The Effects of Retrogressive Thaw Slump Development on Persistent Organic Pollutants in Lake Sediments of the Mackenzie River Delta Uplands, NT, Canada

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Abstract

Using a comparative spatial and temporal analysis on sediment cores from 8 lakes in the Mackenzie River Delta uplands region, NT, Canada, this study assessed how persistent organic pollutant (POP) deposition to lake sediments was affected by: (1) the presence of retrogressive thaw slumps on lake shores; and (2) changes occurring with increased autochthonous primary productivity. POPs examined included polychlorinated biphenyls (PCBs), penta- and hexachlorobenzenes (CBzs), and dichlorodiphenyltrichloroethane and metabolites (DDTs). Surface sediments of slump-affected lakes contained higher total organic carbon (TOC)-normalized POP concentrations than nearby reference lakes unaffected by thaw slumps. Inorganic sedimentation rates were positively related to contaminant concentrations, suggesting that the influx of siliciclastic material reducing organic carbon in slump-affected lake water indirectly results in higher concentrations of POPs on sedimentary organic matter. This explanation was corroborated by an inverse relationship between sedimentary POP concentrations and TOC content of the lake water.

Deposition proxies of autochthonous carbon were not significantly correlated to POP fluxes of surface sediments, and historical profile fluctuations did not coincide with variation in POP deposition. Thus this study does not support the contention that algal-derived organic carbon increases the delivery of organic pollutants to sediments (the algal-scavenging hypothesis), as previously proposed for mercury. Higher POP concentrations observed in surface sediments of slump-affected lakes are best explained by simple solvent switching processes of hydrophobic contaminants onto a lower pool of available organic carbon when compared to neighbouring lakes unaffected by thaw slump development.

Résumé

L'analyse spatiale et temporelle de carottes de sédiments de 8 lacs dans la région du Delta du fleuve Mackenzie, T.N.-O. (Canada) a été effectuée pour évaluer comment la déposition des polluants organiques persistants (POPs) dans les sédiments des lacs a été affectée par : (1) la présence d'effondrements progressifs sur les rivages; et (2) par l'augmentation de la productivité primaire depuis l'aire autochtone. Les POPs étudiés pour cette analyse sont les biphényls polychlorés (BPCs), les penta- et hexachlorobenzènes (CBzs), le dichlorodiphényltrichloroéthane et ses métabolites (DDTs). Les sédiments de surface des lacs affectés par les effondrements montrent des concentrations (normalisées avec le contenu en carbone organique total (COT)) de POPs plus importantes que celles des lacs de référence à proximité. Les taux de sédimentation inorganique étaient positivement corrélés aux concentrations des contaminants. Ceci suggère que l'influx de matériel silicoclastique, réduisant le carbone de nature organique dans l'eau des lacs affectés, se traduit indirectement en concentrations plus élevés de POPs dans la matière organique des sédiments. Cette interprétation est supportée par une relation inversement proportionnelle entre la concentration de POPs dans les sédiments et le contenu en COT de l'eau du lac.

Les indices utilisés montrant la déposition de carbone de l'aire autochtone ne sont pas corrélés significativement aux flux de POPs des sédiments de surface, et le profil des fluctuations historiques ne coïncide pas avec la variation dans les dépositions de POPs. De ce fait, cette étude n'appuie pas la théorie que le carbone organique des algues augmente le transfert des polluants organiques vers les sédiments (hypothèse de l'effet de piégeage), tel que proposée pour le mercure. Les concentrations plus élevées en POP observées dans les sédiments de surface des lacs affectés par les effondrements sont mieux expliquées par des procédés simples de partition des contaminants hydrophobiques sur une

réserve plus faible de carbone organique disponible, en comparaison avec les lacs voisins qui ne sont pas affectés par le développement de ces effondrements.

Acknowledgements

It's been three years since I finally applied to grad school and I can honestly say that my friends were never more relieved. Apparently a few years of continuously debating and questioning if I should do my Masters can be a bit grating for others – who knew? It's odd to think that a small research project back in my last year of high school would spark an interest in contaminant, Arctic and limnological research that would inevitably lead me here.

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I dedicate this work to my Grandmother, who passed before this work and grad school journey began, but always loved and supported me in whatever I endeavoured to do. I hope you would be proud of me.

Sincerely,

David Eickmeyer

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1.0 – Introduction

Two areas of priority for Arctic regions are persistent organic pollutants (POPs) and the impact of current climate warming on landscapes and ecosystems. POPs are ubiquitous contaminants, created and released through anthropogenic activity, which are a concern to both ecosystems and human health due to their persistence, capability of long-range transport, bioaccumulative nature, and toxicity at low concentrations (Stockholm Convention, 2001; El-Shahawi *et al*., 2010). The historical accumulation and persistence of such contaminants has been well documented in both Arctic matrices and food webs (Muir *et al*., 1996; Evenset *et al*., 2004; Rigét *et al*., 2010). The continued presence of POPs in the Arctic is especially concerning where aquatic environments act as important sources of staple foods for indigenous communities (Carrie *et al*., 2010; Donaldson *et al*., 2010). As a result, the indigenous peoples of the Canadian north are amongst the populations on the planet most exposed to POPs (Van Oostdam, 2003; Donaldson *et al*., 2010). With both recent and projected further warming in the north, potential alterations in abiotic transport systems and physical landscapes are predicted to influence both contaminant delivery pathways and fate in the Arctic (Macdonald *et al*., 2005; ACIA, 2005), requiring further study.

1.1 – Sources and Fate of Persistent Organic Pollutants in the Arctic

Halogenated POPs covered under the Stockholm Convention (2001) are a diverse group of synthetic organic compounds that were previously used globally as industrial chemicals and pesticides during the 20th century. Many of these contaminants became distributed throughout Arctic regions, far from major original point source releases, due to degradation resistance and long-range atmospheric transport, facilitated by their semi-volatile nature and affinity for adsorption to organic aerosol particles (de Wit and Muir, 2010; Lohmann *et al*., 2007; El-Shahawi *et al*., 2010). Subsequent atmospheric deposition onto landscape surfaces introduced POPs into Arctic ecosystems where they consequently

became bioaccumulated and biomagnified to high concentrations in food webs, continuing to do so to this day (Macdonald *et al*., 2005; de Wit and Muir, 2010).

Three classes of POPs that have long histories of Arctic contamination are the polychlorinated biphenyls (PCBs), chlorobenzenes (CBzs) and dichlorodiphenyltrichloroethane and degradation metabolites (DDTs). PCBs include a range of 209 congeners, identified by degree and placement of chlorination on the phenyl rings. They were used in a range of industrial applications due to their thermal stability, chemical inertness and high electrical resistivity (Borja *et al*., 2005). Mass production began in the 1930s and peaked during the 1970s, after which their use was phased out due to concerns over their persistence and environmental impacts (Borja *et al*., 2005; IPCS - Ritter *et al*.). Global manufacture was completely ceased in 1993, by which point an estimated cumulative 1326 kt had been produced (Breivik *et al*., 2002). Chronic PCB exposure elicits a broad suite of toxic responses such as immunosuppression, liver, reproductive and developmental toxicity and non-mutagenic cancer promotion (AMAP, 1998; AMAP 2004).

Penta- and hexachlorobenzes, (PeCBz and HCB, herein referred to CBzs), are composed of a single benzene ring with five and six chlorine substitutions, respectively. During the past century, CBzs were most predominately produced as unintentional by-products during production of chlorinated organic compounds, including several pesticides (AMAP, 2004; UNEP, 2007). HCB briefly found limited use as a fungicide during the 1960s (AMAP, 1998). PeCBz was a common component of CBz mixtures used to reduce viscosity of PCB products in electrical transformers and distributed widely (UNEP, 2007). Limited data are available for global production estimates, though HCB emissions in the mid 1990s were estimated to range from 12 – 92 t yr^{-1} (Bailey, 2001) and PeCBz emissions during the past decade were estimated to be 85 kg yr^{-1} (UNEP, 2007), with neither having a single overwhelming source. Chronic PeCBz and HCB exposure results in similar toxic responses such as immunosuppression, reproductive

and developmental effects; HCB has also been identified as a non-mutagenic tumour promoter (AMAP, 2004; UNEP, 2007).

