L. variegatus*	3.14	>90% (peat)	Fen, Northwestern ON*
This study, 2008	Invertebrates	1.2-6.8	25.3-94.6%	Fen, Northwestern ON
Fink, 2008 (unpublished)	*L. variegatus*	0.95-5.11	10.9-85.4% (peat)	Everglades, FL*
Surette et al. (2002)	Clams, shrimp	<1.0	90% peat	Mill Creek, NB
Surette et al. (2002)	Clams, shrimp	0.80-1.04	0% peat	Mill Creek, NB
Lawrence and Mason (2001)	Amphipod	≈1.0	>2%	Fishing Bay, MA*
Lawrence and Mason (2001)	Amphipod	>100	≤1% (sand)	Patuxent River MA*
Mason and Lawrence (1999)	Clams, amphipods	<1->100	<1-3% carbon	Baltimore Harbor, MD
Tremblay et al. (1996)	Mayflies	2.2-4.9	2-4% carbon	Duncan Lake, QC
Tremblay et al. (1996)	Caddisflies	2.4-4.6	2-4% carbon	Duncan Lake, QC
Beauvais et al. (1995)	Mayflies	0.68-2.87	6-10%	Mississippi River
Tremblay et al. (1995)	Zooplankton	1.35	0.6-63.8%	ON-QC; 73 lakes; (mean)
Lindqvist et al. (1991)	Zooplankton	2.2	≈7-18% carbon	Sweden; 8 lakes (mode)
Lindqvist et al. (1991)	Macroinvertebrates	17.2	≈7-18% carbon	Sweden; 8 lakes (mode)
DiGiulio and Ryan (1987)	Clams	17.7	<20%	Pungo River, NC
DiGiulio and Ryan (1987)	Clams	112	<2%	Pungo River, NC
Wren and MacCrimmon (1986)	Clams	7.37	not stated	Tadenac Lake, ON
Wren and MacCrimmon (1986)	Clams	11.1	not stated	Tadenac Bay, ON
Breteler et al. (1981)	Invertebrates	0.5-5.5	highly organic marsh	Great Sippewissett, MA
Hildebrand et al. (1980)	Invertebrates	1.50-3.71	silt/clay, <44 μm	North Fork Holston River, VA
Chapman et al. (1979)	Tubificids	1.69, 3.98	not stated; <63 μm	Fraser River, B.C
Greichus et al. (1978)	Chironomids	5.2	not stated	Lake Nakuru, Kenya
Greichus et al. (1978)	Benthic insects	3.2	not stated	Lake Nakuru, Kenya

Table 3.7: Laboratory (*) and field MeHg Biota-Sediment Bioaccumulation Factors (BSAFs) (dw unless stated).

Reference	**Organism**	**MeHg BSAF**	**Organic matter**	**Study location**
Trial 1, 2008	*L. variegatus*	NA	>90% (peat)	Fen, Northwestern ON*
Trial 2, 2009	*L. variegatus*	12.9-67.4	>90% (peat)	Fen, Northwestern ON*
Trial 3, 2010	*L. variegatus*	9.92-28.4	>90% (peat)	Fen, Northwestern ON*
Kinetic Trial, 2010, data	*L. variegatus*	8.79±1.76	>90% (peat)	Fen, Northwestern ON*
Kinetic Trial, 2010, model	*L. variegatus*	8.38	>90% (peat)	Fen, Northwestern ON*
This study, 2008	Invertebrates	21.8-106	25.3-94.6%	Fen, Northwestern ON
Fink, 2008 (unpublished)	*L. variegatus*	0.93-45.0	10.9-85.4% (peat)	Everglades, FL*
Lawrence and Mason (2001)	Amphipod	≤10	2-13%	Fishing Bay/Patuxent River, MA*
Lawrence and Mason (2001)	Amphipod	10-1000	≤1 (sand)	Fishing Bay/Patuxent River, MA*
Mason and Lawrence (1999)	Clams, amphipods	<10-100	<1-3% carbon	Baltimore Harbor, MD
Nuutinen and Kukkonen (1998)	*L. variegatus*	11.8 (day 7)	7.1% (3.5% carbon)	Lake Hoytiainen, Finland*
Nuutinen and Kukkonen (1998)	*L. variegatus*	4.1 (day 7)-7.7 (day 14)	17.7% (10% carbon)	Lake Mekrijarvi, Finland*
Tremblay et al. (1996)	Mayflies	21.1-123	2-4% carbon	Duncan Lake, QC
Tremblay et al. (1996)	Caddisflies	44.5-558	2-4% carbon	Duncan Lake, QC
Saouter et al. (1993)	Mayflies	≈22.1 (day 9 ww)	2% organic carbon (silt-clay)	Garonne River, France*

3.3.2 Laboratory and Field Tissue Concentrations

Tissue concentrations of THg and MeHg in *L. variegatus* after 28 day bioaccumulation trials are presented in Fig. 3.3. The *L. variegatus* MeHg concentrations before trials (i.e. culture worms) were significantly higher than after 28 day exposures to experimental sediments (TukeyHSD $p<0.001$, ANOVA $F_{2,20}=40.8$, $p<0.001$), whereas THg concentrations were statistically indistinguishable (ANOVA $F_{3,39}=2.37$, $p=0.085$).

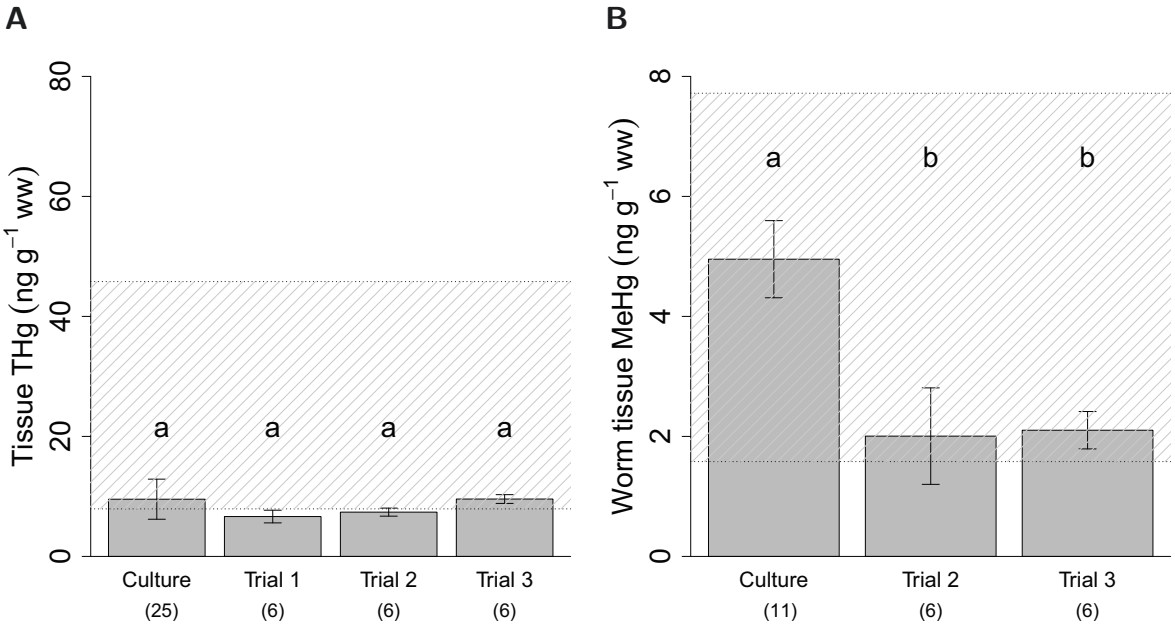


Figure 3.3: Mean±SD (n) tissue concentrations (wet weight) of **A** THg and **B** MeHg in *L. variegatus* before (Culture) and after (Trial) a 28 day exposure to experimental sediments. Hatched area shows range of field invertebrate concentrations (sampled 2008; THg n=7, MeHg n=6). Note y-axis for **A** and **B** intentionally offset by a factor of 10, to visualize %MeHg in tissue. Means with same letter are statistically indistinguishable ($\alpha=0.05$).

The MeHg tissue concentrations from bioaccumulation trials are below the aquatic biota MeHg tissue guideline of 33 ng g^{-1} (ww), as derived to protect Canadian wildlife that consume fish or shellfish from any toxicological effects of MeHg (Environment Canada, 2002). Trial *L. variegatus* tissue concentrations tended to compare with lower concentrations of a limited set of indigenous invertebrates (Fig. 3.3). The percentage of THg present in *L. variegatus* tissue as MeHg was 27% in 2009 and 22% in 2010, being similar to indigenous invertebrates, and lower than cultures (47%, Fig. 3.3).

3.3.3 Sediment Chemistry

Concentrations of MeHg in experimental plot sediment increased over 10-fold the year following the excavation of peat, while both MeHg and THg concentrations at other sites remained relatively constant (Table 3.8). Peat cores sampled in 2010 from unimpacted areas within the peatland (Fig 3.1) were not as low in MeHg concentration as 2008 experimental plot data, but compared well with other sites (Table 3.8). This difference was not readily explained. All sediments from the area were mostly acidic, highly organic and of low mineral content (Table 3.9).

The highest concentration of MeHg measured in sediment was 3.16 ng g^{-1} (dw), being from a pool formed by a beaver dam upstream of mining activity (NW, April 2008). The THg concentration of this sample measured 129 ng g^{-1} (dw, 2.4% MeHg). The dam was removed by road maintenance crews in June 2008. The dam may account for higher SDs in northwest ditch data (Table 3.8). Concentrations of THg in peat and sediments are similar to underlying clay when concentrations are expressed on a per volume basis (Table 3.8), which has been suggested as a more representative presentation of Hg results from peatlands (Grigal, 2003).

Table 3.8: Concentrations of total mercury (THg), methylmercury (MeHg) and bulk density (BD) measured in sediment sampled from sites in Fig 3.1. Confluence pool was where NW ditch, SE ditch and experimental plot ditch intersected. Asterisk; one outlier in data set (271 ng g^{-1} (dw)) was identified and removed (Grubb's test, α=0.05).

	THg (ng g^{-1} dw)				**MeHg (ng g^{-1} dw)**		
Site	Mean	SD	n	**Mean BD ± SD (g cm^{-3} (n))**	Mean	SD	n
2008							
Confluence pool	69.8	9.74	4	0.085 ± 0.021 (2)	1.13	0.847	3
Northwest ditch	77.1	41.1	12	0.174 ± 0.075 (9)	1.13	1.21	10
Southeast ditch	76.6	22.2	10	0.062 ± 0.008 (5)	0.614	0.267	7
Experimental plot	46.6	9.77	2	0.090 (1)	0.025	0.001	2
Clay beneath peat	7.49	NA	1	0.900 (1)	0.003	NA	1
2009							
Confluence pool	76.8	4.50	2	0.085 ± 0.007 (2)	0.501	0.067	2
Northwest ditch	55.3	33.8	5	0.148 ± 0.055 (5)	0.400	0.155	5
Southeast ditch	51.9	12.8	3	0.070 ± 0.010 (3)	0.303	0.145	3
Experimental plot	54.6	6.30	3*	0.070 ± 0.000 (4)	0.184	0.039	4
Drainage ditch	82.2	30.1	3	0.070 ± 0.017 (3)	0.325	0.222	3
2010							
Deep peat cores	61.9	NA	1	0.120 ± 0.014 (2)	0.770	0.210	3
Shallow peat cores	105	NA	1	0.116 ± 0.007 (2)	1.43	0.484	3
Experimental plot cores	81.4	NA	1	0.080 ± 0.000 (2)	1.94	0.416	3
Drainage ditch cores	71.5	NA	1	0.102 ± 0.000 (2)	1.51	0.261	3

Table 3.9: Additional physiochemical data (ranges) for sites sampled in Fig. 3.1. Concentrations expressed as dry weight, except conductivity, pH and redox. Organic matter estimated by loss on ignition (LOI).

Site	Organic matter (LOI%)	pH	Conductivity μS cm^{-1}	Redox mV	Al %	Fe %	S μg g^{-1}	Mn μg g^{-1}	Zn μg g^{-1}	P μg g^{-1}
2008										
Confluence pool (4)	63.3–79.3	5.62–6.13	42.9–59.9	$^{-}$99.9–$^{+}$15.9 (3)	0.38–0.72	0.92–2.05	1120–1730	108–344	38.4–51.0 (4)	382–627
Northwest ditch (12)	25.3–79.5	5.62–6.78	50.6–175	$^{-}$351–$^{+}$88.8 (11)	0.32–1.44	0.64–2.53	681–2780	61.9–857	15.9–102 (12)	232-1170
Southeast ditch (10)	83.1–90.8	5.62–6.36	31.5–107	$^{-}$357–$^{+}$76.5 (8)	0.21–0.56	0.55–1.32	1420–2340	60.9–142	13.9–51.6	261–682
Experimental plot (2)	92.1–93.5	5.59–5.67	22.8–30.3	NA (0)	0.26–0.36	0.60–0.79	1470–1540	105–122	7.18–7.22	360–392
Clay beneath plot (1)	3.3	7.72	214	$^{-}$161	1.92	2.06	755	269	44.5	491
2009										
Confluence pool (2)	77.8–79.5	6.42–6.88	48.8–134	$^{-}$107–$^{-}$40.1	0.37–0.45	1.63–1.72	1860–1910	135–368	43.5–46.6	480–568
Northwest ditch (5)	34.2–82.3	6.22–6.81	39.1–128	$^{-}$121–$^{+}$63.6	0.34–0.89	0.98–1.58	926–1750	98.8–332	23.4–52.8	320–439
Southeast ditch (3)	87.2–93.5	6.31–6.81	20.7–115	$^{-}$61.5–$^{+}$41.8	0.17–0.33	0.60–0.90	1720–2030	69.0–87.1	8.53–32.2	260–377
Experimental plot (4)	93.1–94.6	5.98–6.22	13.0–23.8	$^{+}$61.7–$^{+}$118	0.18–0.25	0.66–0.84	1520–1720	101–155	6.64–7.86	348–413
Drainage ditch (3)	90.5–93.3	6.04–6.28	22.0–53.4	$^{+}$69.9–$^{+}$106	0.21–0.30	0.82-0.94	1670-1940	113–133	6.96–12.3	404–466
2010										
Deep cores (3)	87.7–89.8	6.28–6.31	31.9–34.2	$^{+}$78.8–$^{+}$78.8	NA	NA	NA	NA	NA	NA
Shallow cores (3)	92.3–92.7	5.79–5.94	13.5–14.8	$^{+}$70.7–$^{+}$110	NA	NA	NA	NA	NA	NA
Exp. plot cores (3)	92.8–93.2	6.07–6.11	18.0–19.9	$^{+}$48.1–$^{+}$61.1	NA	NA	NA	NA	NA	NA
Drainage ditch (3)	93.2–93.3	6.02–6.11	13.2–18.6	$^{+}$65.7–$^{+}$94.9	NA	NA	NA	NA	NA	NA

3.3.4 Experimental Kinetic Trial

The uptake of THg by *L. variegatus* from iHg spiked sediment fit a Michaelis-Menton model (Fig. 3.4, adj. r^2=0.928, p<0.001). The accumulation of THg in tissue reached an operationally defined steady state condition within 3 days (Holm adjusted p values), though visually this appeared an underestimation (Fig. 3.4). Using the mean tissue concentration for Day 28, 14 and 7, the model predicted steady state was achieved in 11.5 days, well within the suggested 28 day exposure time.

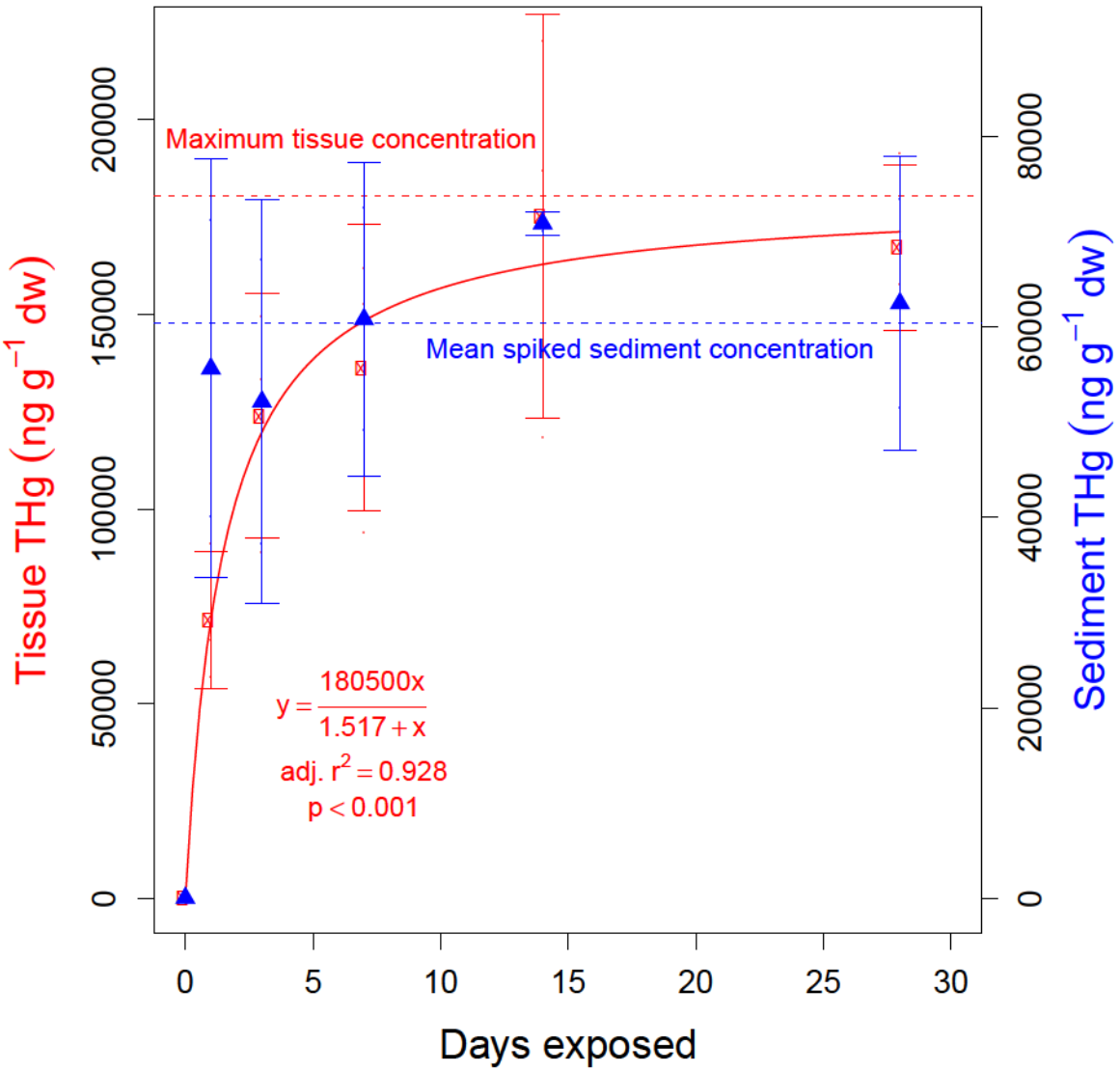


Figure 3.4: Uptake of THg by *L. variegatus* from sediment spiked with 200 μL of 1000 mg L^{-1} iHg per 50 mL aliquot of wet sediment (3.5 g dw; nominal sediment iHg=57 100 ng g^{-1} dw). Error bars are $\pm$ 1SD (tissue n=3; sediment n=2). Dotted red line is the maximum worm tissue concentration estimated from the Michelis-Menton steady state equation. Dotted blue line is the mean of the means of THg concentration measured in spiked experimental sediment for Day 1 to Day 28. Day 0 sediment and tissue concentration were determined before spiking.

The uptake of MeHg by *L. variegatus* from iHg sediment spiked fit a linear model (r^2=0.974, p<0.001), not achieving steady state within 28 days (Fig. 3.5). Although only iHg was added to the sediment, MeHg sediment concentrations also increased linearly (r^2=0.879, p<0.001) over the 28 days (Fig. 3.5). Percent MeHg in worm tissue for Day 1 to 28 was 1.0±0.8, increasing significantly over time (adj.r^2=0.906, p<0.001) from 0.4±0.1 to 2.3±0.4, and lower than bioaccumulation trial and culture percentages (Fig. 3.3).

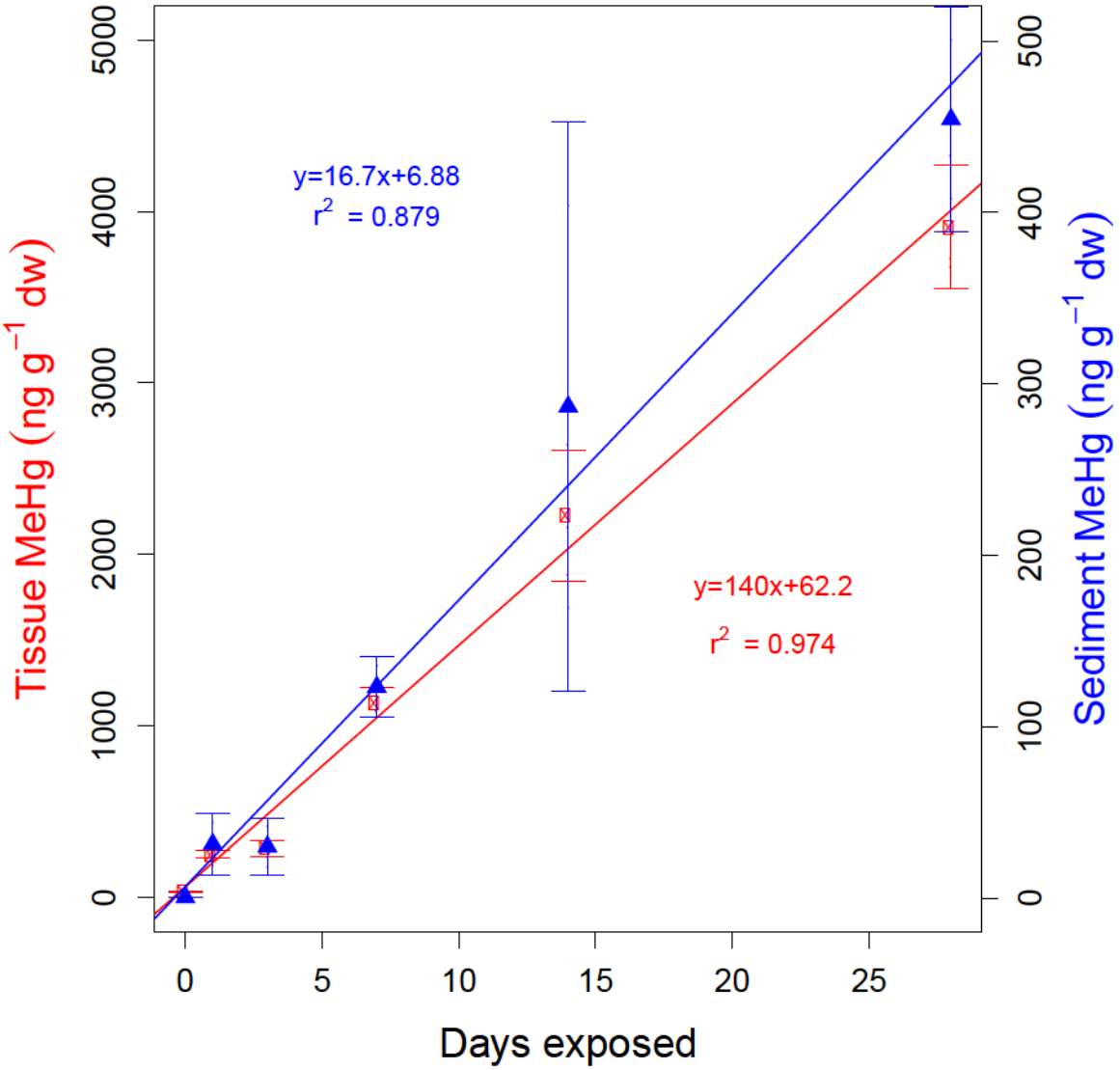


Figure 3.5: Uptake of MeHg by *L. variegatus* from sediment spiked with 200 μL of 1000 mg L^{-1} iHg per 50 mL aliquot of wet sediment. Day 0 MeHg concentration in sediment before spiking was 0.527±0.089 (n=2). Error bars: ±SD (tissue n=3; sediment n=2).

3.4 Discussion

3.4.1 Bioaccumulation of THg

Supporting the hypothesis, three laboratory bioaccumulation trials using sediment from an experimentally wet mined peatland found THg did not bioaccumulate in *L. variegatus* tissue (Table 3.6). Tissue THg concentrations in laboratory exposures (Fig. 3.3), when expressed on a dry weight basis (ww×8.14), were similar to THg concentrations (dw) in sediment (Table 3.4). Laboratory results were supported by site invertebrate data (Table 3.6, Fig 3.3) and other research exclusive of sand only exposures (Table 3.6). McGeer et al. (2003) and DeForest et al. (2007) demonstrated that aqueous phase bioaccumulation potentials significantly decreased with increasing metal (and MeHg) concentrations. Therefore, literature comparisons were restricted to mainly reference and uncontaminated sites, rather than to sites with obviously contaminated sediment. Table 3.6 data compares with Thomann et al. (1995), who calculated a median THg BSAF for marine bivalves of 1.0 using a model that included sediment to water column partitioning, bioconcentration factor, depuration rates, metal assimilation efficiency from food, bivalve feeding rate and growth rate.