DDT was introduced as an insecticide during the 1940s and found wide-scale use in agriculture, forestry and public health applications (AMAP, 1998; Li and Macdonald, 2005). Production and usage peaked during the 1970s before it was phased out and banned in many countries in response to environmental concerns (Li and Macdonald, 2005). Cumulative global production has been estimated to be 4500 kt (Li and Macdonald, 2005); however, DDT is still currently used in some countries under restricted conditions as part of the Stockholm Convention negotiations due to its effectiveness in fighting malaria and other insect-borne diseases (AMAP, 2004). DDT degradation metabolites, dichlorodiphenyldichloroethane (DDD) and dichlorodiphenyldichloroethylene (DDE), display similar physical and chemical properties of the parent compound making them of equal environmental concern, hence their inclusion in environmental monitoring as total DDTs. Chronic exposure to these compounds elicits reproductive and developmental effects in organisms, such as the consequence of egg-shell thinning in birds, as well as immunosuppression, thyroid and adrenal cortex impairment (AMAP, 2004).

During the past two decades, long-term monitoring of Arctic atmospheric contaminants by circumpolar stations has reflected general, albeit slow, consistent declines in PCB and DDT air concentrations (Hung *et al*., 2010). These declines are a consequence of the use restrictions and bans in many countries which began in the 1970s (Muir and de Wit, 2010). Atmospheric CBz concentrations in the circumpolar Arctic, despite either remaining relatively constant or showing slight declines during the 1990s, have recently been observed to be on the rise (Hung *et al*., 2010). Speculation explaining this recent trend includes: (1) increased re-volatilization of previously deposited CBz from recently exposed ocean surfaces due to reduced sea ice coverage; and (2) increased use of chlorinated solvents and pesticides containing CBz impurities (Hung *et al*., 2010).

Subsequent to atmospheric deposition of these POPs into Arctic freshwater ecosystems, their hydrophobicity results in partitioning out of the water column by adsorption to organic matter via a simple solvent switching process (Macdonald *et al*., 2002). Particulate organic matter settling and seasonal phytoplankton dynamics act as key vectors to convey contaminants to the lake bed, causing sediments to become an important sink for POP removal by eventual burial (Karickhoff *et al*., 1979; Lohmann *et al*., 2007). Consequently, sequential layering of lake sediments allows for sediment cores to be useful as historical archives chronicling POP arrival and loading into remote Arctic locations (Blais and Muir, 2001).

1.2 – Changes in Arctic Environments – Permafrost Degradation

The warming of our planet is a well documented phenomenon of the currently changing global climate. During the 20th century, average global surface temperatures rose 0.74°C ± 0.18°C, but changes have been particularly amplified in polar regions (Trenberth *et al*., 2007). For example, the western Canadian Arctic has experienced average winter air temperature increases of 3 – 4 °C over the past 50 years (ACIA, 2004).

Observed fluctuations in circumpolar permafrost surface temperatures have also been consistent with changing Arctic air temperature trends (Lachenbruch and Marshall, 1986; Pavlov, 1996; Smith *et al*., 2005). Considering that approximately 24% of exposed land in the Northern Hemisphere is underlain by permafrost (Zhang *et al*., 2000), climate models project that vast areas of Arctic landscapes will be affected by active layer deepening, hydrological and biogeochemical dynamic modifications, and organic carbon loading to aquatic ecosystems (Anisimov *et al*., 2001; Zhang *et al*., 2006; ACIA, 2005). The resultant permafrost thaw has already led to increased thermokarst activity, a subsidence and deformation of the landscape into irregular terrain (Nelson *et al*., 2001).

In the Mackenzie River Delta uplands, NT, retrogressive thaw slumps along tundra lake shorelines are a common form of observed thermokarst (Kokelj *et al*., 2009a). The susceptibility of this area to warming conditions has already been demonstrated by the observed increase in both thaw slump initiation events and the expansion rate of the developing slumps (Lantz and Kokelj, 2008). The delivery of material released from the thaw slump into the lake results in elevated water ionic concentrations, pH, conductivity and total sedimentation rates, and reduced dissolved organic carbon (DOC), water colour, turbidity and sediment total organic carbon (TOC) content (Kokelj *et al*., 2005; Deison *et al*., 2012). Noted declines in lake ionic concentration, hardness and alkalinity relative to thaw slump age suggest that water chemistry of affected lakes may gradually revert to pristine conditions subsequent to slump stabilization (Kokelj *et al*., 2009b). However, due to the polycyclic nature of thaw slump development, accelerated instances of reinitiation events are anticipated with continued global warming (Kokelj *et al*., 2009a).

1.3 – Impacts on Carbon Cycling

The fluctuating limnological conditions of these slump-affected lakes may further compound expected shifts in carbon cycling currently occurring in Arctic lakes due to warming conditions. Reduced ice cover, lengthened growing seasons and changes in light penetration have already been observed to increase autochthonous primary productivity and influence community structure complexity in northern lakes (Smol *et al*., 2005; Karlsson *et al*., 2005). It is also anticipated that aquatic ecosystems will receive increased inputs of organic matter and inorganic nutrients, mobilized by accelerated microbial activity in the surrounding soil catchments (Karlsson *et al*., 2005; ACIA, 2005).

When inorganic siliciclastic material released from a thaw slump enters the adjacent lake, it has the capacity to reduce the DOC content in the water column, as noted above (Kokelj *et al*., 2005). Thompson *et al.* (2008) demonstrated that when inorganic material exposed by a thaw slump was added

to pristine tundra lake water in mesocosm experiments, it resulted in increased water clarity due to organic material settling out. It was reasoned that: (1) fulvic and humic acids are known to react with metals and cations due to their aromatic structures; and (2) DOC readily binds to fine-grain clay particles which subsequently flocculate out of the water column (Thompson *et al*., 2008). These processes would result in reducing the amount of available DOC remaining in the water column and increasing its sedimentation when mixed with the influx of ion-rich clays released by the thaw slump.

1.3.1 – Algal-Scavenging Hypothesis

One concern is that these effects on carbon cycling within the aquatic system could impact how contaminants partition between abiotic and biotic compartments, providing one explanation for higher POP concentrations observed in Mackenzie River burbot (*Lota lota*) in recent decades (Carrie *et al*., 2010). Stern *et al*. (2005) postulated that climate-driven increases of algal primary productivity could lead to increased scavenging of contaminants from the water column and accelerating sedimentary deposition; however, this is a contentious proposal and is still being debated as implications translate into lake sediment used as historical contaminant deposition proxies may overestimate original atmospheric POP concentrations.

Much of the research on the algal-scavenging hypothesis has focussed on mercury accumulation in sediment of northern lakes, reporting significant relationships between mercury and algal-derived organic matter proxies (Stern *et al*., 2009; Jiang *et al*., 2011; Outridge *et al*., 2007). However, these early studies were limited to one or two sites, as understandable in early exploratory investigations. A recent multisite study of lakes across the Canadian Arctic demonstrated that algal organic matter does not always explain mercury deposition to sediment despite increased primary productivity (Kirk *et al*., 2011), with greater variation explained by lake-specific characteristics such as catchment inputs and sedimentation rates.

Work by Stern *et al*. (2005) and Outridge *et al*. (2009) each compared fluxes of algal organic matter and various POPs in one Arctic lake sediment core, with mixed conclusions. To the best of our knowledge, a multisite analysis for algal-scavenging of halogenated organic contaminants in Arctic lakes has not yet been investigated.

1.4 – Thesis Objectives and Hypotheses

This research was conducted in an effort to understand and document changes occurring in Arctic tundra lakes experiencing retrogressive thaw slump development in the Mackenzie River Delta uplands, NT. This was in collaboration with partners at Aboriginal Affairs and Northern Development Canada (Yellowknife, NT), Queen's University (Kingston, ON), Carleton University (Ottawa, ON) and the Geological Survey of Canada (Calgary, AB). Study sites were located within the Inuvialuit Settlement Region, NT and sampled with permission through the Aurora Research Institute – Aurora College (Northwest Territories Scientific Research Licence No. 14908).

1.4.1 – Persistent Organic Pollutant Deposition and Thaw Slump Development

The first objective was to determine historical POP depositions to lake sediments and how they were affected by thaw slump development along lake shorelines. Based on results of previous studies, it was hypothesized that slump-affected lakes would have different POP concentrations in sediment than undisturbed reference lakes.

1.4.2 – Persistent Organic Pollutant Deposition and Algal-Scavenging

The second objective was to determine how POP deposition to lake sediments related to autochthonous primary productivity, as assessed by historical sedimentary organic matter proxies. Based on results of previous studies, it was hypothesized that sedimentary fluxes of POPs would be correlated with algal-derived organic matter.