The laboratory THg BSAFs reported here are not surprising given the high organic content in sediments around the experimental peat mining site (Table 3.9). Several studies suggest that increased sediment organic matter reduces the uptake of THg by benthic organisms. Breteler et al. (1981) found that THg concentrations did not increase in fiddler crabs (*Uca pugnax*) nor ribbed mussels (*Modiolus demissus*) when their marsh soils received high and extra high doses of a Hg containing fertilizer. In extensive work in British estuarine sediments, Langston (1982) reported that THg in the tissue of bivalves (*Scrobicularia plana* and *Macoma balthica*) may accumulate to high levels from organic-poor sediments of only moderate Hg contamination whereas accumulation may be effectively inhibited in animals exposed to more highly contaminated yet organic rich surface sediments. Microcosm experiments by Lawrence and Mason (2001) found that increased organic matter content in sediments led to an exponential decrease in the bioaccumulation of iHg and MeHg by amphipods, confirming their previous field observations (Mason and Lawrence, 1999).

Few THg studies for bioaccumulation potentials from organic "peat-type" sediments exist. Unpublished bioaccumulation results were kindly made available by Fink (pers.

corr., 2008) who exposed *L. variegatus* for 28 days to Florida Everglades peat. The non-normalized THg BSAF averaged 1.7±1.3 (10 sites), being inversely related to LOI (ρ=-0.73, p=0.02). Fink's BSAFs and LOI concentrations (10.9-85.4%) were similar to this study (Tables 3.6 and 3.9, respectively). Sediment cores from the Pungo River, NC, which received drainage from a dry peat harvesting operation, had THg concentrations ranging from 40 to 193 ng g^{-1} (dw) (DiGiulio and Ryan, 1987), similar to this study site (Table 3.8). The THg in clam tissue ranged from 25 to 32 ng g^{-1} (ww), higher than bioaccumulation trial *L. variegatus*, but similar to site invertebrates (Fig. 3.3). DiGiulio and Ryan (1987) determined Hg was associated with organic matter and concluded a significant Hg impact to receiving systems due to peat mining was unlikely. Similar conclusions were drawn by Surette et al. (2002) studying a New Brunswick active peat mining site (dry harvesting), who failed to find elevated THg concentrations in the tissues of sand shrimp, mummichog or blue mussels (20, 40, 30 ng g^{-1} ww, respectively) sampled from impacted sediment sites with 90% peat content.

Sediment collected during this research, being low in THg (Table 3.8) and high in organic matter (Table 3.9), coupled with experimental and field THg BSAFs near unity, suggests THg bioaccumulation from peat and "peat-type" sediments as not an issue for peat mining activities at this site, in agreement with DiGiulio and Ryan (1987) and Surette et al. (2002). Steady-state kinetics (Fig. 3.4) further suggest that THg concentrations in benthic invertebrates that may be exposed to such sediments from peatland disturbances can be predicted from THg concentrations in peat. However, Mason and Lawrence (1999) found a decoupling between THg and MeHg bioavailability in low carbon ($\leq$3.5%), estuarine surface sediments, noting impact evaluations based only on THg data would be unreliable. It is unknown to what extent such decoupling would occur in higher organic matter, freshwater sediments.

3.4.2 Bioaccumulation of MeHg

The hypothesis was not supported by experimental or field MeHg BSAFs. Three laboratory bioaccumulation trials using sediment from an experimentally wet mined peatland found MeHg in *L. variegatus* tissue was 10 to 70 times the sediment concentration (Table 3.7). Laboratory BSAFs were supported by site invertebrate and literature data (Table 3.7). Bioaccumulation was evident (Table 3.7) despite the high organic matter content (Table 3.9) and low MeHg concentration (Table 3.4, 3.8) of "peat-type" sedi-

ments. Saouter et al. (1993), in silt-clay sediment spiking experiments, found Hg accumulation was greater in mayfly tissue when Hg was introduced to sediment in the organic (MeHg) form, rather than when added as iHg. Later work quantified the bioaccumulation of sediment bound MeHg as 20 times that of sediment bound iHg (Odin et al., 1995). Binding constants for MeHg to organic matter are reportedly lower than those for iHg species (Khwaja et al., 2006, 2010). Therefore, increased sediment bioavailability and/or formation of MeHg under experimental conditions may account for higher MeHg BSAFs than THg BSAFs determined in my trials.

This research appears as to be the first formal report of MeHg experimental bioaccumulation potentials from "peat-type" sediments. The peatland research by DiGiulio and Ryan (1987) could not detect MeHg in either sediments or clams (detection limit (DL)=25 ng g^{-1}) and Surette et al. (2002) did not include MeHg analysis. Experimental and invertebrate MeHg BSAFs were within the ranges provided by Fink (unpublished, 2008) for Everglades peat (Table 3.7). Fink data (n=8) had no correlation with LOI (ρ=-0.38, p=0.36), though the highest MeHg BSAF (45.0) was associated with the lowest LOI (10.9%).

Lower bioaccumulation potentials were associated with higher organic matter content in other studies. In Chesapeake Bay, MD, MeHg BSAFs decreased exponentially with sediment organic matter (Mason and Lawrence, 1999). Nuutinen and Kukkonen (1998) specifically examined tissue concentrations of MeHg in *L. variegatus* exposed to sediments spiked with MeHg where two lake sediments had varying organic matter (LOI=7.1% and 17.8%). Like the kinetic trial here, their MeHg tissue concentrations increased linearly over time, with less bioaccumulation (lower slope) occurring in lake sediment with more organic matter (Nuutinen and Kukkonen, 1998). However, Nuutinen and Kukkonen (1998) did not report MeHg sediment concentrations over time. Lawrence and Mason (2001) also used spiked sediments (33.7±7.4 ng g^{-1} ww), reporting a MeHg BSAF for estuarine amphipods (*Leptocheirus plumulosus*) of around 10 when LOI was between 2% and 6%. For sand exposures (LOI ≤1%), the MeHg BSAF increased exponentially from 10 to 1000 (as estimated from Fig. 2, (Lawrence and Mason, 2001)). Their MeHg BSAF was near unity when the organic matter content was greater than 10%. The relationship of MeHg BSAF and organic matter observed by others should be confirmed with *L. variegatus* under experimental or field conditions by measuring the bioaccumulation potential of "peat-type" sediments mixed with sand or other low carbon sediments. Such scenarios would occur if particulate matter in peat mining runoff waters (Chapter 2 and Chap-

ter 4) entered area lakes or rivers. Decreased tissue MeHg and %MeHg in culture worms occurred after exposure to peat (Fig 3.3), perhaps due to ingestion of sediment organic matter. Further depuration kinetic trials (EPA, 2000c; ASTM, 2010) are required.

The kinetic trial showed that MeHg concentration in *L. variegatus* tissue equilibrates to MeHg concentration in sediment within days (Fig. 3.5). Therefore, peatland disturbances that increase MeHg concentration in "peat-type" sediments would likewise increase the MeHg concentrations in benthic invertebrate tissue, and should be avoided during wet peat mining. Invertebrate MeHg tissue concentrations can be predicted to vary with, and remain higher than, MeHg concentrations in organic sediment by one to two orders of magnitude.

3.4.3 Uptake of THg from Spiked Organic Sediment

The uptake of THg from iHg spiked sediment by *L. variegatus* reached steady state within 28 days (model=11.5 days). Steady state was reached for *Nereis virens* (polycheate worm) before 28 days and in *Macoma nasuta* (bivalve) after 28 days when exposed to New York Harbor sediment (Kennedy et al., 2010). Cardoso et al. (2009) similarly used a Michaelis-Menton equation to describe laboratory Hg bioaccumulation in *Scrobicularia plana* (bivalve). Their research found rapid accumulation (48 h) to contaminated sediments before reaching steady state (5 days). For trials with *Hediste diversicolor* (polycheate), only the lowest THg sediment (70 ng g^{-1} dw, LOI=4.2%) achieved steady state (≈3 days, Fig. 3D, Cardoso et al. (2009)) while a linear THg accumulation over 31 days occurred for two higher concentration sediments (5300, 75,000 ng g^{-1} dw; LOI<10%). Bivalves were noted to feed essentially on sediment particles with which Hg was associated (Cardoso et al., 2009), being a similar major uptake route for THg by *L. variegatus* used here. Cardoso et al. (2009) surmised that different uptake patterns between their bivalves and polycheates were mainly related to different feeding strategies, though ingestion rates, assimilation efficiencies and excretory rates may have contributed to bioaccumulation differences.

The BSAF for THg was two to three times higher in kinetic trials than bioaccumulation trials, although within the range of literature values (Table 3.6). It is probable that iHg spiked to sediment in elevated concentration with a short equilibrium time (48 h), did not permit total binding of Hg species to sediment. From the sediment side, the strength of bonding between Hg and humic substances decreases at higher loadings (Tip-

ping, 2007). Significant porewater phase iHg likely resulted in a higher BSAF. A review of literature by DeForest et al. (2007) reported the lowest empirical bioaccumulation factors (BAFs) for THg (uptake factor of contaminant from water by all modes) was 40,857. Preliminary work during this dissertation (EDTA and DMSA chelation trials) found THg in *L. variegatus* tissue increased at least 3000% when exposed for 24 h to spiked culture water (20 μg L^{-1} iHg). Standardized equilibrium times for sediment spiking are lacking, though 30 days has been suggested (EPS, 1999; ASTM, 2010). Lengthy equilibrium time was not allowed here in order to confirm whether methylation of iHg in sediment occurred under specific bioaccumulation trial conditions. Therefore, the THg BSAF from this kinetic trial may represent the highest value that can be attained from "peat-type" sediments.

Higher kinetic trial THg BSAFs may also have been due to a re-ingestion of Hg contaminated egested material. *L. variegatus*, living in only upper centimeters of spiked sediment, may have created a micro-climate of elevated Hg concentration relative to lower sediments. Upon trial and kinetic test take down, sediment structure was obviously reworked by *L. variegatus*. Whether reworking of sediments by invertebrates alters the bioavailability of contaminants such as Hg in a highly organic sediment would prove an interesting study. Research suggested that sediments rich in organic content, iron, manganese and hydrous oxides partially retain Hg remobilized by bioturbation, decreasing its bioavailability (Cardoso et al., 2008). Although their "organic" sediment had low LOI (<10%) compared to peat, it has been shown here that BSAF are not different than sediments with marginal organic matter (Table 3.6). In either case, THg was not measured in porewater nor top layer sediment and such monitoring is recommended for future trials.

3.4.4 Uptake of MeHg from Spiked Organic Sediment

The uptake of MeHg from iHg spiked sediment did not reach steady state in *L. variegatus* tissue after 28 days exposure, but increased linearly. However, MeHg BSAF remained low (<10, Table 3.7) and nearly constant (Fig 3.5), apparently because MeHg in sediment also increased linearly and tissue concentration equilibrated rapidly. Linear uptake for *L. variegatus* in lake sediments spiked with organic Hg was reported by Nuutinen and Kukkonen (1998). Steady state MeHg tissue concentrations were reported as 28 days or less for polycheates and clams exposed to New York Harbor, NY sediments (Kennedy

et al., 2010). Though Kennedy et al. (2010) MeHg tissue data was fit to non-linear one compartment models suggested by ASTM (2010), some linearity qualitatively appears in their Figures C5, C9, D5 and D9. Kennedy et al. (2010) sediment concentrations were also suspect (MeHg concentrations 10× that of THg) and MeHg was not measured at specific time intervals. Thus, BSAFs were not estimated for that data.

Nuutinen and Kukkonen (1998) exposed *L. variegatus* for 14 days to lake sediments spiked with ^{14}C-MeHg. Nuutinen and Kukkonen (1998) nominal sediment concentrations of 90 and 106 ng g^{-1} (dw) were approximate to sediment concentration at Day 10 of my kinetic trial (Fig. 3.5), suggesting the concentrations in spiked sediment were not exorbitantly high. It was estimated from Fig. 2 model slopes in Nuutinen and Kukkonen (1998) that *L. variegatus* accumulated 95 ng MeHg ng^{-1}tissue (dw) day^{-1} from higher organic sediment (LOI=17.8%) and 160 ng MeHg ng^{-1}tissue (dw) day^{-1} from lower organic matter sediment (LOI=7.1%). An accumlation rate of 140 ng MeHg ng^{-1}tissue (dw) day^{-1} during the kinetic trial of my study was within that range, though higher than expected given that LOI was >90%.

Adding elevated concentrations of iHg spiked to experimental sediment confirmed methylation was possible during laboratory bioaccumulation trials as sediment MeHg increased by 3 orders of magnitude over the nominal concentration by Day 28. Since sediment was collected fresh and spiked within hours, a healthy bacterial population would be present. Production of MeHg by sulphate-reducing bacteria (SRB) (Compeau and Bartha, 1985; Gilmour et al., 1992) or Fe(III)-reducing bacteria (FeRB) (Rother and Cornel, 2004) likely occurred since sulphate concentrations in renewal water (mean= 5.36 mg L^{-1}) were sufficient to stimulate methylation by SRB (Ullrich et al., 2001; Mitchell et al., 2008a). Contrary to methylation observed here (Table 3.4, Fig. 3.5), Saouter et al. (1993) and Nuutinen and Kukkonen (1998) reported demethylation of MeHg in sediments. However, methylation in sediment was observed in littoral zone mesocosms at the Experimental Lakes Area (ELA) receiving isotopically enriched iHg as simulated rainfall (Orihel et al., 2006). It was later shown that added MeHg bioaccumulated in zooplankton after 2-4 weeks and was present in virtually all invertebrates after 10 weeks (Orihel et al., 2007). Ideally, suitable site water and experimental conditions resulting in minimal sediment methylation/demethylation should be sought for laboratory studies, though numerous processes are poorly understood (EPA, 2007).

A substantial decrease in MeHg concentration in *L. variegatus* tissue from cultures after exposure to both experimental and organic sediments (Fig. 3.3, Table B.1) suggests

factors that cause a decrease in sediment MeHg concentration may lower MeHg concentrations in invertebrate tissue. The reasons why %MeHg was twice as high in culture worms than organisms exposed to experimental sediment for 28 days was not evaluated, but in-tank methylation is suspected. A decrease in the percent MeHg in tissue during the bioaccumlation trials suggests that MeHg was removed from *L. variegatus* tissue at a faster rate than other forms of Hg or that MeHg was converted to another Hg species within *L. variegatus* itself. Further work on depuration rates and bioenergetics of various Hg species for *L. variegatus* are required, especially since equilibrium over a 28-day period was not confirmed in the kinetic trial.

I suggest bioaccumulation trials assessing MeHg uptake from sediments include the sampling of sediment throughout the trial, whether or not tissue is sampled during these intervals. Sampling of porewater is also recommended (ASTM, 2010), though logistically, it may be difficult to collect sufficient sample volume at time points during an exposure without disrupting organisms. Suitable control sediment and *L. variegatus* food, both free of THg and MeHg are also required for future work with low THg and MeHg sediments. These could not be found during the course of this research and Mr. Fink had likewise been unsuccessful in these pursuits (pers. corr.). Initial chelation trials with EDTA and DMSA to reduce initial Hg burdens in *L. variegatus* were unsuccessful (unpublished).

3.4.5 Implications for Wet Mining Peat

Bioaccumulation results reported here and elsewhere suggest that invertebrate populations will assume a THg tissue concentration similar to its sediment THg concentration (Table 3.6). Therefore, the concentration of THg in peat-type organic sediments can be used directly to estimate the concentrations of THg in benthic invertebrate species whose main food source is the sediment itself. There seems little concern that extracting peat through wet mining would adversely affect the concentrations of THg in invertebrate tissues when compared to those already present in natural habitats adjacent to peatlands.

The bioaccumulation of MeHg can also be predicted from sediment MeHg concentrations. As shown here, MeHg BSAFs are likely to be higher than those for THg, even in sediments with >90% organic matter (Table 3.6). Tissue concentrations of sediment dwelling invertebrate populations are expected to respond rapidly to changing concentrations of MeHg in sediments (Fig 3.5). Negative impacts would be expected if wet peat

extraction results in increased sediment methylation. Methylation occurs when soils are flooded by beaver or hydroelectric dams (Ullrich et al., 2001). While recent studies suggest that additions of Hg from atmospheric sources lead to an increase in MeHg in the tissues of aquatic species (Driscoll et al., 2003; Orihel et al., 2006; Harris et al., 2007; Orihel et al., 2007), I suggest that mechanisms altering MeHg concentrations in organic sediments not be overlooked. These include, but may not be limited to, increases in temperature, increases in pH, changes in sulfate/sulphide ratio and changes in redox potential (EPA, 2007). Laboratory bioaccumulation and kinetic trials were found to be useful tools to assess sediment methylation and bioaccumulation potential.

3.5 Conclusions

Experimentally derived, 28 day BSAFs values for THg for *L. variegatus* exposed to sediments impacted by an experimental wet extraction of peat ranged from 0.91 to 1.59, within the range determined for a limited number of benthic invertebrates collected near the site (1.2 to 6.8). Based on a kinetic trial, THg in *L. variegatus* tissue reached a steady state within 11.5 days when exposed to the same sediment spiked with iHg. Using the experimental and field BSAFs coupled with the low concentrations of THg in area peat, benthic invertebrate tissue THg concentrations are not predicted to increase if wet peat mining were to occur at this site.

Experimentally derived, 28 day BSAFs values for MeHg for *L. variegatus* exposed to the same sediments ranged from 9.91 to 67.4, within the range determined for a limited number of benthic invertebrate samples (21.8-106). The MeHg BSAFs found here were higher than THg BSAFs. Based on a kinetic trial, the uptake of MeHg by *L. variegatus* may not have reached a steady state when exposed to the same sediment spiked with iHg. The MeHg concentration in spiked sediment also increased linearly, resulting in a constant BSAF over the 28 day trial. Therefore, peatland disturbances that increase MeHg sediment concentration would immediately increase MeHg in benthic invertebrate tissue. At this site, laboratory and field invertebrate tissue concentrations were about 4× less than the Canadian aquatic biota guideline of 33ng g^{-1} (ww).

Laboratory methods to experimentally determine BSAFs were newly established at Lakehead University over the course of this research. Issues that may impede laboratory bioaccumulation studies for Hg BSAFs include a lack of suitable negative control sediments, detectable background THg and MeHg in *L. variegatus* cultures and poten-

tial methylation of Hg in sediment during exposures. While the first two appeared of little concern here, the methylation of laboratory sediment remains troublesome for accurate MeHg BSAFs. Ranges should be reported and qualified if sediment methylation is observed.

Chapter 4

Treatment of Peat Mining Process Waters with Acrotelm Hummock Peat: An Initial Assessment

4.1 Introduction

Canada possesses approximately 30% of the world's total peat reserve, second only to Russia (NWWG, 1988). Though Canadian peatlands contain an estimated 153.7 GT of carbon (Tarnocai, 1998), its recent use has been limited to horticultural products rather than energy (Daigle and Gautreau-Daigle, 2001). Current energy concerns could alter peat use in Canada at any time, particularly in northern, isolated communities with abundant peat resources.

A Canadian company (Peat Resources Ltd.) has developed a proprietary technique to wet mine and pelletize peat for use as a combustible fuel. Though wet mining peat for energy was used in the former USSR for over 40 years, the practice is quite uncommon (Tibbetts, 1986). Pellets from processing wet peat may be utilized as a local energy source, being amenable to combustion in both small scale generators (Obernberger, 1998) and large thermal plants (OME, 2006).

Compared to the commonly employed methods of dry harvesting peatlands, wet mining advantages include a longer processing season and an extraction of peat from areas with coarse woody debris and not amenable to drainage (Monenco, 1981b). A general lack of knowledge on wet mining has resulted in environmental impacts for an industry

in Ontario to be extrapolated from dry harvesting research (Gleeson et al., 2006).

One wet mining environmental concern is the fate of peat mining process water (PMPW) generated from squeezing and pelletizing wet peat (Monenco, 1986). The PMPWs summarized in Monenco (1986) were found to possess solids, nutrients, metals, colour and pH at levels that do not meet current Canadian Water Quality Guidelines (CWQG) for direct discharge. Industry-proposed treatment involves distributing PMPW onto an adjacent intact peatland, where natural filtration may or may not improve PMPW quality. On-site treatment would maintain the portability of current wet mining technology, thus reducing transportation of wet peat, process waters and/or pellets. The proposed treatment appeared plausible since numerous studies have highlighted the benefits of peat as a filter to remove chemicals of concern from a variety of industrial and municipal waste streams (Viraraghavan, 1991; Couillard, 1991, 1994; Bhatnagar and Minocha, 2006).

To directly address the lack of knowledge concerning the quality of PMPW from northwestern Ontario peat in terms of pH, alkalinity, conductivity, metals (including methylmercury (MeHg)), nutrients, solids and organics, experimental wet peat mining was conducted. The selected fen was identified as possessing high value energy peat (DST, 2005) and ideally situated to meet local energy needs (OME, 2006). Acrotelm hummock peat mesocosms were constructed and used off-site in two studies. The main objectives were to (1) determine whether the water quality of local PMPW exceeds current CWQG, (2) determine whether acrotelm peat would significantly remove analytes of concern from dilutions of PMPW (treatments), (3) determine if leachate from acrotelm peat receiving PMPW treatments would exceed CWQG and (4) calculate the efficiency of acrotelm peat to remove analytes from PMPW.

4.2 Materials and Methods

4.2.1 Mesocosm Construction

During the summer of 2008, hummock peat cores were cut by handsaw from an undisturbed area near the wet mined site to precisely fit 25 L plastic buckets (the mesocosms, Fig. 4.1 A). Careful handling prevented any peat compaction or destruction of vegetation. Hummock vegetation was typical for northwestern Ontario, consisting of mainly *Sphagnum* species (e.g. *S. fuscum, S. magellanicum*) interspersed with open poor fen

vegetation (e.g. sedges, ericaceous plants).

Each mesocosm was fitted with a vertical piezometer (Fig. 4.1 B). The piezometer had inlet holes over a 15 cm length that were wrapped with 500 μm Nitex. Inlet holes were positioned nearest the base of the bucket. The piezometer was later fitted with a bottom valve protruding through the base to facilitate sampling of mesocosm leachate (Fig. 4.1 C).

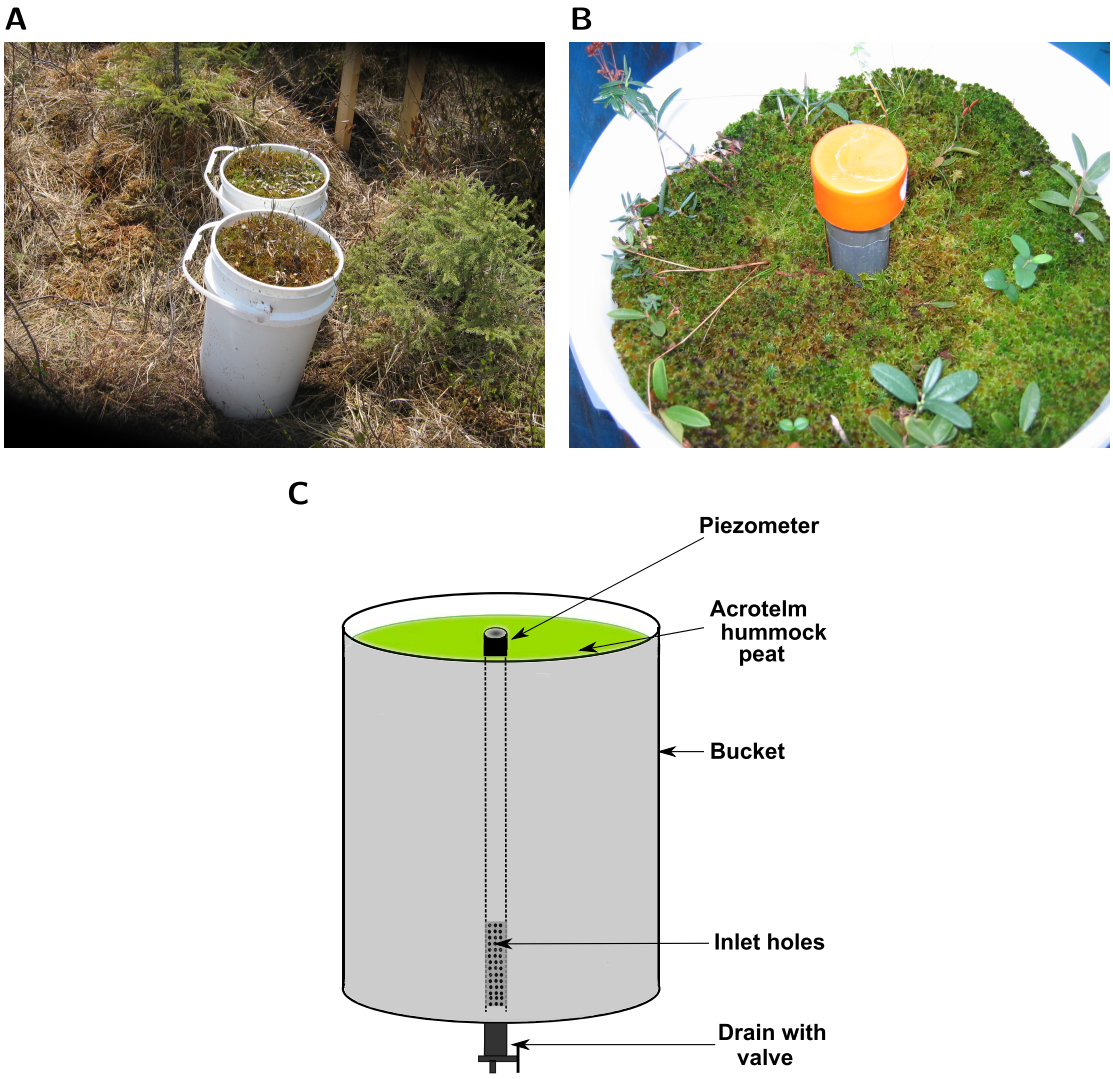


Figure 4.1: **A** Buckets of intact acrotelm peat collected in the field. **B** Mesocosm in the greenhouse. **C** Mesocosm schematic.

A sufficient number of mesocosms were constructed to provide replication in both studies. Mesocosms were housed in a greenhouse and watered with dilution water as required to prevent dessication. The depth to water table (DWT) was measurable via

the piezometer and, for this research, was calculated as the difference from the peat surface to the water surface.

Initial chemical analysis of leachate found significant differences (analysis of variance (ANOVA), $p \leq 0.05$) between mesocosms that may have affected the final interpretation of results. However, an equilibrium period ($\approx$60 d) that consisted of dilution water applications and drainage of leachate corrected this statistical difference. Mesocosm DWT before and after studies was kept constant (Table 4.1).

Table 4.1: Mean ± SD of mean treatment group depth to water table (DWT) for Study 1 encompassing pre-treatment through post-treatment time period (n=43). Dilution water was used to dilute peat mining process water (PMPW) to specified percentages.

Treatment Group	**DWT (cm)**
T0 (0% PMPW)	20.5 ± 3.4
T1 (100% PMPW)	20.4 ± 3.0
T2 (50% PMPW)	20.9 ± 2.5
T3 (33% PMPW)	19.2 ± 3.1

4.2.2 Experimental Design

Overview

First, PMPW was extracted from wet mined peat and its water quality (pH, alkalinity, conductivity, metals (including MeHg), nutrients, solids and organics) compared to current CWQG. Then, PMPW was passed through peat mesocosms in two studies. In Study 1, pulses of diluted PMPW (treatments) were applied to mesocosms to determine whether mean concentrations of analytes in mesocosm leachate would be significantly different after two weeks of exposure (ANOVA). Mesocosm leachate concentrations were also compared to CWQG. Solids were qualitatively observed in mesocosm leachate after each pulse was applied. Therefore, Study 2 was conducted to quantify the relative amount of solids and organics eluting after every pulse of 100% PMPW was applied to mesocosms in rapid succession. Removal efficiencies of analytes were calculated for both studies. Specific details for each step follow.

Process Water Extraction

Catotelm peat was wet mined in spring 2008 from a poor fen near Upsala, ON (40°57′33″N, 90°6′20″S). Peat was mined with a backhoe excavator (Fig. 4.2 A) and transported off site in large metric tonne bags with clean plastic liners (Fig. 4.2 B), where it was mechanically dewatered hydraulically (Fig. 4.2 C). Process waters were combined to produce one 900 L batch of PMPW that was stored protected from light. Pond water pumps were used to mix PMPW when aliquots (Fig. 4.2 D) were sampled. Aliquots for chemical analysis were taken during dewatering and during both mesocosm studies.

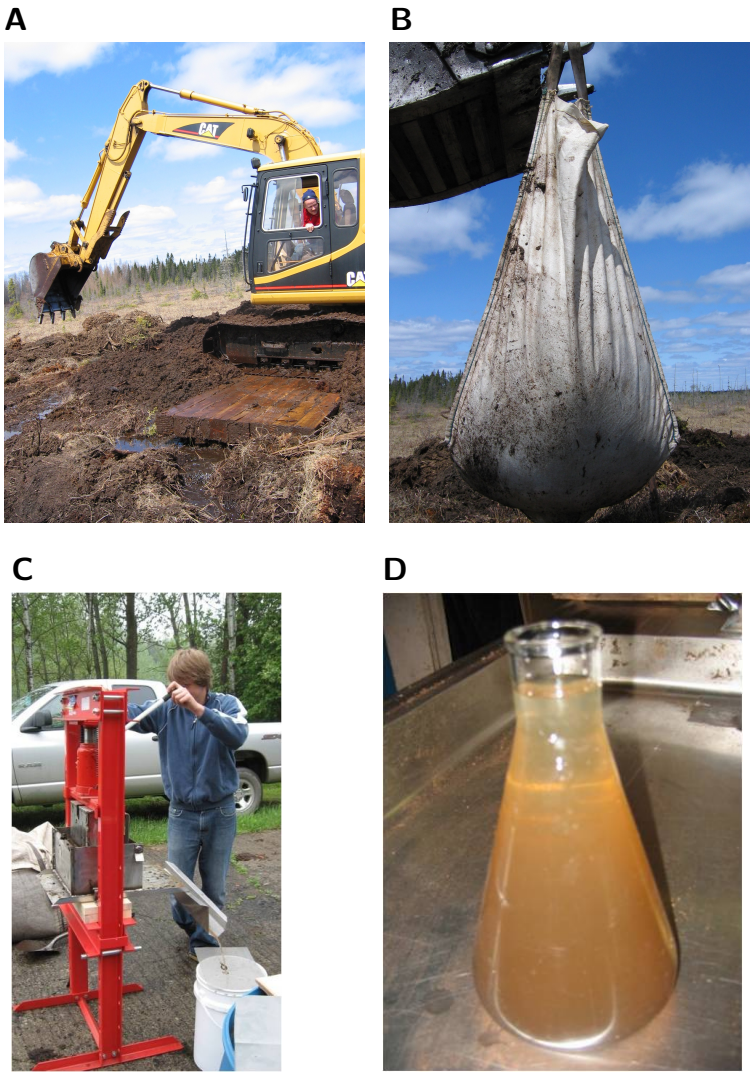


Figure 4.2: **A** Wet mining peat. **B** Peat bagged for processing. **C** Hydraulic peat dewatering. **D** Aliquot of peat mining process water (PMPW).

Mesocosm Study 1:

Study 1 was conducted to test whether groups of mesocosms receiving different concentrations of PMPW would differ significantly in the mean concentrations of analytes in leachate. Mesocosms were randomly assigned to four treatment groups: T0 control, T1 100% PMPW, T2 50% PMPW and T3 33% PMPW (each group n=6). Treatment groups received 4 L pulse impacts of diluted PMPW or control water (dilution water) on nine days over a 14 d period. Dilutions of PMPW were prepared by mixing appropriate volumes of PMPW and dilution water in batches as required. Each pulse impact was equivalent to 138 L of treatment water applied per cubic metre of acrotelm peat and limited by the volume capacity of the mesocosm.

The procedure on days pulse impacts were applied to mesocosm treatment groups (Days 1, 2, 3, 4, 7, 8, 9, 10, 11) was as follows: First, DWT and peat height was measured. Then, 4 L of diluted PMPW or control water was applied (the pulse) to each mesocosm surface with a watering can. Finally, sufficient mesocosm leachate was drained within 1 h of application to restore DWT. Drainage of leachate was assumed to mimic natural water table movement, being similar to changes in water tables observed by Heikurainen et al. (1964) in laboratory water additions to woody sedge-*Sphagnum* profiles.

Mesocosm leachate was sampled for analysis on Day 0 (pre-exposure) and Day 14 (post-exposure). Analytes measured were pH, redox, conductivity, alkalinity, solids, dissolved organics, anions, cations, metals (and MeHg) and nutrients (total nitrogen (TN), total phosphorus (TP), ammonia).

Mesocosm Study 2:

Study 2 was shorter (<3 h) and quantified the relative amount of solids and organics eluting in mesocosm leachate as successive, rapid pulses of 100% PMPW were applied. Triplicate mesocosms (Section 4.2.1) were used (peat volume 0.028±0.002 m^3). Each batch of 100% PMPW used for each replicate was analyzed (Table C.3). Chemically stable leachate concentrations were attained with dilution water additions before 100% PMPW was applied. The total volume of 100% PMPW used was 40 L.

For each replicate, mesocosm leachate was first sampled (I). Next, three 2 L pulses of dilution water were applied to the mesocosm surface with immediate leachate sampling after each pulse (D). Finally, twenty 2 L pulses of 100% PMPW were applied with

immediate leachate sampling after each pulse (P). On each leachate sample, total solids (TS), total suspended solids (TSS), dissolved organic carbon (DOC), particulate organic carbon (POC) and colour were measured. Metals and nutrients were determined on initial leachate samples of the third replicate, but trends for those analytes appeared similar to Study 1 and not reported.

4.2.3 Site Water and Dilution Water

Water chemistry from two reference sites (surface water and peatland porewater) within 300 m of the mining operation were available from the coincident research project (Chapter 2), providing ambient background concentrations (Table 4.2). Dilution water was dechlorinated L. Superior municipal water (Table 4.2) and used to maintain mesocosm DWT and dilute PMPW for Study 1 treatments.

Table 4.2: Mean ± SD (n) for analytes in reference site waters and dilution water (n=2). Reference site surface water was sampled from a pre-existing drainage ditch (circa 1940's) receiving upland flow from the study peatland. Reference site porewater was taken 50 cm below the peat surface, upfield from the mining site. Reference sites were sampled in 2008.

Analyte (units)	**Surface water**	**Peat porewater**	**Dilution water**
pH	6.04±0.32 (40)	5.76±0.05 (9)	7.45
Alkalinity (mg L^{-1} $CaCO_3$)	12.5±9.97 (40)	18.1±2.1 (9)	45.3
Conductivity (μS cm^{-1})	30.7±18.9 (40)	41.5±4.6 (9)	108
TSS (mg L^{-1})	2.1±1.9 (40)	4.6±2.7 (9)	<2.0
True Colour (TCU)	119±39.9 (40)	138±27.7 (9)	1.0
DOC (mg L^{-1})	13.2±5.1 (40)	12.1±4.9 (9)	2.2
POC (mg L^{-1})	11.4±5.1 (40)	14.8±5.2 (9)	<1.0
Redox (mV)	225±45 (27)	159±53.1 (8)	682
Reduced Fe (mg L^{-1})	0.731±0.573 (27)	2.18±0.52 (8)	<0.5
Chloride (mg L^{-1})	0.23±0.20 (40)	<0.05(9)	3.42
Sulphate (mg L^{-1} as SO_4)	0.13±0.18 (40)	<0.05(9)	3.36
Al (μg L^{-1})	49±19 (40)	39±10 (9)	8
Ba (μg L^{-1})	6±4 (40)	7±1 (9)	10
Ca (mg L^{-1})	3.98± 2.76 (40)	4.66±0.69 (9)	14.2
Fe (mg L^{-1})	0.851±0.812 (40)	2.72±0.57 (9)	0.003
Hg (ng L^{-1})	2.49±0.83 (27)	2.33±1.88 (8)	<0.50
MeHg (ng L^{-1} as Hg)	0.083±0.035 (27)	0.065±0.075 (8)	<0.030
K (mg L^{-1})	0.12±0.11 (40)	<0.10 (9)	0.56
Mg (mg L^{-1})	1.35±0.86 (40)	1.55±0.21 (9)	2.84
Mn (μg L^{-1})	37±49 (40)	97±17 (9)	<1
Na (mg L^{-1})	0.06±0.24 (40)	0.70±0.06 (9)	3.26
S (mg L^{-1})	0.31±0.80 (40)	0.33±0.49 (9)	1.32
Zn (μg L^{-1})	38±14 (40)	33±10 (9)	32
TN (mg L^{-1} as N)	0.454±0.174 (40)	0.668±0.053 (9)	0.168
TP (μg L^{-1} as P)	9±9 (40)	12±16 (9)	46

The following analytes were shown to have >75% of their measurments below analytical detection limits (DLs) (DL given in parentheses): nitrate as N (9 μg L^{-1}), nitrite as N (10 μg L^{-1}), As (5 μg L^{-1}), Be (2 μg L^{-1}), Cd (1 μg L^{-1}), Co (10 μg L^{-1}), Cr (2 μg L^{-1}), Cu (2 μg L^{-1}), Ni (2 μg L^{-1}), Pb (5 μg L^{-1}), Ti (10 μg L^{-1}) and V (6 μg L^{-1}).

4.2.4 Sampling and Analytical Procedures

Mesocosm leachate was sampled from bottom drains fitted to mesocosm piezometers (Fig. 4.1 C). Analytical chemistry was conducted at the Lakehead University Environmental Laboratory (LUEL), with accreditation (pH, alkalinity, conductivity, TN, TP, TSS) and demonstrated proficiency (anions, cations, metals, DOC) through the Canadian Association of Laboratory Accreditation. Further proficiency was demonstrated through the National Water Research Institute (above analytes and true colour, mercury (Hg)). Analyses followed LUELs standard operating procedures which included the use of blanks, analytical duplicates and quality control samples. Mesocosm leachate sample duplicates with concentrations greater than 10× DL had ≤15% relative deviation, exceptions being TN 33%, POC 51% and Zn 31%.

Mesocosm leachate, dilution water and site water were analyzed following the same methodology, as per LUEL. Both Hg and MeHg were determined without filtration where samples were preserved with HCl (pH<2, Fisher, OmniTrace) in amber glass bottles before analysis using atomic fluorescence spectrophotometry (Brooks-Rand Model III) after pretreatment and purge and trap techniques based on USEPA Methods 1631 (EPA, 2002) and 1630 (EPA, 2001b), respectively. Total extractable metal analysis was conducted on samples preserved with HCl (pH<2, Fisher, Tracemetal) in HDPE bottles, digested and concentrated by microwave oven after the addition of HNO_3 (Fisher, Tracemetal) and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). In some cases, analysis required filtration of samples post digestion to prevent instrument damage. Original preserved samples were used to determine reduced iron by the phenanthroline colourimetric method (Varian Cary 50).

The following general chemistries were conducted on unpreserved samples collected in HDPE bottles: The TS were determined gravimetrically after drying at 180°C. The TSS were determined gravimetrically on solids retained by 0.45 μm filters after drying at 105°C. The POC was determined on solids retained by 0.7 μm filters, by difference, after drying then ashing at 575°C. Conductivity was determined by calibrated electrode. Redox potential was determined by probe, verified with Zobell's solution. The pH was determined potiometrically with calibrated electrode prior to alkalinity determined by autotitration (Mettler) to pH 4.5 with 0.02 N H_2SO_4. True colour was determined on filtered samples (0.45 μm) using a spectrophotometer (Varian Cary 50; 456 nm), calibrated with platinum-cobalt standards and reported as true colour units (TCU). Chlo-

ride (Cl^-), nitrate (NO_3^--N), nitrite (NO_2^{2-}-N) sulphate (as SO_4^{2-}) and total ammonia (NH_3-N) were determined on filtered samples (0.45 μm) by ion chromatography (Dionex DX-120). Automated flow injection and colourimetric instrumentation (Skalar Sans^{++}, Netherlands) was used for the following: DOC was determined after online filtration and acidification, releasing CO_2 gas that passes through a membrane into weakly buffered alkaline solution with phenolphthalein indicator for detection and quantification; TP was determined via phosphor-molbdic acid complex after fuming acid digestion with a sulphuric acid/potassium sulphate/mercuric oxide solution; TN was determined by online digestion with potassium peroxodisulphate/sodium hydroxide solution and heating, ultra-violet (UV) radiation with a borax buffer and subsequent nitrate quantification with the Griess reaction after reduction by a cadmium copper reductant.

4.2.5 Statistical Procedures

Analytes were removed from the dataset when >75% of data points were censored by LUEL as below DL, otherwise DL values were set equal to DL/2 prior to statistical analysis. For Study 1, this was applied when both initial and post treatment group leachate met the criteria. Statistics were conducted with R (R Development Core Team, 2010). Results are presented as mean ± SD unless stated. Mesocosm treatment groups were compared using one-way ANOVAs and Dunnett's test.

The 100% PMPW possessed high SD, thus median results were included and used for efficiency calculations in Study 1. Note when a PMPW median is lower than its mean, a more conservative estimate of removal efficiency results (Eq. 4.1). Study 2 100% PMPW means and medians were similar to each other and to Study 1 medians. Therefore, means were used for removal efficiency calculations in Study 2.

4.2.6 Efficiency Calculation

The efficiency of mesocosms to remove analytes from 100% PMPW was calculated in cases where PMPW concentration was greater than leachate concentration after 100% PMPW pulses were applied. Percent removal efficiency (E%) was calculated as

$$E\% = \frac{(C_P - (C_F - C_C))}{C_P} \times 100. \tag{4.1}$$

For Study 1, C_P was the median concentration of PMPW (Table 4.3), C_F was the mean leachate concentration on Day 14 for treatment group T1 (100% PMPW, Fig. 4.3)

and C_C was the mean concentration of all 24 mesocosms before the study commenced (Table C.1). The value of C_C corrects for an analyte concentration in mesocosm leachate prior to pulse impacts being applied. If the equilibrium period with dilution water resulted in C_C being greater than C_P and C_F, a removal efficiency could not be calculated (alkalinity, pH, conductivity, K, Mg, ammonia, Fe, reduced Fe, Mn and MeHg). In the case of Zn, C_C was greater than C_F, but less than C_P, resulting in an efficiency of over 100%. Therefore, 100% of Zn appeared to be retained by mesocosms.

For Study 2, C_P was the mean concentration of 100% PMPW used for that replicate (Table C.3), C_F was the mean concentration of the last ten mesocosm leachates sampled (i.e. steady state) and C_C was the mean concentration of leachate sampled after each application of dilution water.

4.3 Results

4.3.1 Process Water Quality

For PMPW produced in this study, pH was below and mean Al, Fe, Hg, Zn, TP and TSS concentrations exceeded CWQG (Table 4.3). True colour in PMPW was higher than a CWQG based on reference site true colour (119 TCU). Copper and Pb were below laboratory DLs (2 μg L^{-1} and 5 μg L^{-1}, respectively) to assess any impact. Other analytes below DL (in parentheses) were nitrite as N (10 μg L^{-1}), As (5 μg L^{-1}), Be (2 μg L^{-1}), Cd (1 μg L^{-1}), Co (10 μg L^{-1}), Ti (10 μg L^{-1}) and V (6 μg L^{-1}).

The PMPW results here for colour were higher than similar dewatering techniques (Washburn & Gillis, 1983; ORF, 1984; Monenco, 1986), while solids, ions and nutrients were similar or lower (Table 4.3). The following were noted for (ORF, 1984) data: *i*) TSS methodology used 1.5 μm pore size filters, larger than 0.45 μm used here, *ii*) TN data were reported as total Kjeldahl nitrogen (TKN), thus excludes inorganic N, *iii*) for low severity heat processing, small batches of well decomposed raw peat (≈300 g) were first diluted with distilled water, heated to 170°C, then cooled before "processing" in Buchner funnels with Whatman #1 filters, which would have removed particulate matter causing a low bias, and *iv*) the rotary mechanical press was a novel design, best suited for producing process water by dewatering fibrous and less humified peat on a small scale (17.5 cm diameter press, #35 mesh screens), rather than from more humified peat as ideal for energy biomass and processed here.

Table 4.3: Chemistry of peat mining process water (PMPW) (mechanical dewatering) including means reported by (a) Washburn & Gillis (1983) mechanical dewatering pressate waters with no pretreatment, (b1) ORF (1984) mechanical dewatering with low severity heat pretreatment and (b2) ORF (1984) mechanical dewatering with rotary press. (c) Canadian Water Quality Guidelines (CWQG) (CCME, 2007): (d) CCME (2001), (e) CCME (2004), (f) CCME (2002). Dashes no data.

	This study					
Analyte (units)	Mean±SD (n)	Median	Washburn & Gillis (1983)[a]	ORF (1984)[b1]	ORF (1984)[b2]	CWQG[c]
pH	5.49±0.40 (5)	5.55	—	4.74	4.30	6.5–9
Alkalinity (mg L^{-1} $CaCO_3$)	9.14±4.90 (5)	7.70	—	—	—	—
Conductivity (μS cm^{-1})	35.6±4.5 (8)	37.0	—	—	—	—
True Colour (TCU)	532±328 (8)	447	—	280	320	not > ref site[d]
DOC (mg L^{-1})	20.1±2.0 (7)	20.3	136	—	—	
TOC (mg L^{-1})	—	—	—	230	7200	—
POC (mg L^{-1})	407±333 (8)	335	—	—	—	—
Redox potential (mV)	399±128 (3)	395	—	—	—	—
Reduced Fe (mg L^{-1})	2.42±1.15 (3)	2.06	—	—	—	—
Chloride (mg L^{-1})	0.71±0.32 (5)	0.75	—	<1	<1	—
Nitrate (mg L^{-1} as N)	0.554±0.581 (5)	0.330	—	<1	<1	2.93
Sulphate (mg L^{-1} as SO_4^{2+})	2.82±1.45 (5)	2.45	—	8.6	29	—
Ammonia (mg L^{-1} as N)	<0.010 (2)	<0.010	—	6	<1	0.019
Al (mg L^{-1})	1.39±0.80 (5)	1.38	4.72	<0.5	0.08	0.005
Ba (μg L^{-1})	49±19 (5)	56	21000	—	—	—
Ca (mg L^{-1})	10.76±4.53 (5)	11.44	—	18	11	—
Cr (μg L^{-1})	15±27 (5)	4	52	<30	10	Cr(III) 8.9, Cr(IV) 1.0
Cu (μg L^{-1})	6±3 (5)	6	<20	<30	<10	2 (soft water)
Fe (mg L^{-1})	4.36±2.23 (5)	4.89	2.03	1.6	1	0.300
Hg (ng L^{-1})	37.1±16.6 (5)	27.7	<1000	300	<100	26.0
MeHg (ng L^{-1} as Hg)	0.485±0.368 (4)	0.498	—	—	—	4
K (mg L^{-1})	0.90±0.94 (5)	0.51	0.75	1.5	2.0	—
Mg (mg L^{-1})	1.45±0.37 (5)	1.57	—	1.6	3.2	—
Mn (μg L^{-1})	109±66 (5)	87	45	80	100	—
Na (mg L^{-1})	0.791±0.054 (5)	0.800	—	<1	8.8	—
Ni (μg L^{-1})	9±7 (5)	7	<4	40	20	25
S (mg L^{-1})	1.803±0.585 (5)	1.860	—	—	—	—
Zn (μg L^{-1})	55±7 (5)	57	24	60	120	30
TN (mg L^{-1} as N)	7.92±6.25 (5)	5.30	38.1	18	207	—
TP (μg L^{-1} as P)	303±212 (5)	315	1000	—	4600	10–20[e]
TSS (mg L^{-1})	432±381 (10)	307	—	19	14300	ambient+5[f]
TS (mg L^{-1})	303±95.7 (6)	289	—	387	14400	(f)

4.3.2 Differences in Mesocosm Leachate Concentrations

In Study 1, significant differences among mesocosm treatment group leachate concentrations were found for TSS, POC, DOC, true colour, Hg, Al, Na, chloride, TN and TP (Fig. 4.3) after pulses of diluted PMPW were applied over a two week period. Though Na and chloride differed significantly ($p<0.001$), these analytes were higher in dilution water (Table 4.2) than PMPW (Table 4.3) and not considered further.

A clear decrease in leachate concentration occurred when PMPW was diluted (Fig. 4.3). Pearson correlation coefficients were highly significant ($p\leq0.001$) between TSS and POC (0.761), DOC (0.878), true colour (0.787), Hg (0.834), Al (0.925), TN (0.865) and TP (0.741) for post mesocosm treatment leachate concentrations (n=24), and significant for MeHg (0.546, $p=0.006$).