1.5 – Note Regarding Included Authors

Many individuals were instrumental in coordinating and completing this research, and as such will be included as authors in future publications. Their names have been included in these thesis chapters for completeness and in recognition of their contributions. However, the writings contained within this work are the sole contribution of the author of this thesis, prior to potential input from associated authors for future publications.

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2.0 Spatial assessment of the interactions of polychlorinated biphenyls and organochlorine pesticides with the organic matter in sediment of retrogressive thaw slump-affected lakes of the Mackenzie River Delta uplands, NT, Canada

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2.1 – Abstract

Using a comparative spatial analysis on surface sediment from 8 lakes in the Mackenzie River Delta uplands, NT, we examined how the presence of retrogressive thaw slumps on lake shores affected persistent organic pollutants (POPs, including polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides) depositing to lake sediments. Sediments of slump-affected lakes contained higher total organic carbon (TOC)-normalized POP concentrations than nearby reference lakes unaffected by thaw slumps. Mean focus-corrected inorganic sedimentation rates were positively related to contaminant concentrations, explaining 54 – 98% of the variation in POP concentration in sediment, suggesting that reduced organic carbon in slump-affected lake water results in higher concentrations of POPs on sedimentary organic matter. This explanation was corroborated by an inverse relationship between sedimentary POP concentrations and TOC content of the lake water. Inferred chlorophyll *a*, S2 (mostly algal-derived carbon) and S3 (mostly terrestrially-derived carbon) fluxes to sediment were not significantly correlated to POP fluxes. Thus this study does not support the contention that algal-derived organic carbon increases the delivery of organic pollutants to sediments (the algal-scavenging hypothesis), as previously proposed for mercury. Higher POP concentrations observed in surface sediments of slump-affected lakes is best explained by simple solvent switching processes of hydrophobic contaminants onto a lower pool of available organic carbon when compared to neighbouring lakes unaffected by thaw slump development.

2.2 – Introduction

Two areas of concern for Arctic regions are persistent organic pollutants (POPs) and the impact of current climate warming on landscapes and ecosystems. POPs are ubiquitous contaminants, created and released through anthropogenic activity, which are a concern to both ecosystems and human health due to their persistence, bioaccumulative nature, and toxicity at low concentrations (Stockholm Convention, 2001; El-Shahawi *et al*., 2010). The historical accumulation and persistence of contaminants, such as polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides, has been well documented in both Arctic matrices and food webs (Muir *et al*., 1996; Evenset *et al*., 2004; Rigét *et al*., 2010). The continued presence of POPs in the Canadian Arctic is especially concerning where aquatic environments act as important sources of staple foods for indigenous communities (Carrie *et al*., 2010; Donaldson *et al*., 2010).

Global warming has been well established over the past century (Trenberth *et al*., 2007). In the western Canadian Arctic, the average winter temperature has increased between 3 – 4 °C over the past 50 years (ACIA, 2004). Shallow permafrost temperatures show warming trends consistent with Arctic air temperatures (Smith *et al*., 2005). This warming results in permafrost thaw (Nelson *et al*., 2001), causing increased thermokarst activity. In the Mackenzie Delta uplands, NT, retrogressive thaw slumps along lake shorelines are a common form of thermokarst (Kokelj *et al*., 2009a). The influx of thaw slump material into the lake increases pH, base ion concentrations and total sedimentation rates, and decreases dissolved organic carbon (DOC), water colour, turbidity, and sediment total organic carbon (TOC) content (Kokelj *et al*., 2005; Deison *et al*., 2012).

The changing limnological conditions and lengthened growing seasons due to rising temperatures influence autochthonous primary productivity and particle flux in Arctic lakes (Macdonald *et al*., 2005; ACIA, 2005; Smol *et al*., 2005). One concern is that these effects on carbon cycling within

the aquatic system could impact how contaminants partition between abiotic and biotic compartments, providing one explanation for higher POP concentrations in Mackenzie River burbot (*Lota lota*) in recent decades (Carrie *et al*., 2010). Several studies have suggested that increased phytoplankton biomass may be scavenging contaminants from the water column and accelerating sedimentary deposition (Outridge *et al*., 2007; Stern *et al*., 2009; Stern *et al*., 2005), providing a basis for the algal-scavenging hypothesis (Stern *et al*., 2005).

Most studies of algal-scavenging have focused on mercury (Hg) accumulation in northern lakes, reporting significant relationships between Hg and algal-derived organic matter proxies (Outridge *et al*., 2007; Stern *et al*., 2009; Jiang *et al*., 2011). However, a recent multisite study of lakes across the Canadian Arctic demonstrated that algal organic matter does not always explain Hg deposition to sediment despite increased primary productivity (Kirk *et al*., 2011). Work by Stern *et al*. (2005) and Outridge *et al*. (2009) each compared fluxes of diatoms and various POPs in one Arctic lake sediment core, however to the best of our knowledge, a multisite spatial analysis for algal-scavenging of halogenated organic contaminants in Arctic lakes has not yet been conducted.

The objectives of this study were: (1) to determine the effects of thaw slump development on POP deposition in lakes; and (2) to test the algal-scavenging hypothesis by determining whether sedimentary fluxes of POPs are correlated with S2 (algal-derived) organic matter. This study used various characterized organic matter proxies and focussed on contamination by atmospherically-deposited PCBs, hexa- and pentachlorobenzenes (CBzs), and dichlorodiphenyltrichloroethane and metabolites (DDTs).

2.3 – Methods

2.3.1 – Study Area

Sediment cores were examined from eight lakes chosen along a transect of the uplands east of the Mackenzie River Delta between Inuvik and Richard Islands, NT, Canada (Figure 2.1). Four lakes with thermokarst activity along their shorelines were paired with four lakes without slumping as reference lakes, based on similarities in location and physical characteristics in previous work by Lantz and Kokelj (2008). For each pair, lakes with thaw slumps, referred to as slump-affected lakes, are labelled "b" lakes and undisturbed (reference) lakes are labelled "a" lakes. Physical characteristics and lake locations are detailed in Table 2.1.

2.3.2 – Sample Collection

A sediment core was collected from the deepest basin of each lake in the summers of 2007 and 2008 using a Glew gravity corer, and subsectioned into 0.25 cm intervals from 0 – 15 cm, then 0.5 cm intervals for the remainder (Glew *et al.*, 2001). Sediment samples were stored in Whirl-Pak bags and frozen. Subsamples of sediment were freeze-dried for radiometric dating, organic carbon determination and inferred chlorophyll *a* analysis (Deison *et al.*, 2012).

From the centre of each lake, 1 L samples of surface water were collected in acid pre-rinsed bottles during the summer of 2011. A 150 ml subsample from each lake was then filtered through a 47 mm, 0.45 µm Sartorius acetate filter. The filtrate was collected and stored in the dark at 4 °C for analysis of DOC. A 150 ml subsample from each lake was also filtered through a pre-combusted 47 mm, 0.45 µm Whatman GF/F filter. The filter was subsequently frozen for particulate organic carbon (POC) analysis. Analysis for DOC and POC were performed by the National Laboratory for Environmental Testing (NLET, Burlington, ON, Canada). TOC was calculated by the summation of DOC and POC concentration for each individual lake.

2.3.3 –Sediment Dating

Sediment cores were radiometrically dated via gamma (γ) spectroscopy by determining unsupported ^{210}Pb activity profiles, as described in Appleby (2001) to establish sediment age and sedimentation rate. In brief, homogenized samples from 12 – 15 interval depths per core were freeze-dried and packed into centrifuge tubes to a height of 2 cm. Tubes were then sealed in epoxy resin and allowed to sit for a minimum of 21 days to allow radioisotopes to reach secular equilibrium. Samples were then counted for 23 hours (82,800 seconds) on a digital high purity germanium well detector (DSPec Model # GWL-120230, Ortec, Oak Ridge, TN, USA) using Maestro Version 6.08 (Advanced Measurement Technology Inc., Oak Ridge, TN, USA) to determine activities of ^{210}Pb and ^{137}Cs, following the methods of Appleby (2001). ^{226}Ra activity was determined by measuring the emissions of its daughter isotope ^{214}Pb.