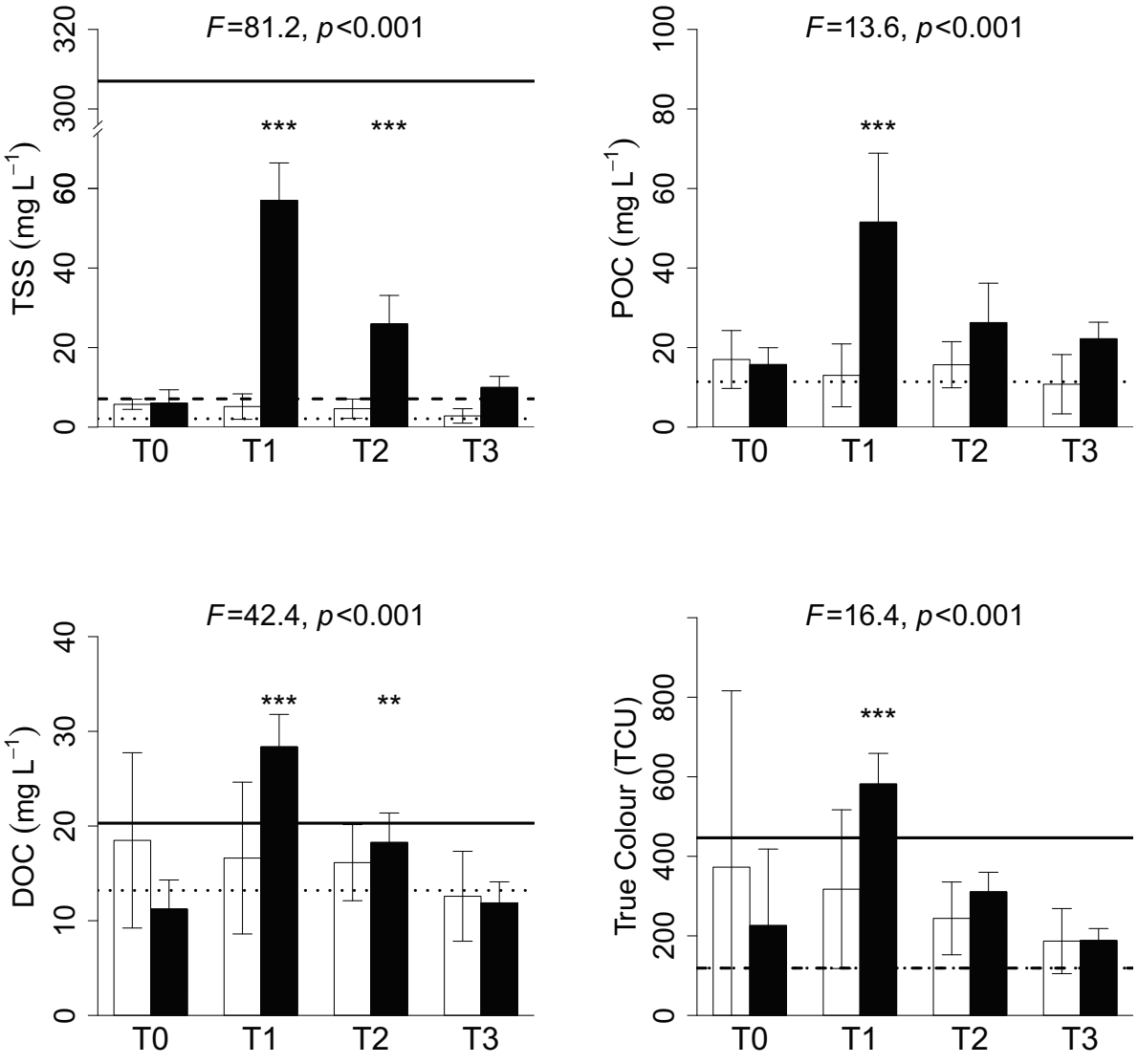
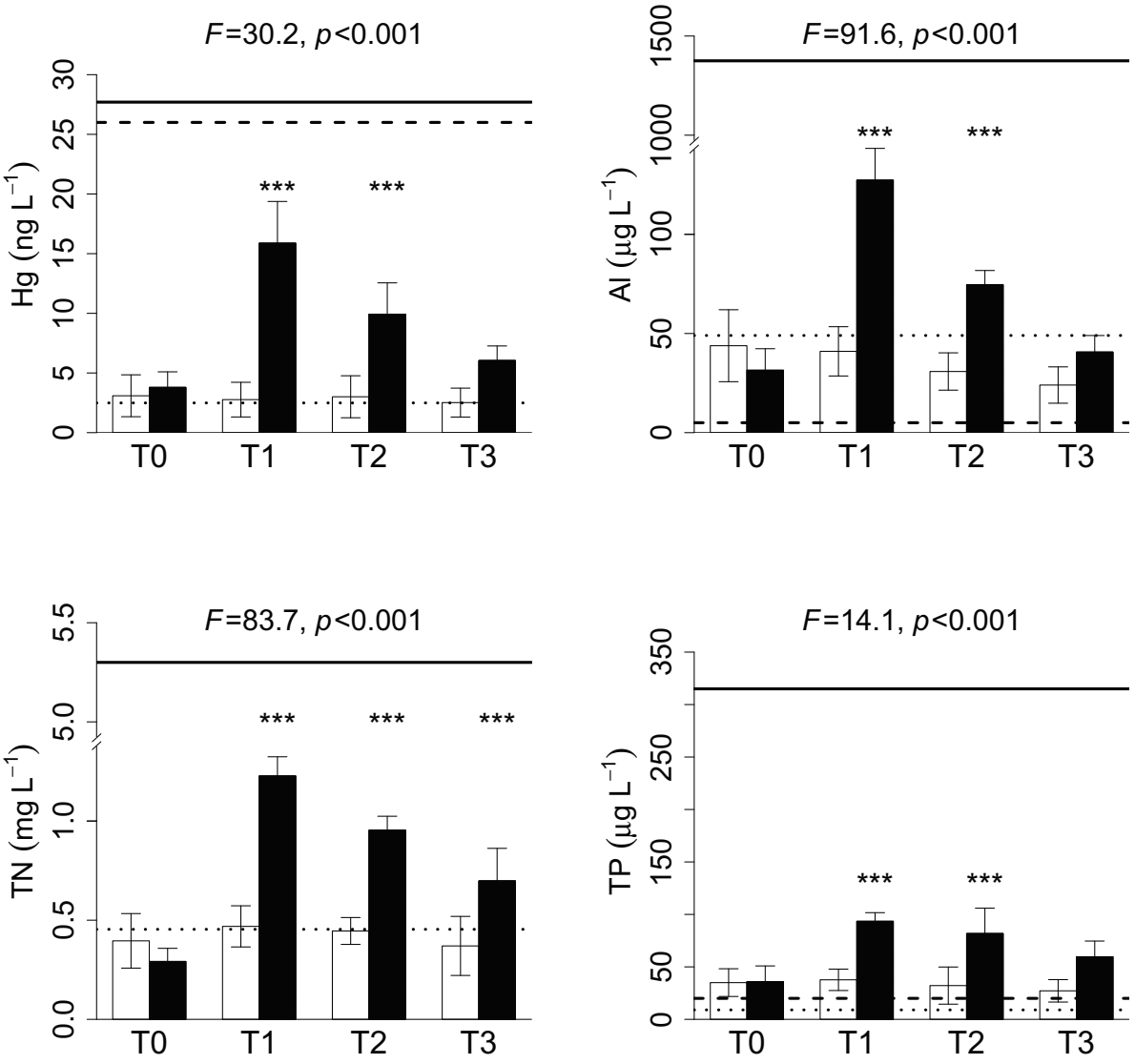


Figure 4.3: Continued next page.



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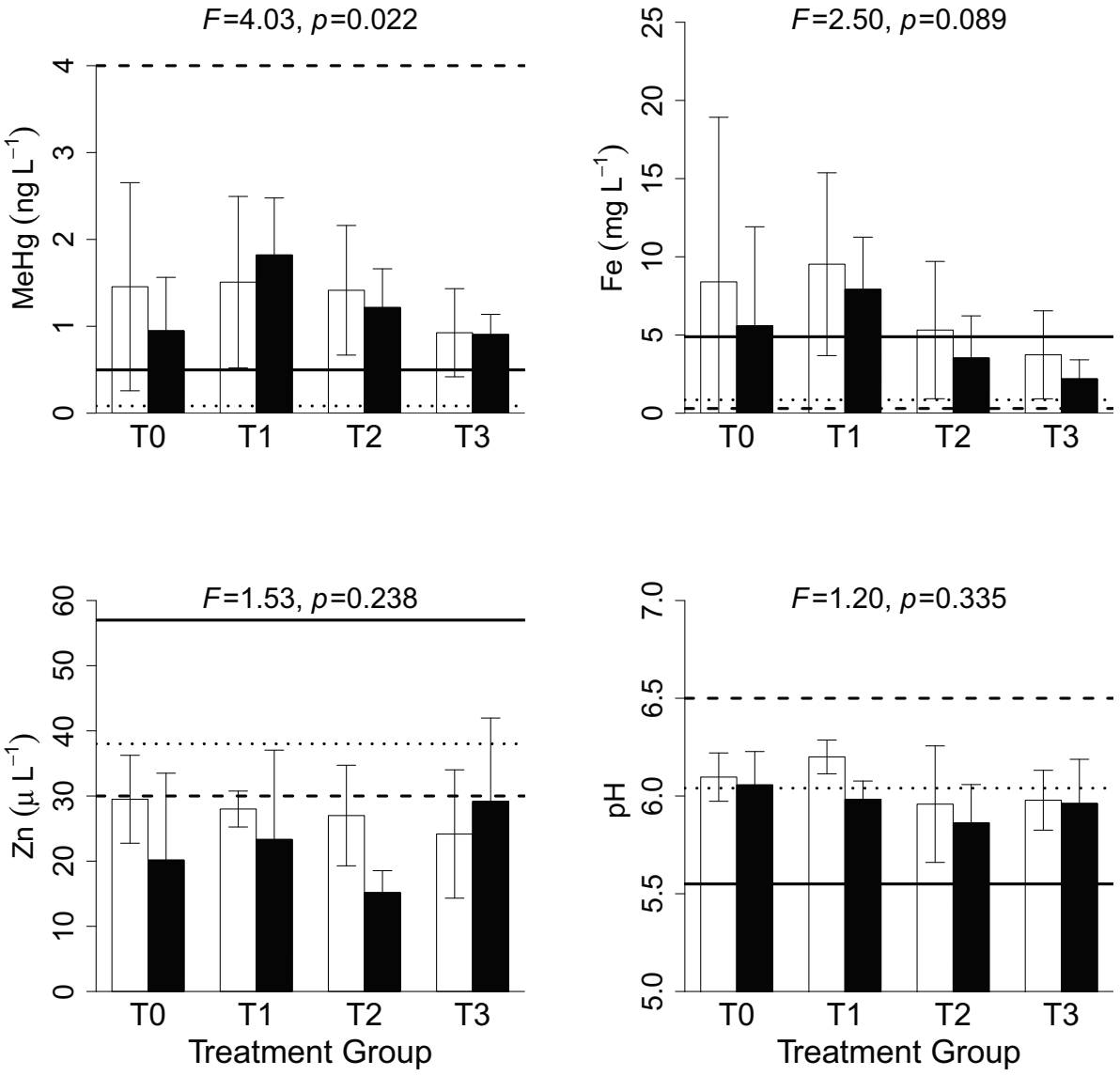

Figure 4.3: Study 1 mean ± SD mesocosm leachate concentrations pre-exposure (hollow bars) and post-exposure (black bars) to pulses of diluted PMPW. Treatment groups (n=6): T0 Control (100% dilution water; 0% PMPW); T1 100% PMPW (0% dilution water); T2 50% PMPW (50% dilution water); T3 33% PMPW (67% dilution water). Solid line: PMPW median concentration (note y-axis breaks for TSS, Al and TN). Dashed line: Canadian Water Quality Guidelines (CWQG) if applicable (CCME, 2007). Dotted line: mean concentration of reference outflow (Table 4.2). F values (ANOVA) for post-exposure with asterisks for significance compared to T0 (*** $p \leq 0.001$; ** $p \leq 0.01$; * $p \leq 0.05$.

Initial Study 1 mesocosm peat depth was 44.0 ± 3.3 cm and peat volume was 0.029 ± 0.002 m^3. The DWT and concentrations of analytes in mesocosm leachate among treatment groups before treatments were not significantly different (Appendix C.1). Change in peat height before the study period to after the study period ranged from an increase of 1.5 cm to a decrease of 3.4 cm (n=24), and not significant ($F_{3,20}$=1.35, p=0.286). Deleterious effects to acrotelm vegetation were not qualitatively evident after 14 day exposure to PMPW.

4.3.3 Peat Filtration Capacity

Though solids were evident in Study 1 mesocosm leachate, 100% breakthrough of TSS, POC and TS did not occur when 40 L of 100% PMPW was applied in successive 2 L pulses over a brief time (≤3 h), as determined in Study 2 (Fig. 4.4). Mean TSS and true colour concentrations in PMPW for replicate applications ranged from 99.4 to 344 mg L^{-1} and 202 to 306 TCU, respectively, exceeding CWQG. A leaching of organic analytes was observed in Study 2 (Fig. 4.4), as in Study 1. True colour in mecocosm leachate replicates was 81.7%, 35.1% and 30.6% higher than PMPW. For DOC, only one replicate showed leaching, being 18.5% higher in leachate than PMPW.

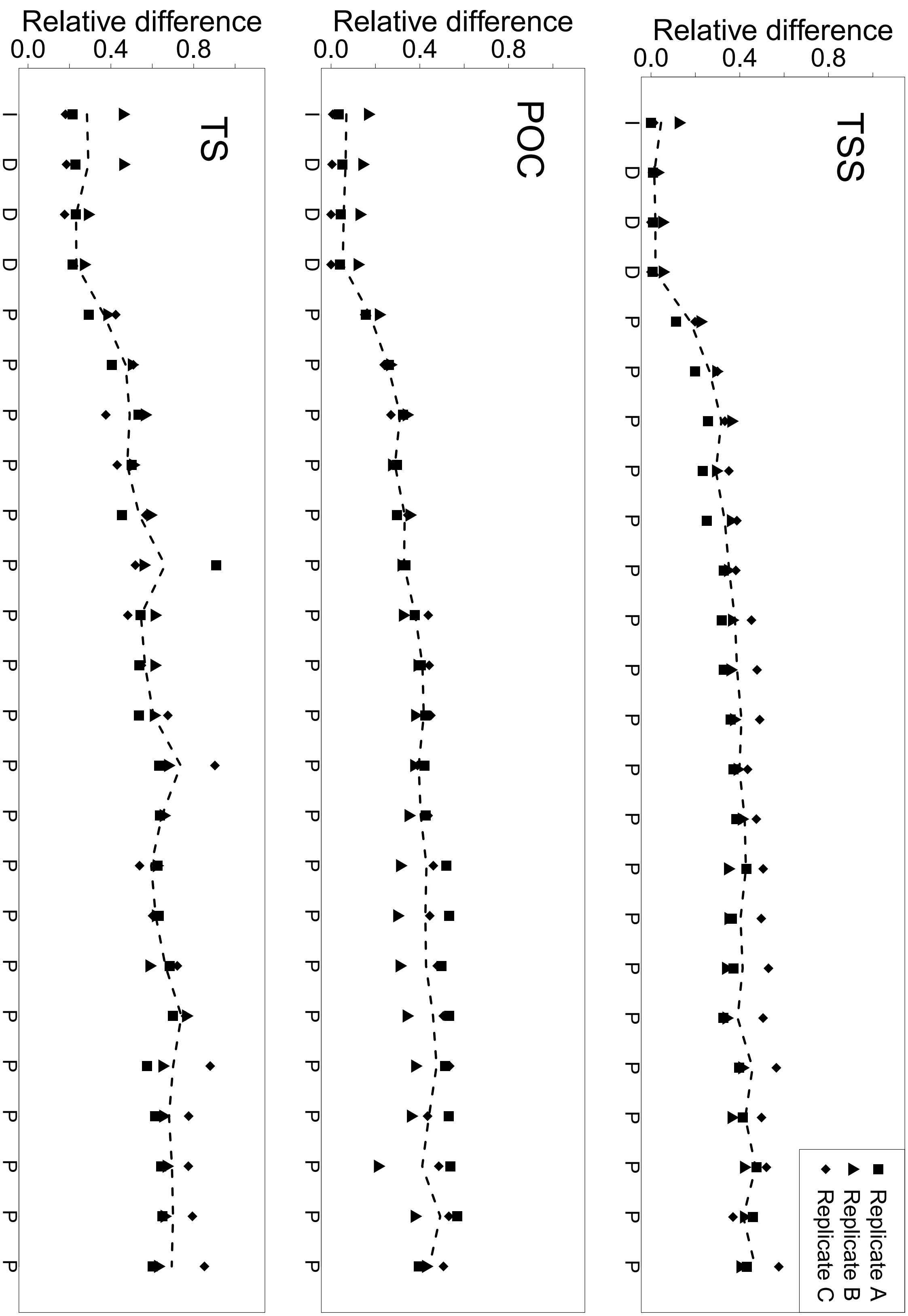

Figure 4.4: Continued next page.

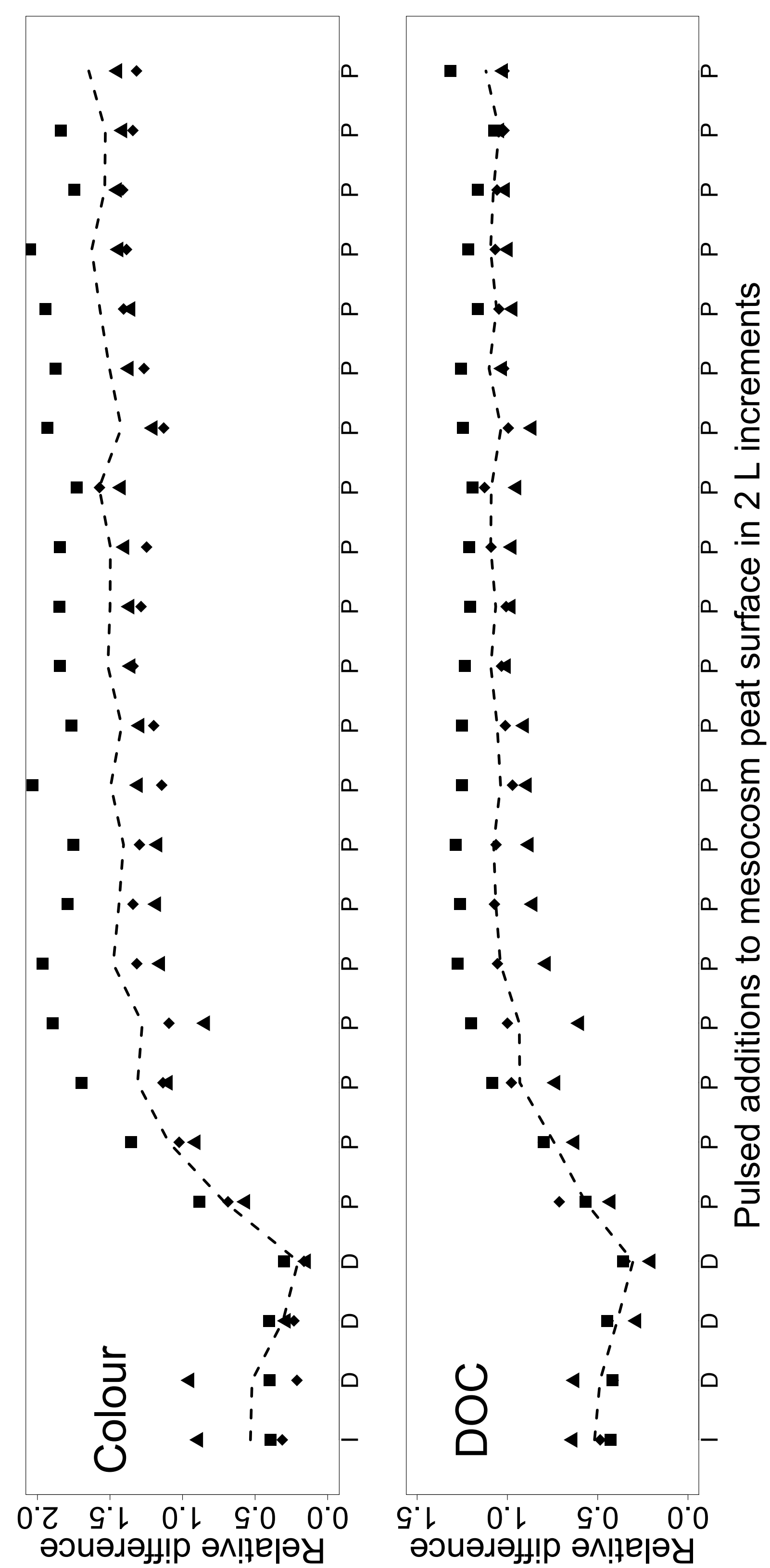

Figure 4.4: Study 2 relative difference in leachate concentration ([mesocosm leachate]/mean [PMPW]) as pulse impacts (2 L aliquots) were applied to the surface of mesocosm peat. Pulse impacts along the x-axis, where I represents the initial mesocosm leachate, D represents leachate after dilution water pulses (control) and P represents leachate after 100% PMPW pulses. Dashed line was the mean of the replicates and relative difference in leachate concentration appeared to reach a steady-state condition.

4.3.4 Removal Efficiencies

Removal efficiencies calculated (Eq. 4.1) for solids in Study 2 were lower that those in Study 1 (Table 4.4). A removal efficiency was not calculated for analytes that leached from mesocosms (DOC and colour) nor analytes with pre-exposure leachate concentrations greater than PMPW (alkalinity, pH, conductivity, K, Mg, ammonia, Fe, reduced Fe, Mn, MeHg, Na and chloride).

Table 4.4: Removal efficiency (%) of analytes from 100% PMPW by peat mesocosms as calculated from Eq. 4.1. Dashes indicate not analyzed.

	Study 1	Study 2		
Analyte		Trial A	Trial B	Trial C
Al	93.2	—	—	—
Ba	91.1	—	—	—
Ca	91.6	—	—	—
S	87.4	—	—	—
Hg	52.9	—	—	—
Zn	100	—	—	—
Sulphate	76.9	—	—	—
TN	84.8	—	—	—
TP	80.8	—	—	—
TSS	82.9	54.9	60.8	45.3
POC	88.8	49.4	73.7	47.2
TS	—	55.7	65.8	43.4

4.4 Discussion

4.4.1 Process Water Quality

Low concentrations of analytes in PMPW observed here, when compared with other studies (Table 4.3) suggests this study represents minimum concentrations of analytes that can expected from dewatering peat by mechanical means. Whether this was a consequence of peat at this site being somewhat "pristine" or a consequence of dewatering methodology, remains unclear. Lower TSS and some adsorbed analytes, such as metals and nutrients, likely occurred in low severity heat pretreatment data, since samples were filtered before analysis (ORF, 1984). Authors also suggested that higher metals for rotary pressed peat (notably Na) occurred since municipal water was used during the process. Nevertheless, any discharge of PMPW with analytes outside the values set by Canadian regulators (Table 4.3) has the potential to degrade receiving water quality. Water quality of process water obtained from any mechanical dewatering of peat will ultimately depend on peat and porewater chemistry in addition to the specific dewatering process employed (Monenco, 1986).

The dewatering of wet mined peat in this study produced effluents with substantial quantities of TS, TSS and POC (Table 4.3). Typical dry peat harvesting activities are known to release particulate matter (Sallantaus, 1984; Winkler and DeWitt, 1985; Shotyk, 1986b; Ouellette et al., 2006; Pavey et al., 2007). Particulate matter from dry harvested peatlands likely caused an alteration in downstream benthic invertebrate and fish communities (Laine and Heikkinen, 2000). Therefore, a removal of solids from PMPW before any direct discharge to receiving water is warranted.

The TN in this PMPW was lower than previously reported (Table 4.3), yet higher than reference site water (Table 4.2). However, TN was not evident as any species with a specific numeric guideline (i.e. ammonia, nitrate, nitrite), though ammonia was detected in heat treated pressate waters (Table 4.3). It was hypothesized that TN in PMPW remained complexed to organic and/or particulate matter and did not pose an immediate environmental concern. However, TP in this PMPW was 15-30× the trigger range that identifies a potential environmental problem for mesotrophic lakes and rivers (CCME, 2004), assuming reference water as mesotrophic based on TP concentrations (Table 4.2). Higher TP was reported by others (Table 4.3) and transport of nitrogen and phosphorus species by organic and particulate matter as a consequence of traditional

peat harvesting has been described elsewhere (Heikkinen, 1994; Kløve, 1998, 2001).

Organic constituents in PMPW (POC, DOC, colour; Table 4.3) would likely alter the spectral quality of receiving water. Water colour has been correlated to primary production, with any significant change in spectral quality from anthropogenic disturbances causing concern (CCME, 2001). Pastor et al. (2003) showed that DOC exerts significant control over productivity, biogeochemical cycles and the attenuation of visible and UV radiation in downstream ecosystems.

The pH of PMPW (Table 4.3), coupled with a low buffering capacity of reference waters (Table 4.2), suggests a direct discharge of PMPW from this study would increase receiving water acidity. As expected, fen peat produced PMPW with a higher pH than bog peats dewatered by others (Washburn & Gillis, 1983; ORF, 1984). Water quality of lakes adjacent to natural peatlands are influenced by those ecosystems, especially with respect to acidity (Keskitalo and Eloranta, 1999), suggesting reference water pH be taken into consideration should it lie outside CWQG. In this case however, reference water pH was still higher than PMPW (Fig. 4.3).

Some increase in metals to receiving waters are expected if PMPW were directly discharged (Table 4.3). It was not surprising that Al, Fe, Hg and Zn in PMPW exceeded CWQG (Fig. 4.3), since reference water had elevated concentrations (Table 4.2). Metals were likely bound to particulate matter (Winkler and DeWitt, 1985). Elevated Hg concentrations downstream of a New Brunswick peat harvesting operation were associated with sediments containing a higher percentage of peat particulates (Surette et al., 2002). Therefore, an increase of Hg species from an Ontario mining operation, as suggested by Gleeson et al. (2006), seems warranted. Whereas, particulate bound Hg from peatlands may not be bioavailable to benthic organisms (DiGiulio and Ryan, 1987; Surette et al., 2002), MeHg in "peat-type" sediments did bioaccumulate in benthic worms (*Lumbriculus variegatus*) under laboratory conditions (Chapter 3). Furthermore, field Biota-Sediment Bioaccumulation Factor (BSAF) for MeHg were greater than 1. The MeHg in PMPW was 5× reference water (Fig. 4.3) and particulate bound MeHg would eventually settle to sediment. Though MeHg in PMPW was less than current CWQG, those guidelines admittedly may not be protective of aquatic life due to food web trophic transfer (CCME, 2003). To fully assess metal impacts, ambient sediment concentrations in the receiving water body should be compared to MeHg in particulate fractions of PMPW and to Canadian Sediment Quality Guidelines. As strongly advocated by Grigal (2003), the bulk densities of discharged peat material and sediment must be considered.

Some treatment of PMPW seems required before discharge. These data, and conclusions by Monenco (1986), agree with a review by Gleeson et al. (2006), who postulated potential cumulative impacts of fuel peat mining in Ontario could include an increase of metals, nutrients, acidity and solids being released to the environment. Results from mesocosm studies assessed the suitability peatlands as primary treatment systems for PMPW.

4.4.2 Mesocosm Leachate Quality

Acrotelm peat hummocks in mesocosms were quite efficient at removing large amounts of analytes (Table 4.4). The first research to critically study the use of an adjacent peatland as a primary treatment method for sewage from a work camp was in the James Bay region of northwestern Quebec (Dubuc et al., 1986). Authors calculated average reduction percentages greater than 90% for Ca, Mg, TP and TN. They also reported a reduction in total carbon of 70.6%, with no evidence of organic constituents leaching. High removal efficiencies in that research were likely the result of an initial settling of solids in septic tanks. Furthermore, dilution of wastewater along the 1.5 km treatment peatland by groundwater flows could not be discounted (Dubuc et al., 1986).