Sedimentation rates and age were determined using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978) as calculated by ScienTissiMe (Scheer Software Solutions, Barry's Bay, ON, Canada). ^{137}Cs activity was used to validate ^{210}Pb dating profiles, due to its peak maximum in 1963 from atmospheric fallout caused by nuclear weapon-testing detonations (Appleby, 2008). For the spatial analysis, a geometric mean sedimentation rate (g m^{-2} yr^{-1}) was determined over the top 5.5 cm of each sediment core. Focus factors (FF) were calculated by dividing the deposition rate of unsupported ^{210}Pb in surface intervals of each sediment core by the estimated atmospheric unsupported ^{210}Pb deposition rate at this latitude (50 Bq m^{-2} yr^{-1}, Omelchenko *et al.*, 1995):

$$FF = \frac{unsupported\ ^{210}Pb\ inventory\ (Bq\ m^{-2}) \times\ ^{210}Pb\ decay\ constant\ (0.03114\ yr^{-1})}{50\ Bq\ m^{-2}\ yr^{-1}}$$

Sedimentation rates and FF are detailed in Table 2.1.

2.3.4 – Organic Geochemistry Analysis

Rock-Eval®6 (Vinci Technologies, France) pyrolysis analysis was performed on interval depths of each sediment core by the Geological Survey of Canada in Calgary, AB to determine quantities and qualitative sources of organic matter based on thermal degradation. Analysis was performed following the method outlined in Lafargue *et al*. (1998) and specified by Sanei *et al*. (2005). An internal shale standard (9107, Geological Survey of Canada – Calgary) was used for quality control.

Sediment samples (30 – 50 mg) were placed in a pyrolysis oven, under inert atmosphere (N_2), and heated from 100 – 650 °C at a programmed rate of 25 °C per minute. Hydrocarbons (HC) released were measured using flame ionization detection (FID). CO and CO_2 released by oxygen-bearing organic compounds were measured by online infrared (IR) detectors. Samples were then transferred to an oxidation oven and heated from 400 – 850 °C in air, incinerating any residual organic carbon. CO and CO_2 released were again measured by IR detection. TOC (% DW) of the sediment was determined by the total amount of organic carbon released during both pyrolysis and oxidation.

HC released over 300 °C during pyrolysis is referred to as the S2 fraction, consisting of the kerogen remaining after labile hydrocarbons volatilized off (Lafargue *et al*., 1998). The S2 fraction is released due to the thermal cracking of high-molecular weight, hydrogen-rich macromolecules forming the structure of algal cell walls (Carrie *et al*., 2012; Sanei *et al*., 2005). S2 is referred to as 'algal-derived' carbon, and thus can be used as a proxy of historical autochthonous primary productivity (Brazeau *et al*., 2013; Kirk *et al*., 2011; Outridge *et al*., 2007).

The S3 fraction consists of the CO and CO_2 produced during the pyrolysis of oxygen-bearing organic compounds in the kerogen (Lafargue *et al*., 1998). This organic matter is composed of carbohydrates and lignins from terrigenous sources (Carrie *et al*., 2012; Carrie *et al*., 2009), and thus can be used for a proxy of allochthonous carbon inputs or 'terrestrially-derived' organic matter in the sediment.

2.3.5 – Organic Contaminant Extraction and Analysis

PCBs and OCs were extracted from sediment samples using accelerated solvent extraction (ASE), isolated using gel permeation chromatography (GPC) and silica gel fractionation, and analysed using gas chromatography – micro electron capture detection (GC-μECD). Briefly, sequential core interval samples were combined to create a pooled sample with approximately 0.25 g of TOC. Samples were homogenized with Hydromatrix™ diatomaceous earth (Varian Inc., Palo Alto, CA, USA), spiked with a PCB/OC recovery standard and extracted by ASE (ASE-200, Dionex Corporation, Sunnyvale, CA, USA) using a solution of 1:1 hexane:dichloromethane (DCM) followed by 1:1 acetone:DCM. Samples then underwent liquid-liquid extraction with DCM to remove contaminants in co-extracted water, followed by passing through a sodium sulphate bed to remove remaining water.

Following a slightly modified US Environmental Protection Agency (EPA) Method 3640 A, sulfur and other matrix materials were removed by running samples on Envirogel™ GPC columns (Waters Corporation, MA, USA) with DCM as the mobile phase delivered by an Agilent 1100 Series preparative HPLC system (Agilent Technologies, Santa Clara, CA, USA). Samples were then eluted through 8 g activated silica gel columns (Grade 635, 60 – 100 mesh, 60 Å) with hexane followed by 1:1 hexane:DCM to separate the PCBs from most OCs in different fractions. Each sample fraction was evaporated to a final volume of 0.5 ml in 2,2',4-trimethylpentane and spiked with octachloronaphthalene (OCN) as an internal standard.

Aliquots of the final extracted samples were analysed on a Hewlett Packard (HP) 6890 GC and an HP G2397A ^{63}Ni μECD detector (Agilent Technologies) following US EPA Method 508.1. Separation was completed on a DB5-MS+DG column (Agilent Technologies) with H_2 as the carrier gas. OC standards for GC-μECD calibration were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Recovery spike OC standards, OCN and all PCB standards were purchased from Ultra Scientific (North

Kingstown, RI, USA). The congeners and compounds monitored for ΣPCBs, ΣCBzs and ΣDDTs are detailed in Supplemental Table S2.1, along with detection limits. Method limits of quantification were based on a signal to noise ratio of 3, and were below 0.15 ng g^{-1} TOC.

Samples were blank corrected to remove effects of background contamination. Recovery spikes reflected a mean recovery of 91.1 – 112.7% for PCBs and 63.6 – 84.9% for OCs (n = 56) and thus were not recovery-corrected. Due to the limited amount of sample, replicate extractions (n = 11) were performed on Standard Reference Material® (SRM) 1944 (organic contaminants in New York/New Jersey waterway sediment) from the National Institute of Standards and Technology (Gaithersburg, MD, U.S.A.). Mean recovery (± 1 SD) of ΣPCBs for replicates was 90.4 ± 12.7% of certified SRM values.

2.3.6 – Inferred Chlorophyll a in Sediment

Visible reflectance spectroscopy (VRS) was used to infer chlorophyll *a* content in sediment by the Paleoecological Environmental Assessment and Research Laboratory (PEARL, Queen's University, Kingston, ON, Canada), following methods outlined in Michelutti *et al.* (2010). In brief, sediment samples were freeze-dried (0.2 – 1.0 g DW), sieved (125 µm mesh) and analyzed on a FOSS NIRSystems Model 6500 rapid content analyzer. Examination of the distinct reflectance peaks between 650 and 700 nm on the spectra allowed for the determination of both chlorophyll *a* and its diagenetic derivatives (pheophytin *a* and pheophorbide *a*), thus allowing for an inferred total chlorophyll *a* content and accounting for degradation (Michelutti *et al*., 2010; Wolfe *et al.*, 2006).

2.3.7 – Cumulative Inventory Calculations and Statistical Analyses

Over the top 5.5 cm of each sediment core, cumulative inventories were calculated for each contaminant, chlorophyll *a*, S2 and S3 carbon fractions using the following equation:

$$Inventory = \sum C_{\mathrm{dw}} I_{\mathrm{dw}}$$

where C_{dw} is the concentration (per g DW) for each interval, and I_{dw} is the interval DW (g). Total DW and TOC amounts were calculated for each sediment core inventory to determine final concentrations of each variable for spatial analysis. Fluxes were then calculated by multiplying DW-normalized concentrations by the sample focus-corrected sedimentation rate.

All data were analysed using SPSS 16.0 (IBM Corporation, Armonk, NY, U.S.A.). Simple linear regressions were used to analyze the relationships between each contaminant, sedimentation rate, water TOC, chlorophyll *a*, sediment TOC content, S2 and S3 carbon fractions. Student's t-tests were used to test the difference in contaminant concentrations and fluxes between slump-affected and reference lakes. Concentrations and fluxes were $\log_{10}$ transformed prior to t-tests to equalize variances.

2.4 – Results and Discussion

2.4.1 – Persistent Organic Pollutants in Surface Sediment

Both reference and slump-affected lakes were found to have a similar range of surface sediment concentrations of ΣPCBs, on a dry weight basis (Table 2.2), to previously studied lakes in the Mackenzie River Delta region (AMAP, 2004; AMAP, 1998). Values were an order of magnitude higher than reported concentrations in remote northern Alaskan lakes (Allen-Gil *et al*., 1997), but lower than much larger lakes in western NT (Muir *et al*., 1996). Concentrations of ΣDDTs and ΣCBzs in study lakes were also similar, on per g DW basis (Table 2.2), to previously reported values in lakes of northern Alaskan and the Mackenzie River Delta region (Allen-Gil *et al*., 1997; AMAP, 2004). In comparison with those studies that also report organic carbon content, lakes from this study contain POP concentrations an order of magnitude lower when normalized to TOC (AMAP, 1998). Due to the propensity for POPs in lake systems to adsorb to organic matter, comparisons of TOC-normalized POP concentrations better reflect the interactions of these contaminants with the carbon cycle in these aquatic systems.