Observed efficiencies were also consistent with previous research employing peat to treat other wastewater types. In column experiments, Ringqvist et al. (2002) found poorly humified peat removed 77-98% of Zn from sulphide mine tailings and 46-56% from landfill leachate, with higher metal removal from wastewater using peat as an adsorbant compared to inorganic adsorbants investigated. In batch experiments, Viraraghavan and Kapoor (1995) found Hg was reduced by 71.6% when wastewater was spiked to 1 mg THg L^{-1} and treated with peat. In field trials, Toth (1980) calculated 99.2-99.4% of TP in sewage sludge as retained by fen soils. Kangsepp and Mathiasson (2009) found vertical flow peat filters reduced TP by 58% and 63% in municipal waste water while full scale peat and organic biofilters used to treat metal recycling landfill leachate removed 37 to 73% of various metals. Authors also found reductions of TN (25%), DOC (30%) and suspended solids (38%).

High removal efficiencies (Table 4.4) did not translate into leachate water quality that would meet CWQG for TSS, true colour, pH, TP, Al, Fe and Zn (Fig. 4.3, 4.4). As explained previously for untreated PMPW, receiving water quality should be considered for analytes such as pH, Al, Fe and Zn. Furthermore, dilution effects surmised by Dubuc

et al. (1986), and that likely occurred in Toth (1980) (based on maintained water levels), may similarly occur in treatment peatlands filtering PMPW. Study 1 showed a simple dilution of PMPW to 33% reduced not only TSS below CWQG, but resulted in mesocosm leachate not differing significantly from controls for all analytes, with the exception of TN (Fig. 4.3). Though dilution may produce PMPW treatable by peat, McLellan and Rock (1988) noted a desorption of metals of up to 50% when deionized water was applied to spent peat columns filtering landfill leachates. Such long term desorption should be explored furthur, using elution waters characteristic of peatland ecosystems (e.g. rainwater, ground water, peat porewater, snow melt).

This research demonstrated that solids in PMPW and mesocosm leachate were at levels detrimental to receiving water bodies (Table 4.3, Fig. 4.3, 4.4). Solids removal should be a focus for wet mining industries and some sort of primary treatment of PMPW seems warranted before peatland filters are considered, especially since these concentrations were initially lower than those produced by others (Table 4.3). In addition, a release of solids to the environment represents a loss of product to industry. Research on ideal settling pond design was conducted by Kløve (1997) and may be of some value to PMPW primary treatment.

Colour clearly leached from mesocosm peat in Study 1 (Fig. 4.3) and Study 2 (Fig. 4.4), while results for DOC were less consistent. Kalmykova et al. (2009) also noted a leaching of DOC from peat filters receiving various effluents, and associated with higher metal concentrations in eluate. It is hypothesized here that exposure of peat mesocosms to PMPW increased the humification of peat, thus releasing organic constituents. Losses of carbon to the atmosphere from constructed wetlands receiving peat mining runoff waters were measured (Liikanen et al., 2006), an indication of peat degradation.

The necessary mixing and dilution of PMPW for homogenization produced aerobic conditions (Tables 4.2, 4.3, C.1, C.2), that would also decompose peat in mesocosms. Any decomposition of hummock peat increases its amorphous nature, thus reducing the size of pore spaces within the peat matrix and enhancing its effectiveness as a sorbent (Couillard, 1994). Peat mesoscoms were exposed to PMPW for a longer period in Study 1 (14 d) than Study 2 ($\approx$3 hr). Therefore, peat decomposition may explain the higher removal efficiencies of solids in Study 1 than Study 2 and the increased leaching of DOC in Study 1 than Study 2. Changes in physical peat properties (e.g. bulk density, peat chemistry) exposed to PMPW should be included in future work.

4.5 Conclusions

Process water produced by mechanically dewatering peat should not be directly discharged to water bodies according to current CWQG. This research provides some local insight into whether PMPW quality would be sufficiently improved by filtration through intact acrotelm hummocks. Two mesocosm studies showed that high levels of particulate matter present in PMPW (TSS, POC), though removed in high quantities (45-83% and 47-89%, respectively), were still present in mesocosm leachate at levels that would be detrimental to aquatic life. Furthermore, organic constituents measured as true colour and DOC increased in concentration in mesocosm leachate, being above concentrations found in PMPW and in exceedance of CWQG.

High removal efficiencies for nutrients (TN 84.4%, TP 80.8%) were determined, but eutrophication of receiving water remains a concern. High percentages of metals were also removed by peat mesocosms. Based on both CWQG and reference site concentrations, the concentrations of metals found in mesocosm leachate do not pose a threat to aquatic systems, with the possible exception of MeHg.

Wetlands have traditionally been employed as tertiary and not primary filtration systems. Although it was anticipated that constructed peatlands or the use of peat filters could improve the water quality of PMPW by reducing concentrations of solids, nutrients and metals, some primary treatment of PMPW to remove solids seems required. Simple dilution of PMPW, improved process control by industry or settling ponds are possible solutions.

Chapter 5

Using a Sugar Solution to Facilitate Separation of *Lumbriculus variegatus* from Organic Sediments

5.1 Introduction

Sediments are a primary sink for Hg species and can be a production site for methylmercury (MeHg) (Jensen and Jernelov, 1969; Ullrich et al., 2001). Quantifying Biota-Sediment Bioaccumulation Factors (BSAFs) experimentally by measuring tissue concentrations of total mercury (THg) and MeHg in benthic organisms that directly ingest these sediments is an important first step to understanding initial transfer of Hg species from sediments to food webs. Wetlands and peatlands have been identified as important sinks of Hg (Grigal, 2003) and sources of MeHg to boreal forest ecosystems (St. Louis et al., 1994). Research questions concerning the bioaccumulation of THg and MeHg after wet peat mining, particularly from highly organic matter discharged to downstream ecosystems, have been posed (Chapter 3).

Bioaccumulation methodology (EPA, 2000c) utilizes the benthic oligochaete *Lumbriculus variegatus* (California blackworms) as the test organism. After a 28 d exposure to test sediments, organisms must be retrieved in order to measure concentrations of analytes of concern in tissue. Peat and its associated organic particulates can be quite fibrous in texture, closely resembling that of vermiform invertebrates. An efficient isolation of *L. variegatus* from such sediments has proven a monumental task. Gut purging of

organisms prior to tissue analysis is also recommended (EPA, 2000c), implying organisms must survive their separation from sediment.

Several strategies for benthic organism isolation from organic detritus have been suggested in the literature and include kerosene and ethanol (Barmuta, 1984), staining dyes (Mason and Yevich, 1967; Lackey and May, 1971), elutriators (Magdych, 1981) and flotation with sugar solution (Anderson, 1959). It was presumed solvents and dyes would cause *L. variegatus* mortality, had a greater potential to alter tissue concentrations and involved costly chemicals not readily available. A benthic elutriator constructed as per Magdych (1981) was briefly evaluated then dismissed, being messy, awkward to clean, physically damaging to *L. variegatus* and failing to retain lighter peat particulates. Therefore, sugar solution was evaluated.

As per Anderson (1959), most organic debris has a specific gravity greater than 1.12, while invertebrates are less than this value. Therefore, placing organic sediments in a solution of higher specific gravity would result in most invertebrates floating to the surface while most detritus sinks. However, after time in a hypertonic solution, organisms would shrink by fluid loss, increase in specific gravity and sink (Anderson, 1959). Invertebrate fluid loss raised the question of whether concentrations of THg and MeHg in *L. variegatus* tissue would be affected, thus making sugar flotation unsuitable. Whereas numerous researchers mention employing the technique for field invertebrate studies (Lackey and May, 1971; Cowell et al., 2004; Wills et al., 2006; Swanson, 2011), no studies have employed the method for bioaccumulation studies, nor examined its effect on organism tissue concentrations of THg and MeHg. Therefore, several experiments were conducted to (1) estimate lethal time (LT) toxicity values for *L. variegatus* in 300 g L^{-1} sugar solution, (2) calculate the percent recovery and time to recover organisms from organic sediment using sugar flotation, and (3) determine if any significant difference in THg and MeHg tissue concentration existed after organisms were exposed to control and sugar solutions.

5.2 Methods

5.2.1 Culturing and Spiking of *L. variegatus*

Mass cultures of mixed-age *L. variegatus* (subclass Oligochaeta) were initiated at Lakehead University from organisms received from United States Environmental Protection

Agency (USEPA) Duluth, MN. Cultures were maintained in flow through aquaria with L. Superior dechlorinated municipal water (DMW) (hardness 45.6 mg L^{-1} as $CaCO_3$, alkalinity 46.7 mg L^{-1} as $CaCO_3$, pH 7.25), maintained at 23±3°C on a 16:8 hr light:dark cycle. Substrate was shredded brown paper towel and cultures were fed two to three times weekly with commercially available trout chow.

Homogeneous and detectable concentrations of THg and MeHg in *L. variegatus* tissue were desired for these experiments. Therefore, aliquots of organisms from culture were spiked with inorganic and organic Hg. For THg spiked organisms, approximately 26 g (ww) of *L. variegatus* from culture were placed in 2 L of 20 μg g^{-1} THg solution (1000 mg Hg L^{-1} (Fisher CSM114-100) diluted in DMW) for 24 hr. Light aeration via a pasteur pipette was required as the first spiking attempt without aeration resulted in severe organism mortality. For MeHg spiked organisms, approximately 26 g (ww) of *L. variegatus* from culture were placed in 2 L of 4 ng L^{-1} MeHg solution (1.0 mg MeHg L^{-1} (Brooks-Rand Labs custom order) diluted in DMW) for 24 hr. (aerated). Spiked organisms were rinsed at least thrice with DMW and held in fresh DMW until their same day use. Separate batches of MeHg spiked organisms were prepared for aqueous and sediment exposure experiments (Section 5.2.6).

5.2.2 Test Sediment and Sediment Exposures

The sediments referred to herein were homogenized composite ponar grab samples of catotelm peat (1-2 m below the water table, 2009) that had been exposed and re-flooded during an experimental peat mining operation (Chapter 2). Total organic matter content was greater than 90% (loss on ignition, 550°C). Sediment had been stored frozen until use. Worms were exposed to sediment that was not seived nor manipulated, except for removal of coarse woody debris. This fen "peat-type" sediment originated from decaying plant material of mostly *Sphagnum* and *Carex* species.

L. variegatus were exposed to sediments in 300 mL test chambers (flow through beakers) to which 100 to 150 mL of sediment and 100 to 150 mL of overlying water (DMW) had been added. Overlying water renewal was provided by a modified automated Zumwalt system (Environmental Consulting and Testing, Michigan; designed as per EPA (2000c), Appendix A). The system was used for sediment bioaccumulation studies (Chapter 3, Fig. 3.2) and housed under the same conditions as *L. variegatus* cultures. The renewal system maintained test chambers and renewal water at 23±3°C. At least

30% of the overlying water was renewed in each beaker every 30 min.

5.2.3 Sugar Solution Preparation

Sugar solution was prepared as per Anderson (1959), in batches as needed. Briefly, about 300±5 g of commercially available refined white sugar was dissolved in 1000 ± 10 mL of DMW in a large beaker with constant stirring. Heating was not required nor recommended as to maintain the solution at room temperature for experiments. Other water for sugar dissolution would be feasible, provided it does not contain analytes of interest, nor possesses other properties detrimental to *L. variegatus*.

5.2.4 Lethal Time Toxicity Test

A LT toxicity test was conducted to determine an appropriate amount of time that can elapse during sugar solution flotation without causing *L. variegatus* mortality. The test was performed on the lab bench at room temperature (21-23°C). Both control and sugar solutions were 23±3°C at the start of the test. Ten organisms per 150 mL of sugar solution were exposed for 2, 4, 8, 16, 32 and 64 min (one solution per time period), prior to a recovery period (60 min) in DMW and assessment for mortality. A control group of 10 organisms was held for 64 min in DMW then transferred to fresh DMW for 60 min prior to assessment. The *L. variegatus* were considered dead if they failed to respond to gentle prodding.

5.2.5 Determining Percent Recovery and Time to Recover *L. variegatus* from Sediment

An attempted recovery of 10 organisms from sediment replicates (≈125 mL, n=4) using 500 mL and 1000 mL of sugar solution was performed. Organisms were exposed to sediment for 72 hr before separation by sugar flotation. Percent recovery was calculated as: (number of organisms recovered)/10×100.

To recover *L. variegatus*, sediment was first poured onto a #60 sieve (250 μm) to remove overlying water. Test chambers were rinsed with a stream of DMW to remove adhered sediment, and likewise sieved. Filtrate was inspected, but never found to contain organisms. Sediment was quickly transferred to a clean white enamel sorting tray

(36×24×5 cm). A dental probe was used to gently scrape adhered sediment from the sieve to the tray.

A known volume of sugar solution was added to sediment to create a sugar solution-sediment slurry. To facilitate flotation, the slurry was gently sloshed and stirred with a dental probe (Anderson, 1959). The *L. variegatus* were immediately removed from the slurry surface with a wide bore pipette. Time was recorded for each worm found. Allotted search time was 20 min. If 10 organisms were found before time expired, an additional 2 min was taken to ensure *L. variegatus* had not replicated over the 72 hr. If time expired before 10 organisms were found, it was assumed the recovery time was 1320 sec (20+2 min) for all remaining organisms. For *L. variegatus* separated with 1000 mL of sugar solution, organisms were immediately placed in a flow-through beakers of aerated DMW (≈175 mL), and mortality assessed after 24 hr.

5.2.6 Assessing Change in *L. variegatus* Tissue Concentration

Spiked *L. variegatus* (Section 5.2.1) were used to ascertain whether sugar flotation altered THg and MeHg concentrations in tissue. If tissue concentrations were not altered during an aqueous exposure to sugar solution, they were assumed unaltered when a sugar solution was used to separate organisms from sediment after a bioaccumulation test.

Aqueous sugar solution exposure

For aqueous only exposures, approximately 1 g (ww) of spiked organisms were exposed for 10 min (<LT50) to either 100 mL of sugar solution (treatment, n=6) or 100 mL DMW (control, n=6). One treatment and one control were exposed simultaneously. After exposure, organisms were immediately rinsed thrice with DMW and placed in beakers with fresh DMW in flow through aquaria for overnight gut purging (>16 hr). This simulated bioaccumulation test procedures (EPA, 2000c). After gut purging, mortality was assessed and *L. variegatus* prepared for THg and MeHg analysis.

Sediment exposure and sugar solution separation

A sediment exposure, similar to bioaccumulation test procedures (EPA, 2000c), was evaluated for MeHg tissue change. Three grams of MeHg spiked organisms were randomly added to 12 replicate sediment test chambers. *L. variegatus* were exposed to sediment

for 24 hr (with water renewal) before two methods were used to separate organisms from sediment.

Random test chambers were selected for manual separation of *L. variegatus* from sediment (control, n=6) or for sugar flotation separation (treatment, n=6). Manual separation was done in white enamel trays with sediment and its overlying water for a maximum time of 30 min. Sugar flotation separation was done in white enamel trays with sieved sediment (#60, to remove overlying water) and 1 L of 300 g L^{-1} sugar solution, to ensure maximum recovery. Maximum sugar solution sorting time was 10 min (<LT50). Sugar solution was reused once. Organisms from each replicate were placed in clean beakers of DMW as they were found. Rinsing, gut purging, mortality assessment and tissue analysis of organisms was the same as per aqueous exposures.

5.2.7 Analytical Methods

The *L. variegatus* for THg and MeHg analysis were weighed wet as per EPA (2000c) into Hg clean glass vials. For THg analysis, tissue was digested 2 to 3 hr at 95°C (complete oxidation) with 3 mL H_2SO_4:7 mL HNO_3 (Fisherbrand, OmniTrace). Digestate was brought to 40 mL final volume with 0.02N BrCl, that was neutralized with hydroxylamine hydrochloride just prior to analysis (EPA, 2001a). Quantitation of THg was by purge and trap on gold sand ($SnCl_2$ reductant) followed by cold vapour atomic fluorescence spectrophotometry (Brooks-Rand, Model III) (EPA, 2001c, 2002). Results are reported as ng g^{-1} (ww).

For MeHg tissue analysis, samples were first freeze dried (Labconco Freezone 12) prior to digestion, but concentrations are reported as ng g^{-1} (ww). Freeze dried tissue was digested in 5 mL of 4N HNO_3 (conc. HNO_3 Fisherbrand, OmniTrace) at 55°C for 16 hr (Hintelmann and Nguyen, 2005). Aqueous phase ethylation on an aliquot of digestate (<100 μL) in acetate buffered Type I water was followed by purge and trap on Tenax traps (Brooks Rand). Quantitation of MeHg was by cold vapour atomic fluorescence after species separation by gas chromatography and conversion to Hg(0) (Brooks Rand, Model III) (EPA, 2001b).

A certified reference material (DORM-2, National Research Council Canada) was used for quality control in addition to method blanks (freeze dried chicken breast), sample duplicates, sample spikes, analytical duplicates and an instrument ongoing precision and recovery sample. Recovery of THg and MeHg for all DORM-2 analyses were within 10%

of the expected value. Relative percent deviation for duplicate sample analysis for THg was 12% and for MeHg was 11%. Relative percent deviation for duplicate analytical analysis for THg was 5.5% and for MeHg was 1.9%. Percent recovery of spiked tissue samples averaged 113% for THg and 107% for MeHg.

5.2.8 Statistical Methods

The LTs with 95% confidence intervals were calculated using the USEPA Probit Analysis Program (Version 1.5), as partial mortality was observed for two exposure times. Other statistics were determined using R (R Development Core Team, 2010). Results are presented as mean ± standard deviation (SD). A one-sided Welch two sample t-test was used to determine whether worm recovery time decreased with an increase in sugar solution volume. Two-sided Welch two sample t-tests were used to compare *L. variegatus* tissue concentrations of THg and MeHg.

5.3 Results

5.3.1 Lethal Times for *L. variegatus* Exposed to Sugar Solution

Lethal times for *L. variegatus* exposed to 300 g L^{-1} sugar solution are presented in Table 5.1, with no mortality in controls.

5.3.2 Recovery of *L. variegatus* with Sugar Solution

There was 100% recovery of *L. variegatus* when 1000 mL of sugar solution (300 g L^{-1}) was used to separate organisms from organic sediment (>90% organic matter, n=4). Average recovery was 92.5±15.0% when 500 mL was used (n=4). No mortality was observed after organisms were held for 24 hr in fresh DMW. Less time was required to recover *L. variegatus* from sediment with 1000 mL of sugar solution than 500 mL (Fig. 5.1).

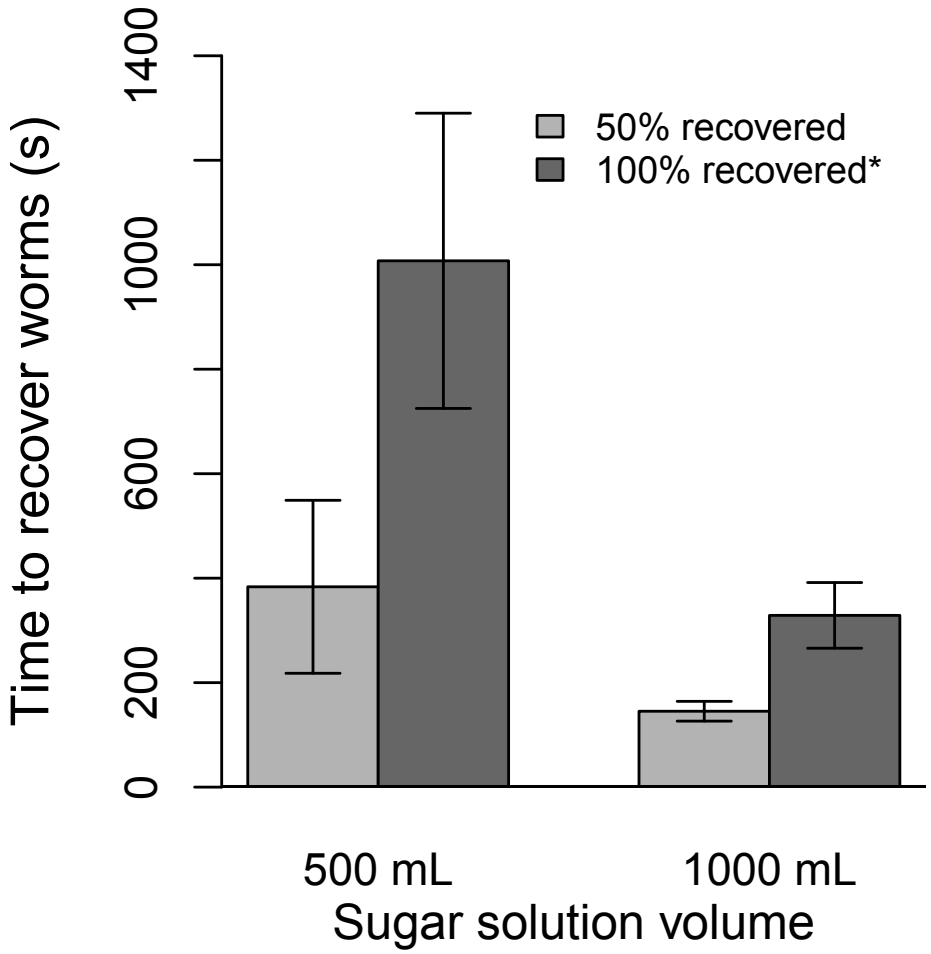

Figure 5.1: Mean ± SD time to recover *L. variegatus* from organic sediment (≈125 mL) using two volumes of 300 g L^{-1} of sugar solution for flotation (n=4). Less time was required to recover *L. variegatus* from sediment when 1000 mL was used compared to 500 mL, for both 50% ($t_{3.08}$=-2.86, p=0.03) and 100% ($t_{3.30}$=-4.69, p=0.007) of the 10 worms initially added to sediment (*less than 100% recovery for 500 mL).

Table 5.1: Estimates of lethal time (LT) with 95% confidence intervals for *L. variegatus* exposed to sugar solution (300 g L^{-1}), followed by 1 hr recovery in dechlorinated municipal water (DMW) (n=10).

		95% Confidence Limits	
End Point	LT (min)	Lower (min)	Upper (min)
LT5	7.26	3.68	9.18
LT10	8.00	4.57	9.93
LT15	8.55	5.26	10.52
LT50	11.31	8.83	14.49
LT85	14.97	12.17	24.32
LT90	15.99	12.89	28.02
LT95	17.64	13.94	34.76
LT99	21.20	15.97	52.67

5.3.3 Tissue Concentrations after Sugar Solution Exposure

Concentrations of THg and MeHg in spiked *L. variegatus* tissue after aqueous exposure to sugar solution and concentrations of MeHg in similarly spiked *L. variegatus* tissue after manual (control) and sugar solution separations from sediment are presented in Fig. 5.2.

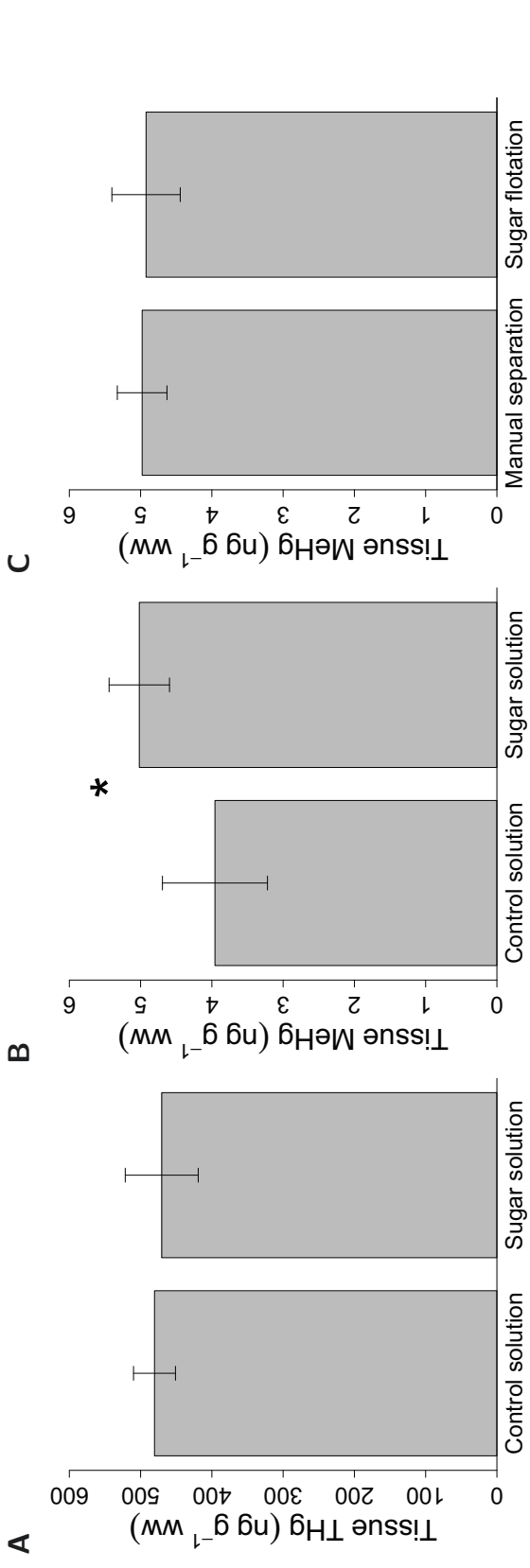

Figure 5.2: A, B: Mean ± SD THg and MeHg concentrations in spiked *L. variegatus* tissue after aqueous exposure to sugar solution (300 g L^{-1}) or control solution (dechlorinated municipal water (DMW)) for 10 min with overnight gut purging, respectively. C: Mean ± SD MeHg in similarly spiked *L. variegatus* tissue after exposure to organic sediment and either manual separation (control) or sugar solution flotation were used to recover organisms. * significant at α <0.05 (A $t_{7.98}$=0.422, p=0.684; B MeHg $t_{7.98}$=-3.06, p=0.016; C $t_{9.13}$=0.227, p=0.825; all n=6).