In general, slump-affected lake sediments had higher concentrations of TOC-normalized POPs than reference lake sediments (Table 2.2). Mean ΣPCB and ΣCBz concentrations were significantly higher in affected lakes (ΣPCB, affected = 89.54 ± 56.09 SD ng g^{-1} TOC, reference = 32.02 ± 15.27 SD ng g^{-1} TOC, t_6 = 2.53, p = 0.045; ΣCBz, affected = 12.65 ± 5.09 SD ng g^{-1} TOC, reference = 2.11 ± 1.00 SD ng g^{-1} TOC, t_6 = 5.47, p = 0.002). Although mean ΣDDT concentrations were higher in slump-affected lake sediments (9.24 ± 5.51 ng g^{-1} TOC) than in reference lakes (4.49 ± 1.66 ng g^{-1} TOC), the difference was not statistically significant (t_6 = 1.82, p = 0.119). Lakes 2b and 36b have ΣDDT concentrations similar to the reference lakes, explaining the lack of significance. However, these two lakes have older, stable retrogressive slump scars where water chemistry could gradually be reverting back to conditions similar to reference lakes (Kokelj *et al*., 2009b), resulting in their similar contaminant concentrations. Comparing lakes with active and stabilized thaw slumps may be informative; however, we were unable to do that here due to sample size limitations.

Previous work on these same lakes by Deison *et al*. (2012) revealed DW-normalized concentrations of both total mercury (THg) and methyl-mercury (MeHg) to be lower in surface sediments of slump-affected lakes than reference lakes. DW-normalized POP concentrations were not found to be significantly different between slump-affected and reference lakes (p > 0.05). Although POP partitioning in aquatic systems is primarily driven by hydrophobic interactions, Hg exists in various oxidation states resulting in complex biogeochemical cycling between biotic and abiotic compartments of the lake (Morel *et al*., 1998), which may explain the different trends observed in Hg and POP concentrations.

Contaminant fluxes were not found to be significantly different between reference and slump-affected lakes (Table 2.3; p > 0.05). This finding indicates that, despite the effect of slump activity on

POP concentrations in lake sediment, the contaminant deposition rates to the sediment were not significantly altered.

2.4.2 – Persistent Organic Pollutants and Sedimentation Relationship

All POP concentrations were found to have significant positive relationships with mean total sedimentation rates (Figure 2.2), explaining 50 – 97% of the variation in concentration. Separating the sedimentation into both organic and inorganic fractions further revealed that inorganic sedimentation rate was correlated to POP concentration in sedimentary organic matter. DW-normalized POP concentrations reflected the same positive relationship with all sedimentation rates, however trends were not significant, $p > 0.05$, with exceptions for ΣPCB and ΣDDT concentrations vs. organic sedimentation rate (Supplemental Figure S2.1). These data contrast with the inverse relationship between total sedimentation rate and DW-normalized Hg concentrations observed by Deison *et al*. (2012), explained as dilution in the sediment by the influx of inorganic material from thaw slump development.

Lake surface water TOC was inversely correlated with sediment POP concentrations (Figure 2.3). Although two of the three POPs do not demonstrate significant relationships ($p > 0.05$), a general trend for all three is apparent. Water TOC content was determined from samples collected in the summer of 2011. If it were available, a long-term temporal record of the water TOC concentrations covering the same decades contained within the sediment core inventories would provide a more representative value than one sampling event, potentially reducing the variation preventing statistical significance for the individual ΣPCB and ΣCBz regressions.

Solvent switching of contaminants in the water can explain the higher concentrations observed in slump-affected lake sediments. The adsorption and accumulation of POPs by DOC and POC in the water column is expected due to their hydrophobicity (Macdonald *et al*., 2002). The reduced DOC and

POC in slump-affected lakes would result in more efficient scavenging of POPs by organic carbon, resulting in higher concentrations of POPs in sedimentary organic carbon in slump-affected lakes. Further, solvent depletion processes (Macdonald *et al*., 2002) would occur via natural sedimentary mineralization of organic matter, causing either continued amplification of contaminants onto more recalcitrant organic carbon pools, or thermodynamically-driven releases into sediment pore water and partitioning into benthos (ACIA, 2005; Macdonald *et al*., 2002).

The amplification of TOC-normalized POP concentrations in the sediment could directly impact food webs within slump-affected lakes. Benthic organisms would consequently be dwelling in more contaminated environments than pelagic equivalents (Macdonald *et al*., 2002). Subsequent consumption of organic matter delivered to the sediment will result in ingestion of increased initial contaminant loads that will transfer up the food chain of these small tundra lakes.

2.4.3 – Persistent Organic Pollutants and Organic Carbon Proxies

Contaminant fluxes were not found to correlate ($p > 0.05$) with inferred chlorophyll *a*, S2, S3 and total organic carbon fluxes (Supplemental Figures S2.2 – 2.5 respectively). Although ΣPCB and ΣDDT fluxes generally presented positive relationships with each measurement of organic carbon, little variation in ΣCBz fluxes was explained by the different carbon fluxes (0.1 – 2.9%). As noted in previous work (Deison *et al*., 2012), fluxes of TOC and S2 were not different for reference and slump-affected lakes and similar observations were noted here for S3 and inferred chlorophyll *a* fluxes (Table 2.3; $p > 0.05$).

There is a possibility that contaminant fluxes for Lake 14b could be considered outliers considering their high positions in Supplemental Figures 2.2 – 2.5, however due to the variability in the small sample size (n = 8), their removal as outliers could not be justified. If Lake 14b is not included, R^2 values for relationships between ΣPCB, ΣDDT and carbon proxy fluxes increase from 0.020 – 0.330 to

0.457 – 0.864, and become either significant ($p < 0.05$) or approaching significant. Relationships with carbon proxy and ΣCBz fluxes remain relatively unchanged if Lake 14b is not included.

If the algal-scavenging hypothesis (increased autochthonous primary productivity causing higher sediment contaminant concentrations via efficient scavenging and deposition) is to be used to explain POP concentrations in the sediment in the same manner as Hg (Outridge *et al*., 2007; Stern *et al*., 2009; Jiang *et al*., 2011), significant positive relationships should be observed between POPs and S2 (algal-derived) carbon . Indeed, if POP concentrations were expressed on a dry weight basis, positive linear relationships were noted in two of the three contaminants (Supplemental Figure S2.6). However, the variability of organic carbon content is not taken into account with DW-normalized POP concentrations. Comparing fluxes of contaminants and S2 carbon, as done by Outridge *et al*. (2009) and this study, addresses this issue. The relationships observed here (Supplemental Figure S2.3) do not provide evidence to support the algal-scavenging hypothesis for ΣPCBs, ΣCBzs and ΣDDTs. Similarly, the temporal study by Outridge *et al*. (2009) also reported no significant correlation between fluxes of S2 carbon, ΣPCBs and ΣDDTs, suggesting the sedimentary profiles were more closely related to trends for global POP production and use. These data also correspond with findings by Kirk *et al*. (2011), who determined that, although significant positive correlations were found between Hg and S2 carbon fluxes in sediment core profiles of 50% of studied Arctic lakes, greater variation in Hg concentrations was explained by lake-specific variables, such as sedimentation rate, and catchment inputs than S2 carbon.

Although S2 carbon concentrations are lower in terrestrial plants than algal matter, allochthonous material is still capable of contributing to S2 levels in sediment if present in considerable amounts (Sanei *et al*., 2012). Previous studies of algal-scavenging in High Arctic lakes (Outridge *et al*., 2007; Jiang *et al*., 2011) have considered S2 carbon to be effectively equivalent to algal productivity by being situated in environments where external plant sources are negligible (Outridge *et al*., 2011).

Considering that organic carbon in these study lakes is predominantly of allochthonous origin (Deison *et al*., 2012), S2 fluxes may not solely reflect algal productivity and thus present the lack of significant relationships with POPs. However, independent measures of autochthonous primary productivity by inferred chlorophyll *a* fluxes also did not have significant relationships with contaminant fluxes (Supplemental Figure S2.2) and do not support the algal-scavenging hypothesis for POPs.

2.5 – Conclusions

This study demonstrates that thaw slump development along lake shores in the Arctic coincides with reduced organic carbon in the water column, affecting organic contaminant dynamics in aquatic ecosystems. Although contaminant fluxes were similar between lakes, sedimentary organic matter from slump-affected lakes contained higher POP concentrations than neighbouring reference lakes. This difference is likely explained by the reduced availability of organic matter for adsorption in the water. Deposition rates of POPs and autochthonous organic matter proxies in lake sediment did not support algal-scavenging as an explanation for POP concentrations.

2.6 – Acknowledgements

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Table 2.1. Location and physical characteristics of 8 study lakes in the Mackenzie River Delta uplands, NT. Thaw slump activity and morphometric data were determined via aerial photograph analysis and ground surveys during 2001 – 2005 (Kokelj *et al*., 2005).

Lake	Latitude (°N)	Longitude (°W)	A_o[1] (ha)	CA[2] (ha)	DA[3] (ha)	Thaw Slump Status	Z_m[4] (m)	FF[5]	Sed Rate[6] (g m^{-2} yr^{-1})
	I. Reference Lakes								
2a	68°30'09.6"	133°39'55.8"	2.0	17.2	—	—	6.1	0.50	244.5
9a	68°58'05.8"	133°53'53.0"	3.1	29.3	—	—	2.7	0.35	210.8
14a	68°31'02.7"	133°44'55.4"	3.4	33.5	—	—	7.5	0.63	158.3
36a	68°30'10.4"	133°42'02.2"	0.8	6.6	—	—	9.5	1.13	78.4
	II. Slump-Affected Lakes								
2b	68°30'26.6"	133°40'08.3"	4.9	15.9	1.0	Stable	3.4	0.87	269.2
9b	68°58'14.1"	133°53'59.2"	3.6	7.2	2.5	Active	3.0	0.64	340.1
14b	68°31'45.4"	133°44'14.8"	9.2	45.1	2.3	Active	10.5	0.91	529.6
36b	68°30'37.6"	133°43'34.9"	3.9	24.4	4.9	Stable	7.4	1.00	153.6

[1] A_o = lake surface area

[2] CA = catchment area

[3] DA = disturbance area of slump

[4] Z_m = maximum lake depth

[5] FF = focusing factor

[6] Focus corrected geometric mean sedimentation rate over the top 5.5 cm core depth was calculated using the CRS model (Appleby and Oldfield, 1978)

Table 2.2. Contaminant concentrations of ΣPCBs, ΣCBzs and ΣDDTs in sediment samples of 8 study lakes in the Mackenzie River Delta uplands, NT. Concentrations were determined by taking inventories of individual contaminants, dry weight (DW) and total organic carbon (TOC) over the top 5.5 cm of each sediment core.

	ΣPCBs[1]		**ΣCBzs[1]**		**ΣDDTs[1]**	
Lake	**(ng g^{-1} TOC)**	**(ng g^{-1} DW)**	**(ng g^{-1} TOC)**	**(ng g^{-1} DW)**	**(ng g^{-1} TOC)**	**(ng g^{-1} DW)**
	I. Reference Lakes					
2a	38.32	2.80	2.34	0.17	6.61	0.48
9a	50.58	9.33	3.40	0.63	4.56	0.84
14a	21.44	3.49	1.53	0.25	4.23	0.69
36a	17.76	2.16	1.15	0.14	2.56	0.31
	II.Slump-Affected Lakes					
2b	71.90	4.57	14.40	0.92	6.51	0.41
9b	77.19	4.65	6.33	0.38	9.43	0.57
14b	169.83	5.33	18.42	0.58	16.84	0.53
36b	39.25	1.78	11.44	0.52	4.16	0.19

[1] Congeners monitored for each contaminant listed in Supplemental Table S2.1

Table 2.3. Organic carbon and contaminant fluxes of ΣPCBs, ΣCBzs and ΣDDTs in sediment samples of 8 study lakes in the Mackenzie River Delta uplands, NT. Fluxes were determined by taking inventories of individual contaminants, carbon fractions and dry weight to determine concentrations over the top 5.5 cm of each sediment core, then multiplying by focus-corrected sedimentation rates.

Lake	ΣPCBs[1] (ng m^{-2} yr^{-1})	ΣCBzs[1] (ng m^{-2} yr^{-1})	ΣDDTs[1] (ng m^{-2} yr^{-1})	S2 Carb[2] (g m^{-2} yr^{-1})	S3 Carb[3] (g m^{-2} yr^{-1})	Chl *a*[4] (mg m^{-2} yr^{-1})	TOC[5] (g m^{-2} yr^{-1})
	I. Reference Lakes						
2a	684.06	41.81	118.09	3.52	2.83	-	17.91
9a	1965.89	132.14	177.24	11.30	5.67	8.51	39.92
14a	552.49	39.58	109.07	5.98	4.50	7.17	25.99
36a	169.17	10.89	24.37	1.27	2.07	2.45	10.05
	II.Slump-Affected Lakes						
2b	1229.61	246.35	111.46	3.33	2.72	5.26	17.30
9b	1581.00	129.57	193.16	5.19	3.17	14.21	20.47
14b	2823.83	306.11	280.16	1.86	3.65	0.69	17.78
36b	272.88	79.44	28.89	0.96	1.51	1.01	7.42

[1] Congeners monitored for each contaminant listed in Supplemental Table S2.1

[2] S2 (algal-derived) carbon

[3] S3 (terrestrially-derived) carbon

[4] Inferred chlorophyll *a*, data for 2a not available

[5] Total organic carbon

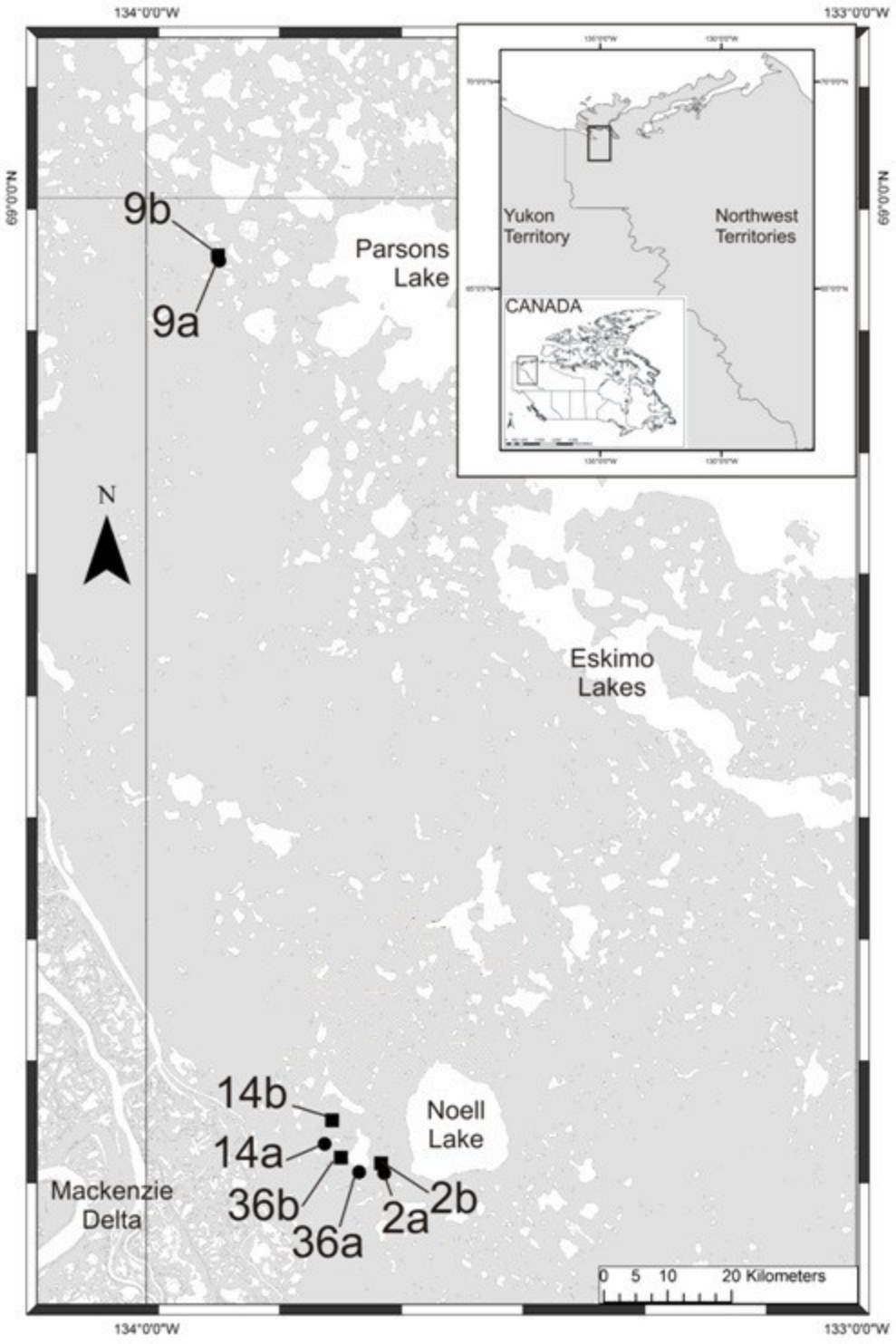


Figure 2.1. Location of the 8 study lakes in the Mackenzie River Delta Uplands, NT. "a" denotes reference lakes and "b" denotes slump-affected lakes.