5.3.4 Specific Gravity of Sugar Solutions

Specific gravity of sugar solution after use for aqueous exposure and THg tissue analysis was 1.095 (n=6) while freshly prepared solution was 1.096 (n=6). Specific gravity of fresh sugar solution for separating *L. variegatus* from sediment for MeHg tissue analysis was 1.096 (n=3). After initial solution use, specific gravity was 1.084 (n=3), and after one reuse, was 1.074 (n=3). All SD were $\leq$0.002.

5.4 Discussion

5.4.1 Sugar Solution Toxicity

When utilizing a sugar solution (300 g L^{-1}) to separate *L. variegatus* from sediment, care must be taken to remove organisms from sediment-sugar solution slurries within about 10 min to improve the survivability of the organisms (Table 5.1). Exceeding the LT50 of 11.3 min is not recommended if the viability of *L. variegatus* is required (i.e. for gut purging). Furthermore, exceeding the LT95 of 17.6 min would result in *L. variegatus* sinking in solution making their observation and retrieval doubtful.

Anderson (1959) found the flotation time of organisms ranged from 5 min (Tubificidae) to 90 min (*Polypedilum sp.*) in sugar solutions with a specific gravity of 1.11. They generally observed that Oligochaetes remained alive for 10 to 15 min and floated for approximately 20 min, as confirmed more precisely here. Benthic organisms with different flotation times likely have different LT values. Therefore, the toxicity of sugar solution requires evaluation and flotation times adjusted accordingly for bioaccumulation tests involving organisms other than *L. variegatus*.

5.4.2 Sugar Solution Slurry for *L. variegatus* Recovery from Organic Sediment

Sugar solution flotation (300 g L^{-1}, specific gravity 1.1) proved an effective and time saving strategy for separating *L. variegatus* from highly organic sediments (Fig. 5.3.2), as may be required for a sediment bioaccumulation test (Chapter 3). At least 1 L of solution per 100 to 150 mL of wet organic sediment should be combined in a typical white enamel sorting tray (36×24×5 cm), with gentle agitation to ensure ample recovery of tissue for subsequent chemical analysis (Fig. 5.1).

Anderson (1959) found 17.4 organisms per minute (mean) using sugar flotation and only 1.2 organisms per minute using manual hand sorting. Although recovery time here averaged 5.5 min when using 1 L of sugar solution (Figure 5.1), "peat-type" sediment was over 90% organic matter with particulates closely resembling *L. variegatus*. Organic detritus still floated in sugar solution, and *L. variegatus* would attach and remain hidden.

Although 100% of *L. variegatus* were generally found before 6 min, only 10 organisms were used per replicate. Experience has shown that 3 to 5 g (ww) of *L. variegatus* added to sediment are required for THg and MeHg analysis, which cannot be 100% recovered in 10 min floation time. Lackey and May (1971) previously noted using sugar solution alone was insufficient, and concluded rose bengal and formalin preservative be used. Pask and Costa (1971) found preserving with 10% formalin also increased recovery using sugar flotation. However, such preservation techniques are not applicable to THg and MeHg analysis (EPA, 2001b,a,c, 2002; Hintelmann and Nguyen, 2005).

To ensure adequate tissue mass for THg and MeHg analysis, I suggest bioaccumulation tests be initiated with sufficient *L. variegatus* to ensure 3 to 5 g will be recovered from each test vessel in 10 min to 12 min. High organic matter content of "peat-type" sediments meets the 50:1 ratio of total organic carbon in sediment to organism dry weight criteria (EPA, 2000c). Additionally, experience has shown sugar flotation for *L. variegatus* recovery from hydrated cattle manure requires less *L. variegatus* per test vessel to obtain sufficient tissue mass. Less detritus floats from the manure substrate as an interference. Furthermore, *L. variegatus* tend to clump together for simple recovery.

5.4.3 Changes in *L. variegatus* Tissue Concentrations

The mean THg concentrations in tissue were not significantly different when *L. variegatus* were exposed to sugar solution (Fig. 5.2A), making sugar flotation suitable for bioaccumulation studies that determine THg BSAFs. Although MeHg concentration in tissue was 27% higher than controls after aqueous exposures to sugar solution (Fig. 5.2B), this was not apparant when *L. variegatus* were exposed to sediment and then separated by flotation with sugar solution (Fig. 5.2C). Therefore, until alternative methods to extract benthos from organic sediment are validated, sugar solution appears applicable to BSAF determinations of THg and MeHg from organic sediments.

The sugar solution separation is advocated here for several reasons. First, aqueous exposure results suggest that sugar flotation may cause a positive bias in MeHg tissue

concentrations. This would result in an environmentally protective estimation of BSAFs. If subsequent work determines a constant bias exists, a correction factor may be applied to the data. Second, there may have been a negative bias in control *L. variegatus* when compared to other MeHg tissue means (Fig. 5.2B,C). However, there is currently no explaination. Third, the use of sugar flotation facilitates the determination of BSAFs from organic sediments that may otherwise remain unknown because of the difficulty in separating invertebrates from those substrates.

It was recognized that *L. variegatus* tissue concentrations evaluated here may be not be representative of THg and MeHg tissue concentrations measured at other contaminated or uncontaminated sites. Therefore, a re-evaluation with tissue concentrations relevant to a site of interest is advised. Further experiments with different analytes of concern at different concentrations with different invertebrate species are recommended.

5.4.4 Reuse of Sugar Solution

The reuse of sugar solution once was feasible for bioaccumulation studies (Chapter 3), saving time, money and resources. After one reuse, the specific gravity was found to decrease (Section 5.3.4), making it less likely to float benthos. Specific gravity would also decrease due to dilution from sediment porewater and overlying water, making it imperative to sieve sediments before sugar flotation.

5.5 Conclusions

In the interest of determining the bioaccumulation of THg and MeHg from organic sediment as found near a peatland in northwestern Ontario, the sugar flotation method of Anderson (1959) as adapted here was suitable. The THg concentrations of spiked *L. variegatus* were not significantly different when organisms were exposed to aqueous sugar solutions (300 g L^{-1}). The MeHg concentrations of spiked *L. variegatus* were not significantly different when organisms were separated from organic sediment by flotation with sugar solution than organisms manually sorted from organic sediment. However, spiked *L. variegatus* exposed to aqueous sugar solutions led to tissue concentrations higher than organisms exposed to control waters.

The final sugar flotation method adopted for THg and MeHg bioaccumulation testing with *L. variegatus* exposed to organic sediments consisted of a 300 g L^{-1} sugar solution

(specific gravity 1.1) prepared with laboratory culture or renewal water. Each exposure vessel of sediment (100-150 mL) was necessarily sieved to remove overlying water and sediment quickly placed in a typical sorting tray (36×24×5 cm). At least 1000 mL of sugar solution was added to create a sediment-sugar solution slurry, decreasing recovery time and increasing percent recovery. Gentle agitation of the sediment-sugar solution slurry facilitated the recovery of organisms. *L. variegatus* were removed to fresh culture or renewal water as found, rinsed then allowed to gut purge. To ensure viable organisms for gut purging, sorting time should not exceed 11 min.

Chapter 6

Conclusions and Future Direction

6.1 Conclusions from this Research

This dissertation has provided a foundation of scientific evidence and methodology upon which future wet peat mining initiatives and regulations can be formulated for northwestern Ontario. A fen, possessing high value energy peat and ideally situated within the Upsala corridor was chosen as the research site to address specific regional interests and concerns. The site was experimentally wet mined and restored by transplantation of the reserved acrotelm layer in 2008. The main research question posed was: **How would wet mining a peatland in the Upsala corridor of northwestern Ontario impact its adjacent ecosystem in terms of water quality and bioaccumulation potential of Hg species?** The impacts to adjacent ecosystems were found to be dependent on the analyte of concern, the manner it was produced and the quality of the receiving ecosystem itself.

Using a Before-After-Control-Impact (BACI) experimental design, significant changes in water quality were found associated with wet peat mining. Porewater in experimental plot (EP) showed significant increases after mining in pH, alkalinity, conductivity, cations (Ca, Mg, K, Na), some metals (Sr, Ba, Mn, Fe) and total nitrogen when compared with reference plot (RP) porewater. However, changes in porewater quality did not clearly translate to significant changes in surface water quality downfield of the mined site. Surface water changes were difficult to interpret due to seasonality with the data set. However, results suggest that solids released during the active phases of wet mining (ditching, extraction) remain a legitimate concern, since total suspended solids (TSS) was positively correlated to Hg. Concentrations of TSS and Hg in surface water from the

mined and restored plot recovered to reference site values within the same season.

Methods to determine Biota-Sediment Bioaccumulation Factors (BSAFs) experimentally were established at Lakehead University over the course of this research. Experimentally derived, 28 day BSAFs values for total mercury (THg) for *L. variegatus* exposed to sediments from the impacted site ranged from 0.91 to 1.59, within the range of indigenous benthic invertebrates (1.2 to 6.8). Experimentally derived, 28 day BSAFs values for methylmercury (MeHg) for *L. variegatus* exposed to the same sediments ranged from 9.91 to 67.4, also similar to benthic invertebrates (21.8-106). Actual tissue concentrations of MeHg were about 4× less than the Canadian aquatic biota guideline of 33ng g^{-1} (ww). A kinetic trial with sediment spiked with inorganic mercury (iHg) showed tissue THg reached steady state in 11.5 d. However, MeHg concentration in *L. variegatus* increased linearly with increased MeHg concentration in sediment. Peatland disturbances that cause MeHg to increase in concentration would likely cause an immediate increased concentration in benthic invertebrate MeHg tissue concentration.

Mechanical dewatering of wet peat produced peat mining process water (PMPW) that should not be directly discharged to limnic systems because it does not meet current Canadian Water Quality Guidelines (CWQG). Mesocosm studies with acrotelm peat demonstrated that high levels of particulate matter present in PMPW (TSS, particulate organic carbon (POC)), though removed in high quantities (45-83% and 47-89%, respectively) was still present in mesocosm leachate at levels that would be detrimental to aquatic life. Furthermore, organic constituents (true colour and dissolved organic carbon (DOC)) increased in concentration in mesocosm leachate, above that found in PMPW and in exceedance of CWQG. High removal efficiencies for nutrients (total nitrogen (TN) 84.4%, total phosphorus (TP) 80.8%) were determined, but eutrophication of receiving water remained a concern. High percentages of metals were also removed. Based on CWQG and reference site concentrations, metals in mesocosm leachate would not pose a threat to aquatic systems with the possible exception of MeHg. Wetlands have traditionally been employed as tertiary and not primary filtration systems. Although it is anticipated that constructed peatlands or the use of peat filters could improve the water quality of PMPW by reducing concentrations of solids, nutrients and metals, some primary treatment of PMPW to remove solids seems required. Simple dilution of PMPW, improved process control by industry or settling ponds are possible solutions. In this respect, the study site chosen for this research may be well suited for field trials, where pre-existing drainage ditch networks would act a "natural" settling ponds.

The sugar flotation method of Anderson (1959) as adapted here for bioaccumulation trials was suitable. The THg concentrations of spiked *L. variegatus* were not significantly different when organisms were exposed to aqueous sugar solutions (300 g L^{-1}). The MeHg concentrations of spiked *L. variegatus* were not significantly different when organisms were separated from organic sediment by flotation with sugar solution, though aqueous only exposures led to tissue concentrations higher than controls. The final sugar flotation method adopted for THg and MeHg bioaccumulation testing with *L. variegatus* exposed to organic sediments consisted of a 300 g L^{-1} sugar solution (specific gravity 1.1) prepared with laboratory culture or renewal water. Each exposure vessel of sediment (100-150 mL) was necessarily sieved to remove overlying water and sediment quickly placed in a typical sorting tray (36×24×5 cm). At least 1000 mL of sugar solution was added to create a sediment-sugar solution slurry, decreasing recovery time and increasing percent recovery. Gentle agitation of the sediment-sugar solution slurry facilitated the recovery of organisms. *L. variegatus* were removed to fresh culture or renewal water as found, rinsed then allowed to gut purge. To ensure viable organisms for gut purging, sorting time should not exceed 11 min.

6.2 Future Research Directions

Future research on environmental impacts associated with wet peat mining in northwestern Ontario needs to be carried out on a larger scale at multiple sites. Sufficient "Before" data (ideally >1 yr) should be collected for such work. The dataset should include both water quality and accurate, real-time hydrology measures or models to calculate fluxes of analytes. Additional piezometer nests should be located in areas upslope of impacts, capturing inflow water quality anticipated to change in response to mining activities. These upslope areas should include those sensitive to Hg methylation and include any anthropogenic inputs. A true bog in the region should be included as a future study site since bog porewater and outflow waters may differ significantly from fens (Gore, 1983; Daigle and Gautreau-Daigle, 2001; Rydin and Jeglum, 2006). Biology, hydrology and geochemistry are intricately linked in peatland systems. Therefore biological data, such as plant and animal species composition and abundance, in areas subject to peat dessication and particulate loading, should be considered. Further speciation of analytes of concern is required. For example, what is the bioavailability of particulate and organically bound MeHg and when pH is increased?

The acrotelm restoration method applied here appeared a reasonable strategy over the short term. Criteria to establish the success of acrotelm restoration for wet mined sites should be developed. These should include biological (e.g. plant species abundance), hydrological (e.g. water table, flow rates) and chemical (e.g. porewater quality) parameters. Such criteria are important if acrotelm transplants continue to be used for drainage ditches at dry harvested sites elsewhere. The practicality of transplanting acrotelm pieces manually, on a larger excavation site, should be considered since it was found to be labour intensive. Other reclamation or rehabilitation schemes, such as blueberry, cranberry and wild rice production may be simpler to conduct on a larger scale. Comparing several strategies and their relative influences on water and sediment quality would help direct future restoration/reclamation plans.

Evaluating the bioaccumulation potential of Hg species when organic debris from peat mining enters water bodies of differing sediment and water quality remains unknown. It was found here that overlying water may enhance the methylation of Hg from "peat-type" organic sediment, thus increasing the tissue concentration of MeHg in invertebrate populations. Therefore, the bioaccumulation potential for a gradient of organic sediment should be tested where the gradient is between the "peat-type" sediment and receiving water sediment. In-situ bioaccumulation studies may be more accurate than laboratory based methods because overlying water and environmental parameters (redox, temperature, pH) can alter sediment chemistry. This becomes especially apparent when analytes are at ambient, rather than grossly contaminated concentrations. In-situ studies would eliminate the need to bring copious amounts of site water back to the lab, where water quality may change during storage.

The sugar flotation method used here was suitable for this research. However, confirmation at varying tissue concentrations with various organisms and various analytes would enable a wider applicability of the methodology to laboratory and field studies. The difficulty in separating sufficient benthos for Hg and MeHg analysis prevents sufficient data being collected to accurately predict bioaccumulation at lower trophic levels. Results for highly organic sediment, such as peat, were found lacking in the literature.

The intricate relationship between biology, geochemistry and hydrology became evident during mesocosm work. It is unlikely that ex-situ mesocoms can reflect true peatland dynamics. Therefore, in-situ mesocosm or smaller scale field trials are recommended to further evaluate treatment peatlands for improving the quality of PMPW. However, the issue of elevated solids in PMPW must be addressed. Additionally, specific details

from industry (total volumes of discharge, area/volume of peat to receive discharge) are needed. Mesocosm studies have suggested peat chemistry may change when receiving PMPW. Long term biological and peat chemistry monitoring programs seem required as some alteration of a peatland's delicate balance may occur after receiving a substantial hydrological input of poor water quality. The BACI design, though more costly, can identify significant changes (biological and/or chemical) that are associated with an impact.

Environmental considerations for wet mining peat in northwestern Ontario have been presented. Academic, government and industry researchers should continue to provide sound science, demonstrate environmental leadership and guide sustainable development of our immense peatland resources of global importance. It appears opportunities in the "Ring of Fire" chromite deposit, located amongst vast expanses of peatlands in northwestern Ontario, may present the next opportunity for sustained peatland research programs.

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Appendix A

Supplemental Information for Chapter 2

Table A.1: Water quality from 25 cm. Significant difference among time periods for means of the differences in concentration (MDC) between experimental plot (EP) or back of experimental plot (BEP) and RP reference plot (ANOVA, Welch t-text, respectively); *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.10$, NS not significant. [a] n=2, [b] n=1 for Before data.

			Before 2007-2008 (n=3)		After 2008 (n=8)		After 2009 (n=4)	
	Analyte	**Signif.**	Mean	standard deviation (SD)	Mean	SD	Mean	SD
Ref.	pH[a]	—	5.85	0.30	5.71	0.24	5.59	0.04
Site	Alkalinity[a] (mg L^{-1} as $CaCO_3$)	—	5.4	1.6	12.9	6.9	8.1	3.9
	Conductivity[a] (μS cm^{-1})	—	16.5	3.0	32.2	13.7	21.6	6.8
	TN[a] (mg L^{-1})	—	0.468	0.392	0.405	0.192	0.264	0.061
	Ca[a] (mg L^{-1})	—	2.30	1.12	4.36	2.18	2.66	1.06
	Mg[a] (mg L^{-1})	—	0.79	0.35	1.43	0.74	0.91	0.32
	K[a] (mg L^{-1})	—	<0.10	NA	<0.10	NA	<0.10	NA
	Na[a] (mg L^{-1})	—	0.68	0.12	0.47	0.04	0.41	0.05
	Sr[a] (μg L^{-1})	—	<5	NA	9	4	5	2
	Ba[a] (μg L^{-1})	—	5	3	8	4	6	1
	Mn[a] (μg L^{-1})	—	78	50	110	58	65	38
	Fe[a] (mg L^{-1})	—	1.16	0.90	3.11	2.04	1.75	0.73
	Al[a] (μg L^{-1})	—	47	36	50	17	45	13
	S[a] (μg L^{-1})	—	130	14	355	639	98	51
	Colour[a] (TCU)	—	36.4	20.6	161	89.8	112	21.9
	Redox[b] (mv)	—	273	NA	201	62	209	21
	MeHg[a] (ng L^{-1})	—	0.300	0.174	0.102	0.061	0.162	0.101
	TSS[a] (mg L^{-1})	—	6.9	6.7	6.6	2.7	8.5	2.7
	TP[a] (μg L^{-1})	—	<5	NA	11	8	25	16
	DOC[b] (mg L^{-1})	—	11.3	NA	14.3	6.2	11.6	2.5
	Hg[a] (ng L^{-1})	—	23.2	13.2	4.15	1.54	5.98	2.88
Exp.	pH	—	5.61	0.16	—	—	—	—
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	6.7	2.3	—	—	—	—
	Conductivity (μS cm^{-1})	—	18.3	4.8	—	—	—	—
	TN (mg L^{-1})	—	0.375	0.265	—	—	—	—
	Ca (mg L^{-1})	—	2.43	0.78	—	—	—	—
	Mg (mg L^{-1})	—	0.90	0.29	—	—	—	—
	K (mg L^{-1})	—	<0.10	NA	—	—	—	—
	Na (mg L^{-1})	—	0.54	0.11	—	—	—	—
	Sr (μg L^{-1})	—	5	2	—	—	—	—
	Ba (μg L^{-1})	—	5	3	—	—	—	—
	Mn (μg L^{-1})	—	69	18	—	—	—	—
	Fe (mg L^{-1})	—	1.29	0.65	—	—	—	—
	Al (μg L^{-1})	—	52	45	—	—	—	—
	S (μg L^{-1})	—	100	62	—	—	—	—
	Colour (TCU)	—	59.1	12.8	—	—	—	—
	Redox[a] (mV)	—	226	4	—	—	—	—
	MeHg (ng L^{-1})	—	0.180	0.031	—	—	—	—
	TSS (mg L^{-1})	—	2.0	1.8	—	—	—	—
	TP (μg L^{-1})	—	10	12	—	—	—	—
	DOC[a] (mg L^{-1})	—	10.6	0.3	—	—	—	—
	Hg[a] (ng L^{-1})	—	5.65	3.85	—	—	—	—
Back	pH	NS	—	—	5.64	0.34	5.58	0.14
Exp.	Alkalinity (mg L^{-1} as $CaCO_3$)	NS	—	—	6.6	2.4	5.0	1.2
Site	Conductivity (μS cm^{-1})	NS	—	—	19.6	3.1	16.6	2.8
	TN (mg L^{-1})	NS	—	—	0.345	0.115	0.246	0.049
	Ca (mg L^{-1})	NS	—	—	2.74	0.79	1.92	0.67
	Mg (mg L^{-1})	NS	—	—	0.67	0.11	0.66	0.16
	K (mg L^{-1})	NA	—	—	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	NS	—	—	0.45	0.04	0.40	0.08
	Sr (μg L^{-1})	NS	—	—	<5	NA	<5	NA
	Ba (μg L^{-1})	*	—	—	5	2	5	3
	Mn (μg L^{-1})	NS	—	—	42	15	26	7
	Fe (mg L^{-1})	NS	—	—	1.30	0.72	0.52	0.28
	Al (μg L^{-1})	NS	—	—	57	36	55	24
	S (μg L^{-1})	NS	—	—	104	63	88	43
	Colour (TCU)	NS	—	—	109	27.0	93.6	20.9
	Redox (mv)	NS	—	—	223	28	193	28
	MeHg (ng L^{-1})	NS	—	—	0.141	0.097	0.096	0.022
	TSS (mg L^{-1})	NS	—	—	9.0	9.2	4.1	1.5
	TP (μg L^{-1})	NS	—	—	5	3	8	3
	DOC (mg L^{-1})	NS	—	—	11.9	2.9	11.6	2.8
	Hg (ng L^{-1})	NS	—	—	3.07	1.24	2.59	1.03

Table A.2: Water quality from 50 cm. Significant difference among time periods for means of the differences in concentration (MDC) between experimental plot (EP) or back of experimental plot (BEP) and RP reference plot (ANOVA, Welch t-text, respectively); *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.10$, NS not significant. [a] n=2 for Before data.

			Before 2007-2008 (n=3)		After 2008 (n=8)		After 2009 (n=4)	
	Analyte	**Signif.**	Mean	SD	Mean	SD	Mean	SD
Ref.	pH	—	5.68	0.10	5.75	0.08	5.70	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	20.3	4.0	18.8	2.0	16.1	2.8
	Conductivity (μS cm^{-1})	—	49.4	11.1	43.6	4.8	36.9	4.5
	TN (mg L^{-1})	—	0.974	0.375	0.649	0.064	0.311	0.014
	Ca (mg L^{-1})	—	6.15	2.59	4.93	0.64	4.14	0.41
	Mg (mg L^{-1})	—	2.01	0.73	1.63	0.20	1.39	0.10
	K (mg L^{-1})	—	<0.10	NA	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	—	1.20	0.55	0.71	0.05	0.56	0.04
	Sr (μg L^{-1})	—	11	4	10	1	8	1
	Ba (μg L^{-1})	—	8	4	8	1	6	1
	Mn (μg L^{-1})	—	139	71	102	15	87	8
	Fe (mg L^{-1})	—	2.97	0.92	2.92	0.48	2.44	0.31
	Al (μg L^{-1})	—	50	31	42	9	35	2
	S (μg L^{-1})	—	130	87	248	441	85	42
	Colour (TCU)	—	132	48.2	148	15.2	114	13.7
	Redox[a] (mv)	—	173	7	151	55	153	51
	MeHg[a] (ng L^{-1})	—	0.055	0.056	0.069	0.072	0.151	0.128
	TSS (mg L^{-1})	—	6.0	5.3	4.5	2.3	3.0	1.9
	TP (μg L^{-1})	—	14	20	7	7	10	4
	DOC[a] (mg L^{-1})	—	17.2	6.4	13.7	4.3	11.7	1.4
	Hg (ng L^{-1})	—	3.54	3.43	2.34	1.87	8.15	6.67
Exp.	pH	—	5.69	0.06	—	—	—	—
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	13.6	3.0	—	—	—	—
	Conductivity (μS cm^{-1})	—	33.1	7.0	—	—	—	—
	TN (mg L^{-1})	—	0.721	0.137	—	—	—	—
	Ca (mg L^{-1})	—	4.09	1.62	—	—	—	—
	Mg (mg L^{-1})	—	1.35	0.42	—	—	—	—
	K (mg L^{-1})	—	<0.10	NA	—	—	—	—
	Na (mg L^{-1})	—	0.54	0.11	—	—	—	—
	Sr (μg L^{-1})	—	8	3	—	—	—	—
	Ba (μg L^{-1})	—	7	3	—	—	—	—
	Mn (μg L^{-1})	—	137	69	—	—	—	—
	Fe (mg L^{-1})	—	3.30	1.74	—	—	—	—
	Al (μg L^{-1})	—	43	29	—	—	—	—
	S (μg L^{-1})	—	113	74	—	—	—	—
	Colour (TCU)	—	107	15.4	—	—	—	—
	Redox[a] (mV)	—	159	1	—	—	—	—
	MeHg[a] (ng L^{-1})	—	0.095	0.005	—	—	—	—
	TSS (mg L^{-1})	—	7.1	5.1	—	—	—	—
	TP (μg L^{-1})	—	20	16	—	—	—	—
	DOC[a] (mg L^{-1})	—	14.3	2.6	—	—	—	—
	Hg (ng L^{-1})	—	5.92	5.62	—	—	—	—
Back	pH	**	—	—	5.89	0.20	5.65	0.04
Exp.	Alkalinity (mg L^{-1} as $CaCO_3$)	NS	—	—	10.0	2.7	5.2	0.9
Site	Conductivity (μS cm^{-1})	NS	—	—	25.0	4.4	16.8	2.7
	TN (mg L^{-1})	***	—	—	0.350	0.058	0.257	0.045
	Ca (mg L^{-1})	NS	—	—	3.66	0.71	2.11	0.36
	Mg (mg L^{-1})	NS	—	—	0.82	0.16	0.52	0.11
	K (mg L^{-1})	NS	—	—	0.08	0.07	0.05	0.00
	Na (mg L^{-1})	*	—	—	0.47	0.03	0.38	0.06
	Sr (μg L^{-1})	NS	—	—	6	2	<5	NA
	Ba (μg L^{-1})	NS	—	—	6	2	3	1
	Mn (μg L^{-1})	NS	—	—	48	20	27	7
	Fe (mg L^{-1})	NS	—	—	1.27	0.31	0.78	0.25
	Al (μg L^{-1})	NS	—	—	38	12	37	5
	S (μg L^{-1})	NS	—	—	94	56	85	40
	Colour (TCU)	*	—	—	107	23.2	101	13.7
	Redox (mv)	NS	—	—	198	40	192	27
	MeHg (ng L^{-1})	NS	—	—	0.137	0.105	0.143	0.091
	TSS (mg L^{-1})	NS	—	—	9.3	8.6	3.2	1.1
	TP (μg L^{-1})	NS	—	—	10	12	10	4
	DOC (mg L^{-1})	NS	—	—	11.9	3.7	11.8	2.3
	Hg (ng L^{-1})	NS	—	—	2.41	1.28	1.42	0.58

Table A.3: Water quality from 100 cm. Significant difference among time periods for means of the differences in concentration (MDC) between experimental plot (EP) or back of experimental plot (BEP) and RP reference plot (ANOVA, Welch t-text, respectively); *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.10$, NS not significant. [a] n=2 for Before data; [b] n=1 for Before data.