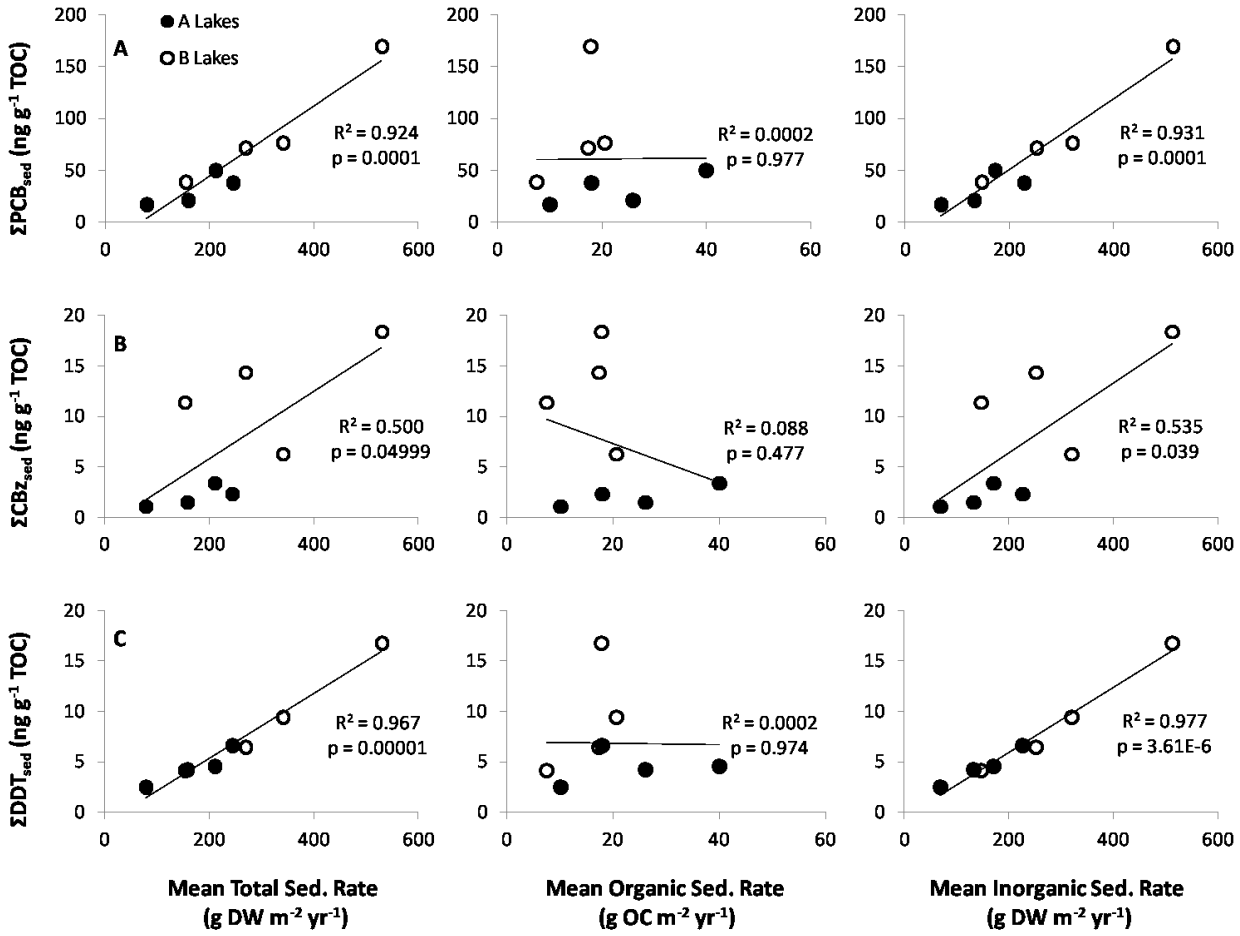


Figure 2.2. Mean total, organic and inorganic sedimentation rates (g m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores (focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb) from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT concentrations (ng g^{-1} TOC), panels A, B and C, respectively. Cumulative inventories of each contaminant and total organic carbon were calculated over the top 5.5 cm of each core to determine concentration. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).