			Before 2007-2008 (n=3)		After 2008 (n=8)		After 2009 (n=4)	
	Analyte	**Signif.**	Mean	SD	Mean	SD	Mean	SD
Ref.	pH	—	6.06	0.02	6.04	0.06	6.07	0.04
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	59.1	3.3	57.5	1.0	43.1	5.0
	Conductivity (μS cm^{-1})	—	118	1.6	118	2.1	87.4	6.7
	TN (mg L^{-1})	—	1.49	0.595	1.60	0.256	0.980	0.146
	Ca (mg L^{-1})	—	14.2	1.57	13.3	0.41	10.6	0.68
	Mg (mg L^{-1})	—	4.13	0.33	3.85	0.15	3.18	0.13
	K (mg L^{-1})	—	<0.10	NA	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	—	2.68	0.75	1.88	0.10	1.31	0.11
	Sr (μg L^{-1})	—	22	2	21	1	16	1
	Ba (μg L^{-1})	—	17	2	17	1	14	2
	Mn (μg L^{-1})	—	131	16	120	9	101	10
	Fe (mg L^{-1})	—	3.47	0.80	3.68	0.16	3.34	0.37
	Al (μg L^{-1})	—	18	11	11	6	20	1
	S (μg L^{-1})	—	80	46	146	218	85	44
	Colour (TCU)	—	98.0	14.4	110	11.3	104	7.4
	Redox[a] (mV)	—	150	16	119	49	132	61
	MeHg (ng L^{-1})	—	0.089	0.095	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	—	2.6	1.5	3.1	0.8	5.5	1.4
	TP (μg L^{-1})	—	9	5	12	11	10	5
	DOC[a] (mg L^{-1})	—	15.4	2.0	11.5	2.9	12.0	0.5
	Hg (ng L^{-1})	—	1.38	0.32	0.59	0.54	<0.50	NA
Exp.	pH	***	5.69	0.02	5.87	0.10	6.06	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	***	22.4	0.5	42.6	5.9	67.7	4.7
	Conductivity (μS cm^{-1})	***	51.6	1.0	89.9	11.3	138	5.9
	TN (mg L^{-1})	***	0.917	0.166	1.40	0.299	1.97	0.427
	Ca (mg L^{-1})	***	6.53	0.85	11.6	2.94	14.1	0.59
	Mg (mg L^{-1})	***	1.89	0.17	3.01	0.65	3.76	0.09
	K (mg L^{-1})	***	<0.10	NA	<0.10	NA	0.17	0.03
	Na (mg L^{-1})	***	0.68	0.20	1.35	0.40	3.95	0.44
	Sr (μg L^{-1})	***	11	2	18	5	22	1
	Ba (μg L^{-1})	**	8	2	16	5	17	2
	Mn (μg L^{-1})	*	99	14	129	32	164	39
	Fe (mg L^{-1})	NS	2.48	0.55	3.34	0.89	3.27	0.28
	Al (μg L^{-1})	NS	27	12	46	42	14	7
	S (μg L^{-1})	NS	100	61	84	57	53	26
	Colour (TCU)	**	98.3	22.3	81.7	7.9	83.9	3.4
	Redox[a] (mV)	*	165	6	151	55	122	60
	MeHg[b] (ng L^{-1})	*	0.051	NA	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	NS	3.8	2.7	17.2	15.8	7.6	5.8
	TP (μg L^{-1})	NS	24	19	19	11	16	9
	DOC[a] (mg L^{-1})	NS	14.6	1.1	10.9	1.7	10.0	0.6
	Hg (ng L^{-1})	NS	5.45	7.68	1.39	1.70	0.80	0.88
Back	pH	***	—	—	6.06	0.09	5.93	0.04
Exp.	Alkalinity (mg L^{-1} as $CaCO_3$)	**	—	—	16.2	4.3	9.8	1.9
Site	Conductivity (μS cm^{-1})	***	—	—	37.5	8.4	24.6	3.9
	TN (mg L^{-1})	*	—	—	0.488	0.263	0.225	0.053
	Ca (mg L^{-1})	NS	—	—	5.78	1.24	3.61	0.58
	Mg (mg L^{-1})	*	—	—	1.14	0.25	0.71	0.09
	K (mg L^{-1})	NA	—	—	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	***	—	—	0.46	0.03	0.38	0.05
	Sr (μg L^{-1})	NS	—	—	9	2	5	1
	Ba (μg L^{-1})	NS	—	—	8	2	5	2
	Mn (μg L^{-1})	NS	—	—	50	10	33	6
	Fe (mg L^{-1})	NS	—	—	1.28	0.31	0.94	0.12
	Al (μg L^{-1})	**	—	—	37	14	27	1
	S (μg L^{-1})	NS	—	—	88	57	78	34
	Colour (TCU)	*	—	—	126.2	23.8	93.6	13.7
	Redox (mV)	NS	—	—	185	54	163	34
	MeHg (ng L^{-1})	NS	—	—	0.039	0.027	0.068	0.023
	TSS (mg L^{-1})	NS	—	—	6.2	7.5	3.2	1.7
	TP (μg L^{-1})	NS	—	—	8	7	7	3
	DOC (mg L^{-1})	**	—	—	14.8	2.8	10.7	1.6
	Hg (ng L^{-1})	NS	—	—	1.96	1.77	0.82	0.45

Table A.4: Water quality from 150 cm. Significant difference among time periods for means of the differences in concentration (MDC) between experimental plot (EP) or back of experimental plot (BEP) and RP reference plot (ANOVA, Welch t-text, respectively); *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.10$, NS not significant. [a] n=2 for Before data.

			Before 2007-2008 (n=3)		After 2008 (n=8)		After 2009 (n=4)	
	Analyte	**Signif.**	Mean	SD	Mean	SD	Mean	SD
Ref.	pH	—	6.24	0.07	6.20	0.06	6.22	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	82.4	2.3	84.1	0.9	75.3	2.2
	Conductivity (μS cm^{-1})	—	167	2.7	168	2.0	143	12.1
	TN (mg L^{-1})	—	2.62	0.629	2.21	0.507	1.59	0.315
	Ca (mg L^{-1})	—	22.2	4.29	19.7	0.39	17.7	0.88
	Mg (mg L^{-1})	—	5.44	0.26	5.33	0.13	4.96	0.21
	K (mg L^{-1})	—	0.13	0.07	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	—	3.48	0.94	2.59	0.09	2.26	0.14
	Sr (μg L^{-1})	—	31	5	29	1	26	1
	Ba (μg L^{-1})	—	27	4	26	1	23	1
	Mn (μg L^{-1})	—	159	42	125	5	115	4
	Fe (mg L^{-1})	—	3.61	1.19	3.86	0.21	3.52	0.16
	Al (μg L^{-1})	—	64	81	16	5	15	2
	S (μg L^{-1})	—	107	68	110	129	78	43
	Colour (TCU)	—	79.0	27.3	102.4	12.7	104.6	6.2
	Redox[a] (mv)	—	152	14	119	57	123	70
	MeHg[a] (ng L^{-1})	—	0.068	0.047	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	—	24.0	28.8	6.6	5.1	4.3	2.4
	TP (μg L^{-1})	—	40	51	26	28	15	18
	DOC[a] (mg L^{-1})	—	17.9	4.2	11.1	3.0	13.0	0.3
	Hg (ng L^{-1})	—	1.74	1.43	0.84	0.87	0.59	0.25
Exp.	pH	***	5.87	0.03	6.06	0.09	6.27	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	***	32.1	1.4	64.1	11.0	107	13.4
	Conductivity (μS cm^{-1})	***	69.9	2.8	131	21.1	218	23.3
	TN (mg L^{-1})	***	0.883	0.311	1.839	0.341	2.23	0.512
	Ca (mg L^{-1})	***	9.40	1.28	17.5	4.35	22.6	1.67
	Mg (mg L^{-1})	***	2.37	0.20	4.02	0.92	5.37	0.44
	K (mg L^{-1})	***	<0.10	NA	<0.10	NA	0.32	0.05
	Na (mg L^{-1})	***	0.84	0.31	1.84	0.62	6.16	0.66
	Sr (μg L^{-1})	***	14	2	25	6	32	3
	Ba (μg L^{-1})	***	11	2	20	5	26	3
	Mn (μg L^{-1})	**	102	24	121	27	145	7
	Fe (mg L^{-1})	*	2.35	0.45	3.24	0.76	3.78	0.17
	Al (μg L^{-1})	NS	46	23	17	8	7	2
	S (μg L^{-1})	NS	87	51	61	36	48	21
	Colour (TCU)	*	85.5	25.1	69.7	24.8	76.3	8.9
	Redox[a] (mV)	**	149	1	143	62	106	73
	MeHg[a] (ng L^{-1})	NS	0.034	0.027	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	*	3.9	3.8	11.4	8.8	5.2	3.0
	TP (μg L^{-1})	NS	15	18	28	17	15	8
	DOC[a] (mg L^{-1})	NS	14.4	1.1	10.7	2.2	9.3	0.7
	Hg (ng L^{-1})	NS	0.99	0.75	1.33	1.85	<0.50	NA
Back	pH	NS	NA	NA	6.15	0.08	6.10	0.11
Exp.	Alkalinity (mg L^{-1} as $CaCO_3$)	NS	NA	NA	21.2	3.7	13.1	2.1
Site	Conductivity (μS cm^{-1})	NS	NA	NA	46.9	7.2	30.3	3.3
	TN (mg L^{-1})	NS	NA	NA	0.633	0.469	0.204	0.043
	Ca (mg L^{-1})	NS	NA	NA	7.42	1.05	4.49	0.51
	Mg (mg L^{-1})	NS	NA	NA	1.40	0.21	0.88	0.09
	K (mg L^{-1})	NS	NA	NA	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	*	NA	NA	0.45	0.05	0.39	0.03
	Sr (μg L^{-1})	NS	NA	NA	10	2	6	1
	Ba (μg L^{-1})	NS	NA	NA	10	1	6	1
	Mn (μg L^{-1})	NS	NA	NA	49	5	35	10
	Fe (mg L^{-1})	NS	NA	NA	1.28	0.24	1.01	0.38
	Al (μg L^{-1})	NS	NA	NA	51	51	29	4
	S (μg L^{-1})	NS	NA	NA	94	76	73	31
	Colour (TCU)	*	NA	NA	129.2	28.4	94.4	15.8
	Redox (mv)	*	NA	NA	183	54	147	37
	MeHg (ng L^{-1})	NS	NA	NA	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	NS	NA	NA	12.0	22.4	3.7	1.3
	TP (μg L^{-1})	NS	NA	NA	8	4	7	4
	DOC (mg L^{-1})	**	NA	NA	14.9	2.5	11.0	1.6
	Hg (ng L^{-1})	NS	NA	NA	1.48	2.52	<0.50	NA

Table A.5: Water quality from 300 cm. Significant difference among time periods for means of the differences in concentration (MDC) between experimental plot (EP) or back of experimental plot (BEP) and RP reference plot (ANOVA, Welch t-text, respectively); *** $p \leq 0.001$, ** $p \leq 0.01$, * $p \leq 0.10$, NS not significant. [a] n=2 for Before data.

			Before 2007-2008 (n=3)		After 2008 (n=8)		After 2009 (n=4)	
	Analyte	**Signif.**	Mean	SD	Mean	SD	Mean	SD
Ref.	pH	—	6.47	0.02	6.47	0.05	6.48	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	—	149	2.1	151	1.0	146	5.3
	Conductivity (μS cm^{-1})	—	298	6.7	300	5.8	294	3.3
	TN (mg L^{-1})	—	3.14	0.971	3.23	0.969	2.19	0.522
	Ca (mg L^{-1})	—	37.6	2.95	35.7	0.58	34.7	1.13
	Mg (mg L^{-1})	—	8.66	0.60	8.47	0.12	8.43	0.24
	K (mg L^{-1})	—	0.29	0.05	0.25	0.02	0.26	0.01
	Na (mg L^{-1})	—	6.16	1.64	4.54	0.15	4.42	0.12
	Sr (μg L^{-1})	—	48	4	46	2	44	1
	Ba (μg L^{-1})	—	55	1	55	2	54	2
	Mn (μg L^{-1})	—	128	15	118	2	115	5
	Fe (mg L^{-1})	—	4.51	1.54	5.13	0.16	4.85	0.33
	Al (μg L^{-1})	—	21	14	12	8	11	3
	S (μg L^{-1})	—	77	40	106	91	65	30
	Colour (TCU)	—	101	45.9	126	10.6	133	9.7
	Redox[a] (mv)	—	136	1	108	83	99	81
	MeHg[a] (ng L^{-1})	—	0.085	0.090	<0.030	NA	0.035	0.015
	TSS (mg L^{-1})	—	9.5	10.3	5.2	2.8	3.6	1.3
	TP (μg L^{-1})	—	39	23	30	29	18	9
	DOC[a] (mg L^{-1})	—	16.1	0.8	11.8	3.2	13.3	0.8
	Hg (ng L^{-1})	—	3.79	5.36	0.90	0.98	0.61	0.42
Exp.	pH	***	6.26	0.02	6.53	0.15	6.96	0.06
Site	Alkalinity (mg L^{-1} as $CaCO_3$)	***	64.4	4.8	159	26.4	246	21.6
	Conductivity (μS cm^{-1})	***	129	7.1	312	46.1	452	18.8
	TN (mg L^{-1})	*	2.12	0.527	2.66	1.19	2.16	0.472
	Ca (mg L^{-1})	***	19.8	4.6	39.4	6.35	60.5	2.87
	Mg (mg L^{-1})	***	3.51	0.17	8.10	1.77	12.7	0.59
	K (mg L^{-1})	***	<0.10	NA	0.34	0.07	0.46	0.02
	Na (mg L^{-1})	***	1.48	0.30	3.86	0.54	8.54	0.75
	Sr (μg L^{-1})	***	24	4	49	8	76	4
	Ba (μg L^{-1})	***	23	2	56	10	85	5
	Mn (μg L^{-1})	***	97	18	156	21	195	6
	Fe (mg L^{-1})	***	2.36	1.75	4.94	0.53	5.44	0.22
	Al (μg L^{-1})	*	49	40	10	5	7	2
	S (μg L^{-1})	NS	90	53	60	34	53	26
	Colour (TCU)	NS	65.5	24.9	101	19.0	113.5	33.0
	Redox[a] (mV)	NS	156	1	88	81	86	85
	MeHg[a] (ng L^{-1})	NS	0.079	0.091	<0.030	NA	0.035	0.040
	TSS (mg L^{-1})	NS	20.5	25.7	5.8	2.7	7.9	1.9
	TP (μg L^{-1})	NS	38	32	47	32	16	8
	DOC[a] (mg L^{-1})	NS	16.9	4.9	10.4	1.2	10.2	0.8
	Hg (ng L^{-1})	NS	4.84	7.25	<0.50	NA	<0.50	NA
Back	pH	NS	NA	NA	6.37	0.07	6.32	0.06
Exp.	Alkalinity (mg L^{-1} as $CaCO_3$)	**	NA	NA	73.3	4.1	45.3	4.8
Site	Conductivity (μS cm^{-1})	***	NA	NA	146	8.1	94.6	12.4
	TN (mg L^{-1})	NS	NA	NA	1.68	0.841	0.813	0.071
	Ca (mg L^{-1})	***	NA	NA	21.2	1.54	13.5	1.93
	Mg (mg L^{-1})	***	NA	NA	4.11	0.28	2.71	0.39
	K (mg L^{-1})	NS	NA	NA	<0.10	NA	<0.10	NA
	Na (mg L^{-1})	NS	NA	NA	1.08	0.09	0.87	0.06
	Sr (μg L^{-1})	***	NA	NA	27	2	16	2
	Ba (μg L^{-1})	***	NA	NA	30	2	20	2
	Mn (μg L^{-1})	***	NA	NA	99	7	64	8
	Fe (mg L^{-1})	**	NA	NA	3.11	0.43	2.13	0.25
	Al (μg L^{-1})	NS	NA	NA	64	64	36	25
	S (μg L^{-1})	NS	NA	NA	105	66	78	36
	Colour (TCU)	NS	NA	NA	102	26.5	100	12.8
	Redox (mv)	NS	NA	NA	152	74	126	57
	MeHg (ng L^{-1})	NS	NA	NA	<0.030	NA	<0.030	NA
	TSS (mg L^{-1})	NS	NA	NA	29.5	39.3	6.2	2.9
	TP (μg L^{-1})	NS	NA	NA	16	17	9	5
	DOC (mg L^{-1})	**	NA	NA	12.1	2.4	12.0	1.0
	Hg (ng L^{-1})	NS	NA	NA	2.55	4.16	0.53	0.33

Table A.6: Comparison of means of the differences in concentration (MDC) in porewater concentrations between the reference plot (RP) and experimental plot (EP) among time periods sampled (Before, After 2008 and After 2009) for piezometers at 100 cm, 150 cm and 300 cm depths for select parameters. (ANOVA, * F statistic based on 2,11 degrees of freedom.)

	Depth of Piezometer					
	100 cm		**150 cm**		**300 cm**	
Parameter	$\boldsymbol{F}_{2,12}$	$\boldsymbol{p}$	$\boldsymbol{F}_{2,12}$	$\boldsymbol{p}$	$\boldsymbol{F}_{2,12}$	$\boldsymbol{p}$
Conductivity	142	<0.001	52.7	<0.001	65.5	<0.001
Alkalinity	132	<0.001	59.4	<0.001	53.4	<0.001
Na	113	<0.001	109	<0.001	105	<0.001
K	91.9	<0.001	78.6	<0.001	31.3	<0.001
pH	54.7	<0.001	39.8	<0.001	38.6	<0.001
Mg	24.7	<0.001	17.3	<0.001	38.5	<0.001
Ca	20.8	<0.001	20.2	<0.001	63.0	<0.001
TN	18.2	<0.001	30.6	<0.001	2.89	0.094
Sr	15.5	<0.001	13.8	0.001	57.3	<0.001
Ba	7.77	0.007	23.5	<0.001	63.7	<0.001
Colour	7.30	0.008	3.02	0.087	0.356	0.708
Mn	6.72	0.011	11.6	0.002	35.4	<0.001
Redox*	6.08	0.017	8.52	0.006	1.80	0.211
MeHg*	5.77	0.021	1.37	0.290	1.58	0.249
log TSS	2.96	0.090	3.06	0.084	1.70	0.224
Al	1.84	0.201	0.546	0.593	6.44	0.013
TSS	1.71	0.222	4.19	0.042	2.43	0.130
Fe	1.43	0.277	3.58	0.060	22.6	<0.001
Hg	1.34	0.299	1.21	0.331	2.48	0.125
TP	0.959	0.411	0.725	0.504	2.35	0.138
DOC*	0.647	0.543	2.73	0.109	1.26	0.322
Cl	0.292	0.752	1.69	0.226	0.134	0.876
S	0.221	0.805	0.094	0.911	1.01	0.392

Table A.7: Comparison of means of the differences in concentration (MDC) in porewater concentration from back of experimental plot (BEP) and RP for time period After 2008 and After 2009 (Welch two sample t-test).

	Piezometer depth									
	25 cm		**50 cm**		**100 cm**		**150 cm**		**300 cm**	
Parameter	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***
Colour	-1.13 (7.07)	0.297	-2.17 (9.99)	0.056	2.77 (9.14)	0.021	2.57 (10.0)	0.028	0.707 (9.96)	0.498
DOC	-0.830 (6.11)	0.438	-0.714 (8.59)	0.494	3.29 (9.98)	0.008	3.98 (9.76)	0.003	3.51 (9.96)	0.006
pH	-0.514 (7.68)	0.621	3.70 (9.79)	0.004	5.78 (8.44)	<0.001	1.04 (4.13)	0.354	1.92 (4.21)	0.124
Alkalinity	-1.11 (8.90)	0.295	-1.26 (9.62)	0.237	-3.61 (7.60)	0.007	-0.49 (9.66)	0.635	5.40 (4.07)	0.005
Conductivity	-1.33 (8.65)	0.216	0.546 (8.30)	0.599	-4.77 (8.62)	0.001	-1.13 (3.87)	0.324	6.38 (5.19)	0.001
TN	-0.502 (7.06)	0.631	-7.36 (6.91)	<0.001	-2.75 (7.16)	0.028	-0.859 (7.03)	0.419	-0.412 (9.85)	0.689
Redox	1.85 (7.40)	0.105	0.316 (6.52)	0.762	1.98 (5.18)	0.102	2.13 (4.27)	0.095	0.867 (7.41)	0.413
TP	1.37 (4.16)	0.241	0.718 (5.94)	0.500	-0.091 (9.17)	0.929	-0.790 (9.93)	0.448	-0.353 (9.03)	0.732
TSS	1.73 (8.55)	0.119	1.54 (7.28)	0.167	1.70 (9.64)	0.120	0.723(7.31)	0.492	1.65 (7.17)	0.142
Hg	1.41 (3.90)	0.233	1.86 (3.19)	0.154	1.40 (9.14)	0.195	1.06 (7.59)	0.320	1.46 (7.54)	0.184
MeHg	1.51 (6.73)	0.176	0.659 (4.12)	0.545	-1.64 (9.31)	0.134	-0.674 (5.72)	0.527	1.03 (6.51)	0.340

Table A.8: Comparison of means of the differences in concentration (MDC) in porewater concentration from back of experimental plot (BEP) and RP for time period After 2008 and After 2009 (Welch two sample t-test).

	Piezometer depth									
	25 cm		**50 cm**		**100 cm**		**150 cm**		**300 cm**	
Parameter	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***	***t* (DF)**	***p***
Ca	-1.26 (7.81)	0.245	1.78 (7.32)	0.116	-1.23 (8.43)	0.253	1.39 (7.54)	0.204	7.20 (8.31)	<0.001
Mg	-1.76 (7.79)	0.117	0.524 (7.34)	0.616	-2.46 (7.96)	0.039	0.912 (6.46)	0.395	8.11 (7.11)	<0.001
K	NA	NA	1.00 (7.00)	0.351	NA	NA	-1.00 (7.00)	0.351	1.67 (7.93)	0.134
Na	-0.074 (7.06)	0.943	-2.20 (9.54)	0.054	-10.1 (8.07)	<0.001	-3.69 (4.70)	0.016	0.986 (9.62)	0.348
Sr	-1.34 (8.45)	0.216	1.71 (9.97)	0.119	-1.45 (9.31)	0.180	1.02 (6.74)	0.342	7.73 (9.78)	<0.001
Ba	-2.17 (8.86)	0.058	1.26 (7.00)	0.247	-0.970 (8.46)	0.359	1.28 (9.75)	0.231	10.2 (9.35)	<0.001
Mn	-1.12 (8.92)	0.293	0.558 (8.83)	0.591	-0.298 (8.64)	0.773	0.846 (4.86)	0.437	9.36 (8.22)	<0.001
Fe	-0.722 (7.49)	0.492	0.020 (8.15)	0.985	-0.008 (4.88)	0.994	-0.420 (4.86)	0.437	3.67 (9.45)	0.005
Al	-0.246 (8.18)	0.812	-1.04 (9.02)	0.325	3.91 (7.14)	0.006	1.17 (7.26)	0.280	1.10 (9.94)	0.299
Cl	0.356 (5.61)	0.735	0.539 (10.0)	0.602	-0.402 (7.18)	0.699	0.021(7.20)	0.984	0.043 (7.06)	0.967
S	-1.10 (6.01)	0.312	-0.999 (7.01)	0.351	-0.623 (7.12)	0.553	-0.199 (7.33)	0.848	-0.527 (7.47)	0.614

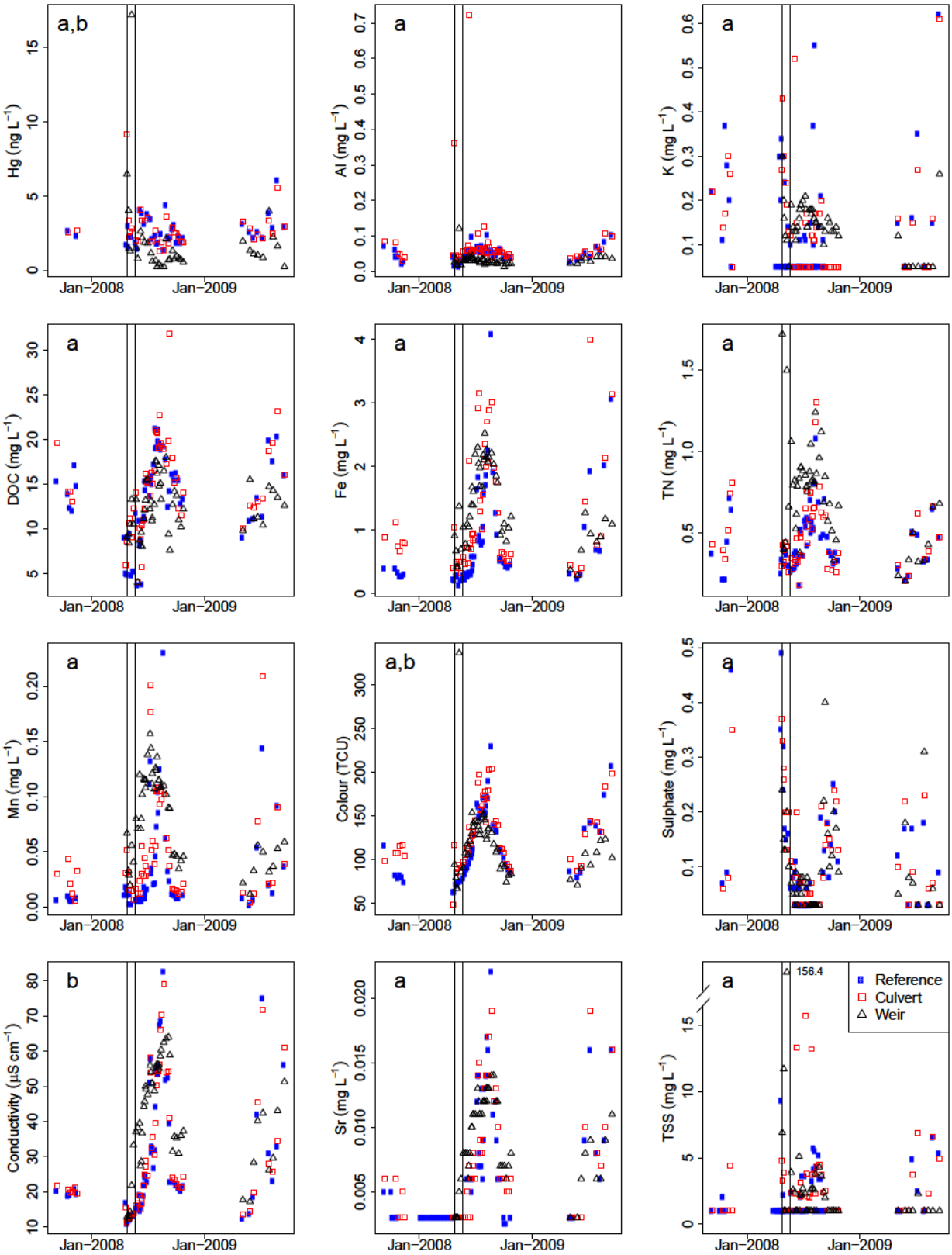

Figure A.1: Continued next page.

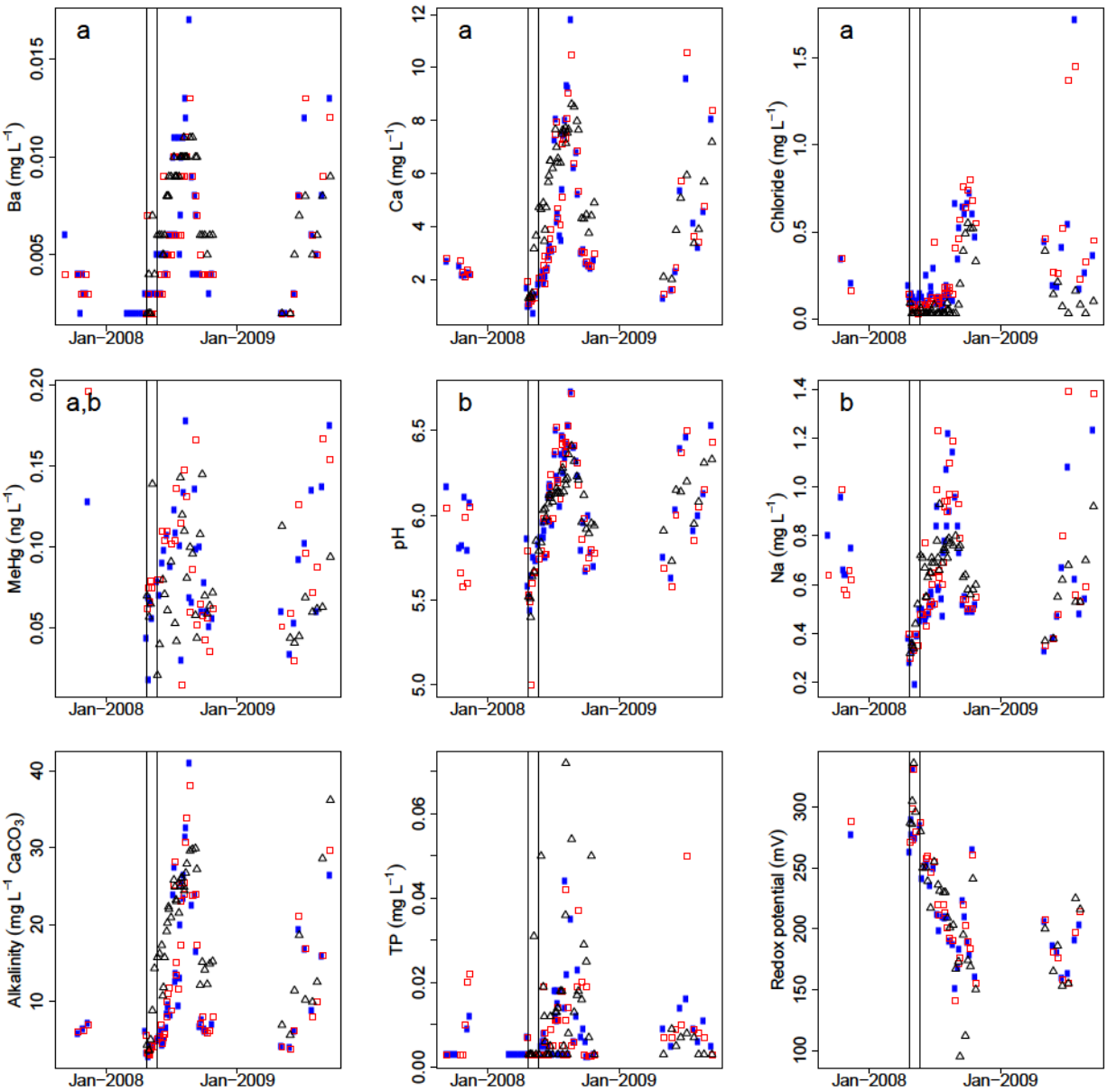

Figure A.1: Concentrations in surface water over time for analytes that showed a significant means of the differences in concentration (MDC) between the weir (**a**, triangles) or culvert (**b**, squares) and the reference site (circles) among time periods (ANOVA). Horizontal lines show start and end of mining/restoration delineating Before, Impact and After.

Tables of Surface Water Statistics

Surface water MDC between the weir and reference site among time periods showed significant differences for numerous analytes (Table A.9), whereas culvert and reference site surface water MDC were significant for pH ($F_{3,51}$=7.40, p<0.001), Hg ($F_{3,34}$=4.39, p=0.010), MeHg ($F_{3,33}$=3.63, p=0.023), colour ($F_{3,51}$=2.59, p=0.063) and Na ($F_{3,51}$=2.51, p=0.069).

Table A.9: Results for means of the differences in concentration (MDC) for weir and reference site surface water among time periods Before, Impact, After 2008 and After 2009 (ANOVA). NS indicates not significant and NA was not applicable.

		Tukey pairwise comparison (p value)		
Parameter	**ANOVA result**	**Impact– After 2008**	**Impact– After 2009**	**After 2008– After 2009**
Hg	$F_{2,33}$=11.1, p<0.001	<0.001	<0.001	NS
Al	$F_{2,45}$=10.8, p<0.001	<0.001	0.002	NS
K	$F_{2,45}$=9.39, p<0.001	0.028	NS	0.001
DOC	$F_{2,45}$=8.89, p<0.001	<0.001	0.004	NS
Fe	$F_{2,45}$=8.27, p<0.001	NS	0.037	<0.001
TN	$F_{2,45}$=6.73, p=0.003	NS	0.003	0.017
Mn	$F_{2,45}$=6.53, p=0.003	NS	NS	0.002
Colour	$F_{2,45}$=6.20, p=0.004	0.016	0.003	NS
Sulphate	$F_{2,45}$=5.55, p=0.007	0.005	0.032	NS
Conductivity	$F_{2,45}$=5.34, p=0.008	NS	NS	0.008
Sr	$F_{2,45}$=5.28, p=0.009	NS	NS	0.007
TSS	$F_{2,45}$=5.06, p=0.010	0.009	0.024	NS
Ba	$F_{2,45}$=4.43, p=0.018	NS	NS	0.013
Ca	$F_{2,45}$=3.87, p=0.028	NS	NS	0.022
Cl	$F_{2,45}$=3.60, p=0.035	NS	0.070	0.047
MeHg	$F_{2,32}$=2.64, p=0.087	NS	0.072	NS

Table A.10: Results for means of the differences in concentration (MDC) for weir and reference site surface water among time periods Before, Impact, After 2008 and After 2009 (ANOVA). NS indicates not significant and NA was not applicable.

		Tukey pairwise comparison (p value)		
Parameter	**ANOVA result**	**Impact– After 2008**	**Impact– After 2009**	**After 2008– After 2009**
TP	$F_{2,45}$=2.32, p=0.110	NA	NA	NA
Mg	$F_{2,45}$=2.30, p=0.112	NA	NA	NA
Alkalinity	$F_{2,45}$=1.72, p=0.191	NA	NA	NA
Na	$F_{2,31}$=1.34, p=0.273	NA	NA	NA
Redox	$F_{2,31}$=1.32, p=0.281	NA	NA	NA
Nitrate	$F_{2,45}$=0.732, p=0.487	NA	NA	NA
Zn	$F_{2,45}$=0.768, p=0.470	NA	NA	NA
S	$F_{2,45}$=0.344, p=0.711	NA	NA	NA
pH	$F_{2,45}$=0.068, p=0.934	NA	NA	NA

Appendix B

Supplemental Information for Chapter 3

Control Results

Control sediment was commercially available manure, with one batch used for Trials 1 and 2 and a new batch used for Trial 3. The Kinetic Trial was run nearly simultaneous as Trial 3, thus did not have a separate control. Sediment data was presented in the Methods Section (Table 3.4).

Table B.1: Control sediment worm tissue concentrations (±SD, n=6) from three Bioaccumulation Trials and the calculated Biota-Sediment Bioaccumulation Factors (BSAFs) (dw). Exposure of *L. variegatus* to control sediment was 28 days. Sediment concentrations are presented in Table 3.4.

	THg	**MeHg**
Post Trial Worm Tissue (ng g^{-1} ww)		
Trial 1	4.66±0.74	NA
Trial 2	5.96±1.49	0.70±0.08
Trial 3	10.2±2.11	0.61±0.11
ASTM (2010) recommendation	<50-1200	NA
BSAF (dw)		
Trial 1	1.13	NA
Trial 2	1.21	4.80–13.5
Trial 3	1.46–2.03	9.44–14.5

Appendix C

Supplemental Information for Chapter 4

Table C.1: Study 1 mesocosm leachate chemistry (mean ± SD) for each treatment group before pulse impacts were applied (n=6). ANOVA results for comparisons among treatments (F, p) are presented. Laboratory analytical detection limits (DLs) provided.

Analyte (units)	100% PMPW (T1)	50% PMPW (T2)	33% PMPW (T3)	0% PMPW (T0)	All	DL	$F_{3,20}$	p
DWT (cm)	17.4 ± 3.6	18.2 ± 3.6	18.0 ± 5.2	17.8 ± 3.2	17.9 ± 3.7	NA	0.046	0.986
Hg (ng L^{-1})	2.77 ± 1.45	3.01 ± 1.76	2.52 ± 1.21	3.09 ± 1.76	2.84 ± 1.47	0.50	0.163	0.920
Alkalinity (mg L^{-1} $CaCO_3$)	31.9 ± 5.7	18.0 ± 11.7	18.7 ± 11.5	25.4 ± 15.6	23.5 ± 14.0	1.0	1.34	0.290
True Colour (TCU)	317 ± 99.6	244 ± 91.5	187 ± 81.8	372 ± 443	280 ± 244	1.0	0.636	0.600
Conductivity (μS cm^{-1})	90.4 ± 31.1	62.8 ± 21.9	65.0 ± 21.5	79.2 ± 29.9	74.4±27.2	1.5	1.42	0.265
DOC (mg L^{-1})	16.6 ± 8.02	16.1 ± 4.02	12.6 ± 4.75	18.5 ± 9.25	16.0 ± 6.8	0.5	0.773	0.522
Redox (mV)	43.0 ± 48.2	86.92 ± 59.8	89.9 ± 35.4	59.1 ± 35.7	69.7 ± 47.2	NA	1.45	0.258
Reduced Fe (mg L^{-1})	6.51 ± 3.70	4.10 ± 3.53	3.00 ± 2.85	5.95 ± 6.52	4.89 ± 4.33	0.050	0.828	0.494
Chloride (mg L^{-1})	4.94 ± 0.47	5.04 ± 0.58	4.53 ± 0.33	5.17 ± 0.54	4.92 ± 0.52	0.05	1.84	0.172
NH_3 (mg L^{-1} -N)	0.064 ± 0.052	0.043 ± 0.069	0.061 ± 0.118	0.019 ± 0.026	0.047 ± 0.071	0.010	0.46	0.715
Al (mg L^{-1})	0.041 ± 0.012	0.031 ± 0.009	0.024 ± 0.009	0.044 ± 0.018	0.035 ± 0.014	0.005	3.08	0.051
Ba (mg L^{-1})	0.014 ± 0.006	0.008 ± 0.004	0.006 ± 0.003	0.012 ± 0.006	0.010 ± 0.006	0.003	3.15	0.048
Ca (mg L^{-1})	5.58 ± 3.02	3.11 ± 2.02	3.10 ± 2.18	4.71 ± 2.29	4.12 ± 2.49	0.005	1.56	0.229
Fe (mg L^{-1})	9.53 ± 5.85	5.31 ± 4.39	3.73 ± 2.81	8.40 ± 10.52	6.74 ± 6.56	0.002	1.00	0.412
K (mg L^{-1})	3.33 ± 0.74	3.77 ± 1.01	3.15 ± 1.08	3.32 ± 0.56	3.39 ± 0.84	0.10	0.558	0.649
Mg (mg L^{-1})	2.05 ± 0.93	1.16 ± 0.76	1.21 ± 0.77	1.65 ± 0.55	1.52 ± 0.80	0.01	1.78	0.183
Mn (mg L^{-1})	0.466 ± 0.161	0.315 ± 0.235	0.232 ± 0.100	0.405 ± 0.262	0.355 ± 0.207	0.001	1.58	0.226
Na (mg L^{-1})	4.09 ± 0.33	3.69 ± 0.33	3.62 ± 0.30	3.79 ± 0.19	3.80 ± 0.33	0.01	2.98	0.056
S (mg L^{-1})	0.648 ± 0.169	0.388 ± 0.121	0.457 ± 0.208	0.487 ± 0.182	0.495 ± 0.188	0.050	2.44	0.094
Zn (mg L^{-1})	0.028 ± 0.003	0.027 ± 0.008	0.024 ± 0.010	0.030 ± 0.007	0.027 ± 0.007	0.001	0.579	0.636
Sulphate (mg L^{-1} as SO_4)	1.11 ± 0.63	0.57 ± 0.35	0.78 ± 0.49	0.78 ± 0.68	0.81 ± 0.55	0.05	0.977	0.423
MeHg (ng L^{-1} as Hg)	1.51 ± 0.99	1.42 ± 0.75	0.93 ± 0.51	1.46 ± 1.20	1.33 ± 0.87	0.030	0.541	0.660
pH	6.20 ± 0.08	5.96 ± 0.30	5.98 ± 0.16	6.10 ± 0.12	6.06 ± 0.20	NA	2.25	0.114
POC (mg L^{-1})	13.0 ± 7.9	15.7 ± 5.8	10.8 ± 7.5	17.0 ± 7.3	14.1 ± 7.1	1.0	0.903	0.457
TN (mg L^{-1} as N)	0.469 ± 0.104	0.446 ± 0.068	0.370 ± 0.149	0.396 ± 0.138	0.420 ± 0.118	0.015	0.866	0.475
TP (mg L^{-1} as P)	0.038 ± 0.010	0.032 ± 0.018	0.027 ± 0.011	0.035 ± 0.013	0.033 ± 0.013	0.005	0.685	0.571
TSS (mg L^{-1})	5.2 ± 3.2	4.6 ± 2.4	2.8 ± 1.8	5.7 ± 1.3	4.6 ± 2.4	1.0	1.82	0.175

The following analytes were shown to have >75% of data censored below DL (DLs given in parentheses): NO_3-N (0.009 mg L^{-1}),NO_2-N (0.010 mg L^{-1}), As (0.005 mg L^{-1}), Be (0.002 mg L^{-1}), Cd (0.001 mg L^{-1}), Co (0.010 mg L^{-1}), Cr (0.002 mg L^{-1}), Cu (0.002 mg L^{-1}), Ni (0.002 mg L^{-1}), Pb (0.005 mg L^{-1}), Ti (0.010 mg L^{-1}) and V (0.006 mg L^{-1}).

Table C.2: Study 1 mesocosm leachate chemistry (mean ± SD) after peat mining process water (PMPW) pulse impacts were applied on nine days over a fourteen day study period (n=6). For laboratory detection limits (DLs) see Table C.1.

Analyte (units)	100% PMPW (T1)	50% PMPW (T2)	33% PMPW (T3)	0% (T0) PMPW	DL	$F_{3,20}$	p
DWT	21.9 ± 3.7	20.0 ± 4.5	20.4 ± 3.1	20.6 ± 3.7	NA	0.302	0.824
Hg (ng L^{-1})	15.88 ± 3.49	9.93 ± 2.62	6.05 ± 1.22	3.80 ± 1.30	0.50	30.2	<0.001
Alkalinity (mg L^{-1} $CaCO_3$)	18.2 ± 5.9	12.7 ± 4.97	15.7 ± 8.2	19.4 ± 8.1	1.0	1.10	0.373
True Colour (TCU)	582 ± 77.1	311 ± 9.23	188 ± 30.0	226 ± 192	1.0	16.4	<0.001
Conductivity (μS cm^{-1})	52.0 ± 10.2	45.4 ± 0.5	51.1 ± 15.4	59.5 ± 14.0	1.5	1.28	0.309
DOC (mg L^{-1})	28.4 ± 3.42	18.3 ± 0.11	11.9 ± 2.22	11.2 ± 3.07	0.5	42.4	<0.001
Redox (mV)	124.9 ± 55.2	149.3 ± 7.9	119.4 ± 41.7	80.6 ± 43.5	NA	1.72	0.195
Reduced Fe (mg L^{-1})	6.74 ± 2.80	3.14 ± 0.99	2.08 ± 1.07	4.37 ± 4.82	0.050	2.66	0.076
Chloride (mg L^{-1})	1.46 ± 0.12	2.62 ± 0.19	3.16 ± 0.16	3.88 ± 0.20	0.05	215	<0.001
NH_3 (mg L^{-1} as N)	0.021 ± 0.038	0.032 ± 0.034	0.086 ± 0.084	0.028 ± 0.014	0.010	2.17	0.123
Al (mg L^{-1})	0.127 ± 0.016	0.075 ± 0.007	0.041 ± 0.008	0.032 ± 0.011	0.005	91.6	<0.001
Ba (mg L^{-1})	0.015 ± 0.003	0.008 ± 0.002	0.006 ± 0.001	0.011 ± 0.006	0.003	6.07	0.004
Ca (mg L^{-1})	5.09 ± 1.30	2.90 ± 0.988	3.16 ± 1.76	3.58 ± 1.55	0.005	2.80	0.066
Fe (mg L^{-1})	7.92 ± 3.34	3.53 ± 2.69	2.20 ± 1.22	5.59 ± 6.33	0.002	2.50	0.089
K (mg L^{-1})	1.49 ± 0.23	2.04 ± 0.65	1.52 ± 0.51	1.83 ± 0.37	0.10	1.89	0.164
Mg (mg L^{-1})	1.77 ± 0.389	1.05 ± 0.356	1.31 ± 0.781	1.25 ± 0.393	0.01	2.10	0.132
Mn (mg L^{-1})	0.381 ± 0.106	0.225 ± 0.098	0.170 ± 0.026	0.282 ± 0.224	0.001	2.71	0.073
Na (mg L^{-1})	1.76 ± 0.148	2.67 ± 0.156	3.00 ± 0.100	3.53 ± 0.12	0.01	190	<0.001
S (mg L^{-1})	0.730 ± 0.153	0.692 ± 0.054	0.663 ± 0.095	0.713 ± 0.141	0.050	0.361	0.782
Zn (mg L^{-1})	0.023 ± 0.014	0.015 ± 0.003	0.029 ± 0.013	0.020 ± 0.013	0.001	1.53	0.238
Sulphate (mg L^{-1} as SO_4)	1.38 ± 0.33	1.39 ± 0.17	1.41 ± 0.31	1.68 ± 0.45	0.05	1.16	0.349
MeHg (ng L^{-1} as Hg)	1.82 ± 0.66	1.22 ± 0.45	0.91 ± 0.23	0.95 ± 0.62	0.030	4.03	0.022
pH	5.98 ± 0.09	5.86 ± 0.19	5.96 ± 0.23	6.06 ± 0.17	NA	1.20	0.335
POC (mg L^{-1})	51.5 ± 17.3	26.3 ± 9.9	22.2 ± 4.2	15.7 ± 4.2	1.0	13.6	<0.001
TN (mg L^{-1} as N)	1.23 ± 0.097	0.954 ± 0.070	0.699 ± 0.164	0.292 ± 0.066	0.015	83.7	<0.001
TP (mg L^{-1} as P)	0.094 ± 0.008	0.082 ± 0.024	0.060 ± 0.015	0.036 ± 0.015	0.005	14.1	<0.001
TSS (mg L^{-1})	57.0 ± 9.4	25.9 ± 7.2	10.0 ± 2.8	6.1 ± 3.3	1.0	81.2	<0.001

The following analytes were shown to have >75% of data censored below DL (DLs given in parentheses): NO_3-N (0.009 mg L^{-1}),NO_2-N (0.010 mg L^{-1}), As (0.005 mg L^{-1}), Be (0.002 mg L^{-1}), Cd (0.001 mg L^{-1}), Co (0.010 mg L^{-1}), Cr (0.002 mg L^{-1}),Cu (0.002 mg L^{-1}), Ni (0.002 mg L^{-1}), Pb (0.005 mg L^{-1}), Ti (0.010 mg L^{-1}) and V (0.006 mg L^{-1}).

Table C.3: Analyte concentration in 100% peat mining process water (PMPW) applied to each replicate (A, B, C) for Study 2; NA was not analyzed.

Analyte (units)	A (n=1) Value	B (n=3) Mean ± SD	C (n=3) Mean ± SD
Hg (ng L^{-1})	NA	NA	27.3 ± 4.76
Alkalinity (mg L^{-1} $CaCO_3$)	NA	NA	7.7 ± 2.9
True Colour (TCU)	217	306 ± 27.2	202 ± 3.60
Conductivity (μS cm^{-1})	NA	NA	27.2 ± 0.2
DOC (mg L^{-1})	20.3	19.0 ± 0.35	18.1 ± 0.53
Chloride (mg L^{-1})	NA	NA	0.95 ± 0.01
NO_3 (mg L^{-1} as N)	NA	NA	0.330 ± 0.002
Al (mg L^{-1})	NA	NA	0.733 ± 0.062
Ba (mg L^{-1})	NA	NA	0.028 ± 0.001
Ca (mg L^{-1})	NA	NA	5.91 ± 0.24
Cr (mg L^{-1})	NA	NA	0.002 ± 0.001
Cu (mg L^{-1})	NA	NA	< 0.002
Fe (mg L^{-1})	NA	NA	2.15 ± 0.12
K (mg L^{-1})	NA	NA	0.47 ± 0.01
Mg (mg L^{-1})	NA	NA	1.07 ± 0.03
Mn (mg L^{-1})	NA	NA	0.045 ± 0.004
Na (mg L^{-1})	NA	NA	0.863 ± 0.006
Ni (mg L^{-1})	NA	NA	0.005 ± 0.002
S (mg L^{-1})	NA	NA	1.28 ± 0.05
Zn (mg L^{-1})	NA	NA	0.052 ± 0.013
Sulphate (mg L^{-1} as SO_4)	NA	NA	3.65 ± 0.06
pH	NA	NA	5.59 ± 0.01
POC (mg L^{-1})	247	94.1 ± 1.4	322 ± 9.5
TN (mg L^{-1} as N)	NA	NA	3.87 ± 0.26
TP (mg L^{-1} as P)	NA	NA	0.611 ± 0.022
TSS (mg L^{-1})	270	99.9 ± 4.4	344 ± 18.5
TS (mg L^{-1})	341	198 ± 6.6	289 ± 69.4