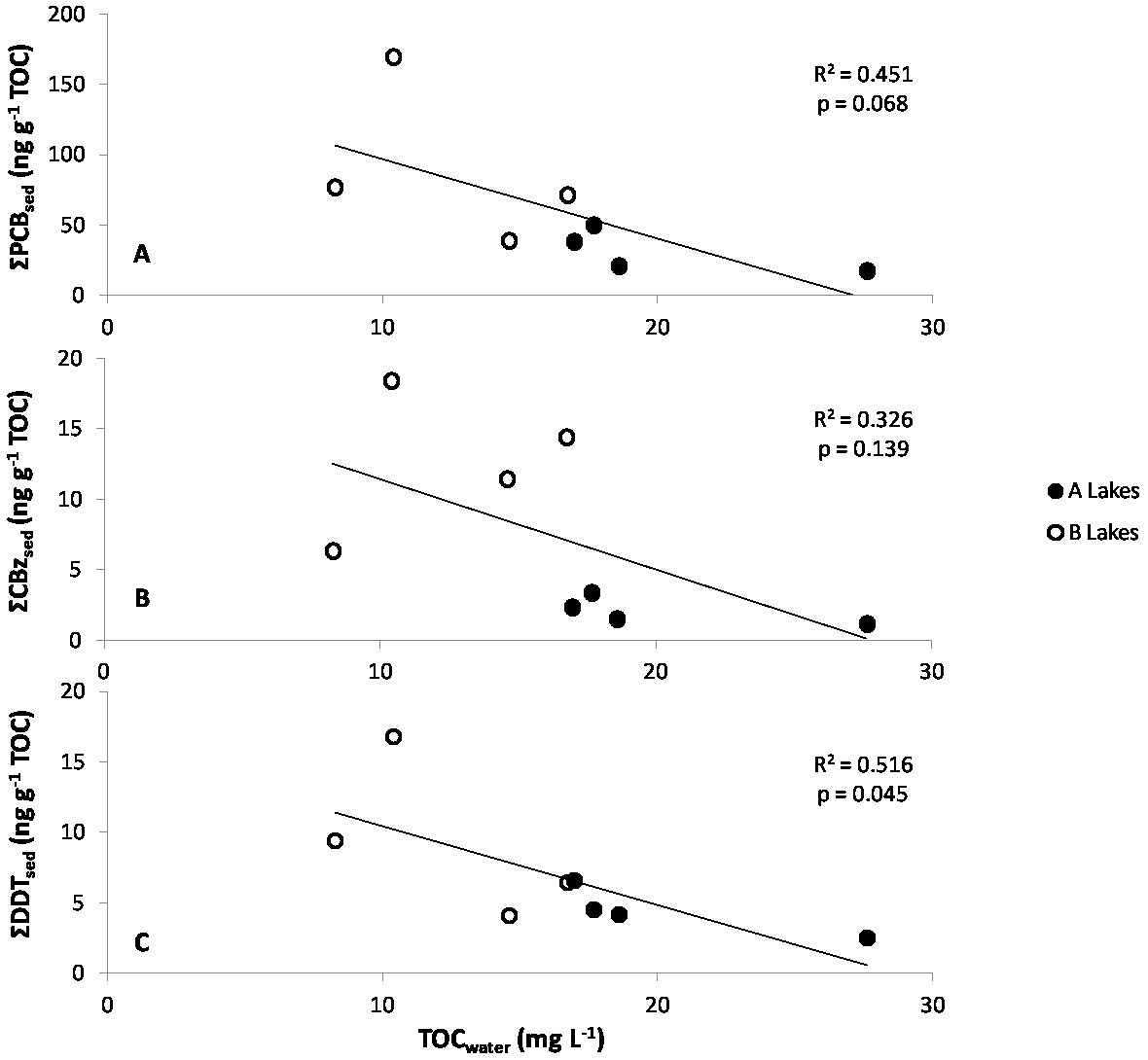
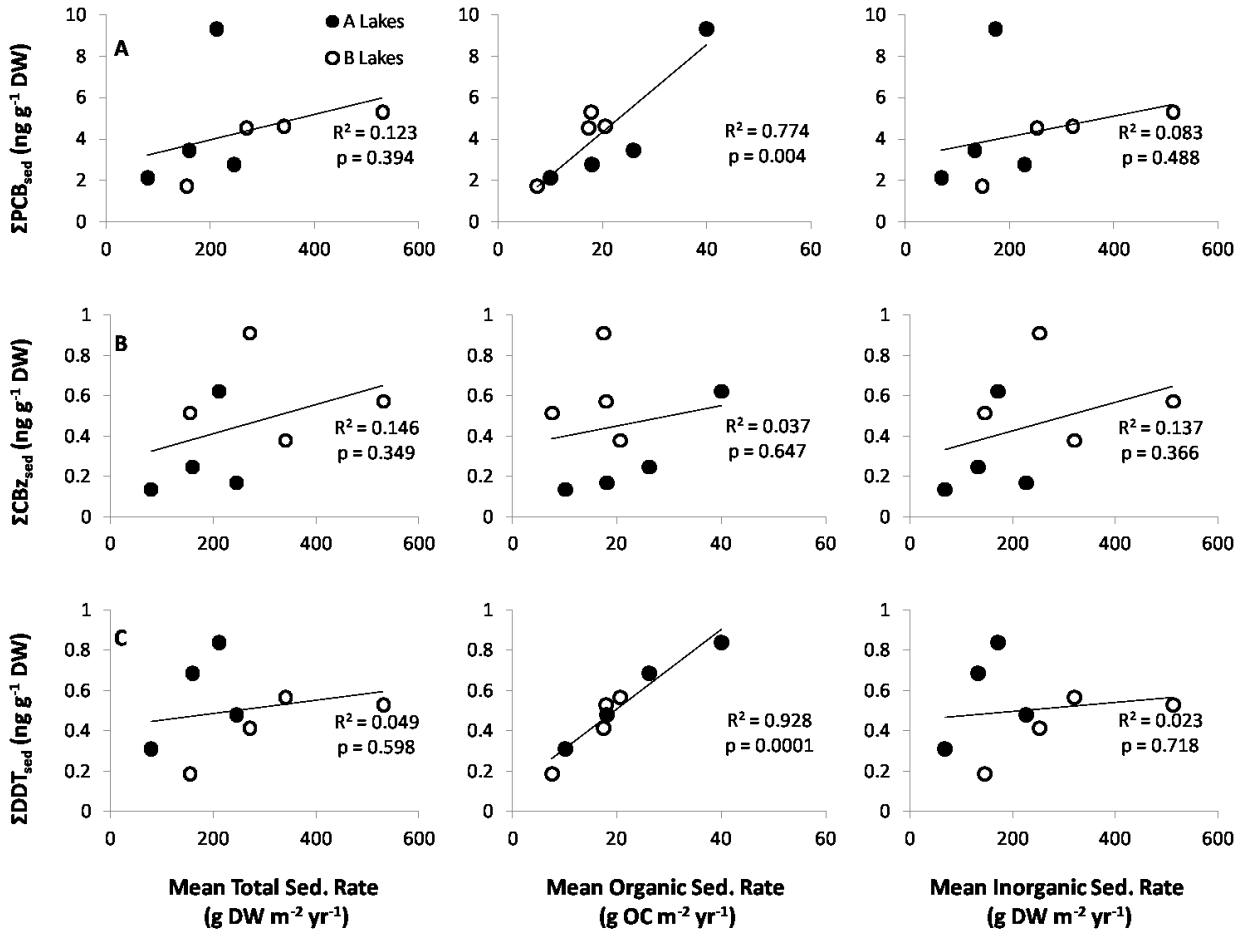


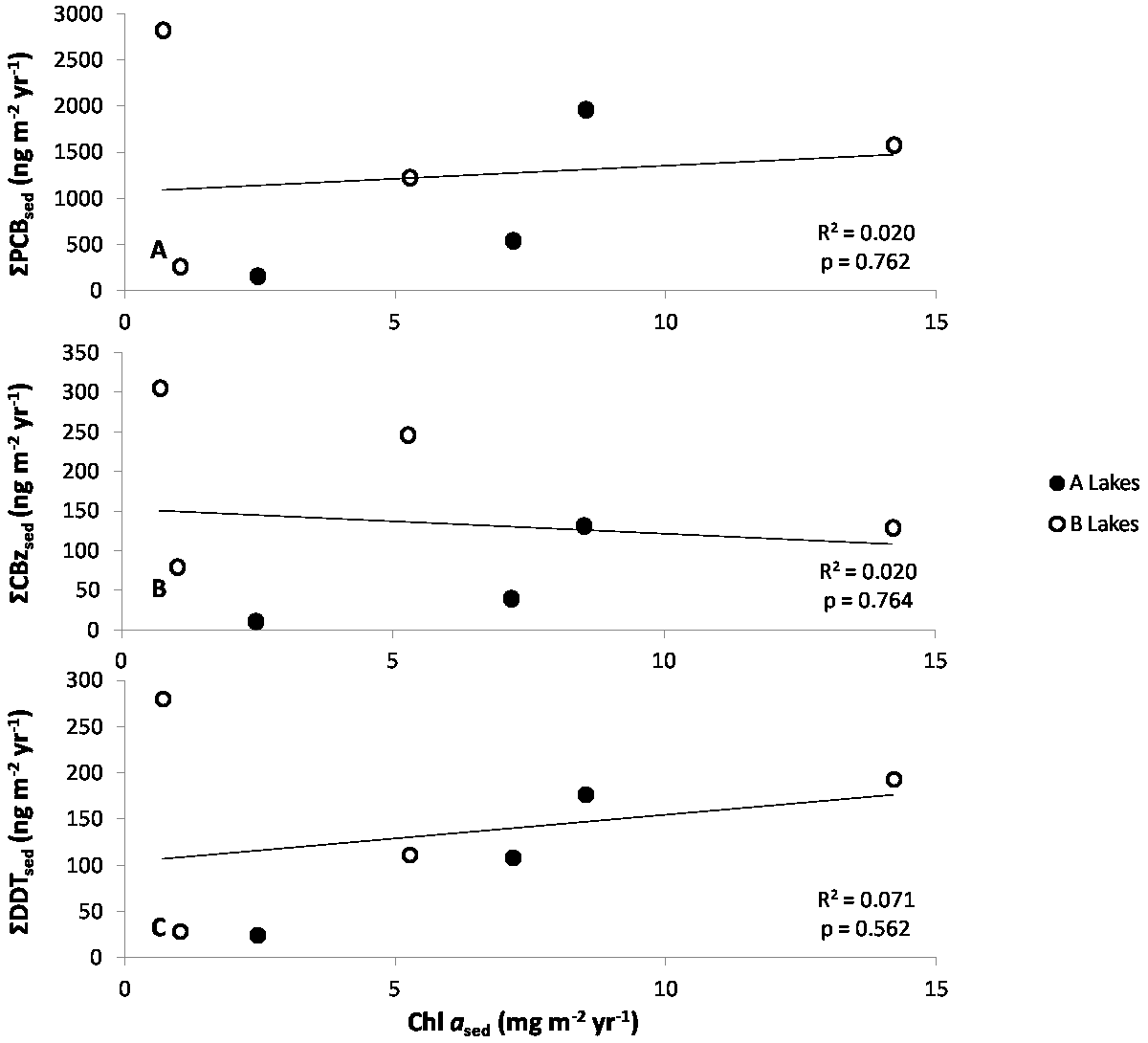
Figure 2.3. Concentration of total organic carbon (mg L^{-1}) in surface waters of 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against surface sediment ΣPCB, ΣCBz and ΣDDT concentrations (ng g^{-1} TOC), panels A, B and C, respectively. Cumulative inventories of each contaminant and total organic carbon were calculated over the top 5.5 cm of each sediment core to determine concentration. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).

Supplemental Table S2.1. Mean method detection limits (MDL) (ng g^{-1} TOC) and congeners monitored for polychlorinated biphenyls (ΣPCBs), chlorobenzenes (ΣCBzs) and dichlorodiphenyltrichloroethane (ΣDDTs) and metabolites.

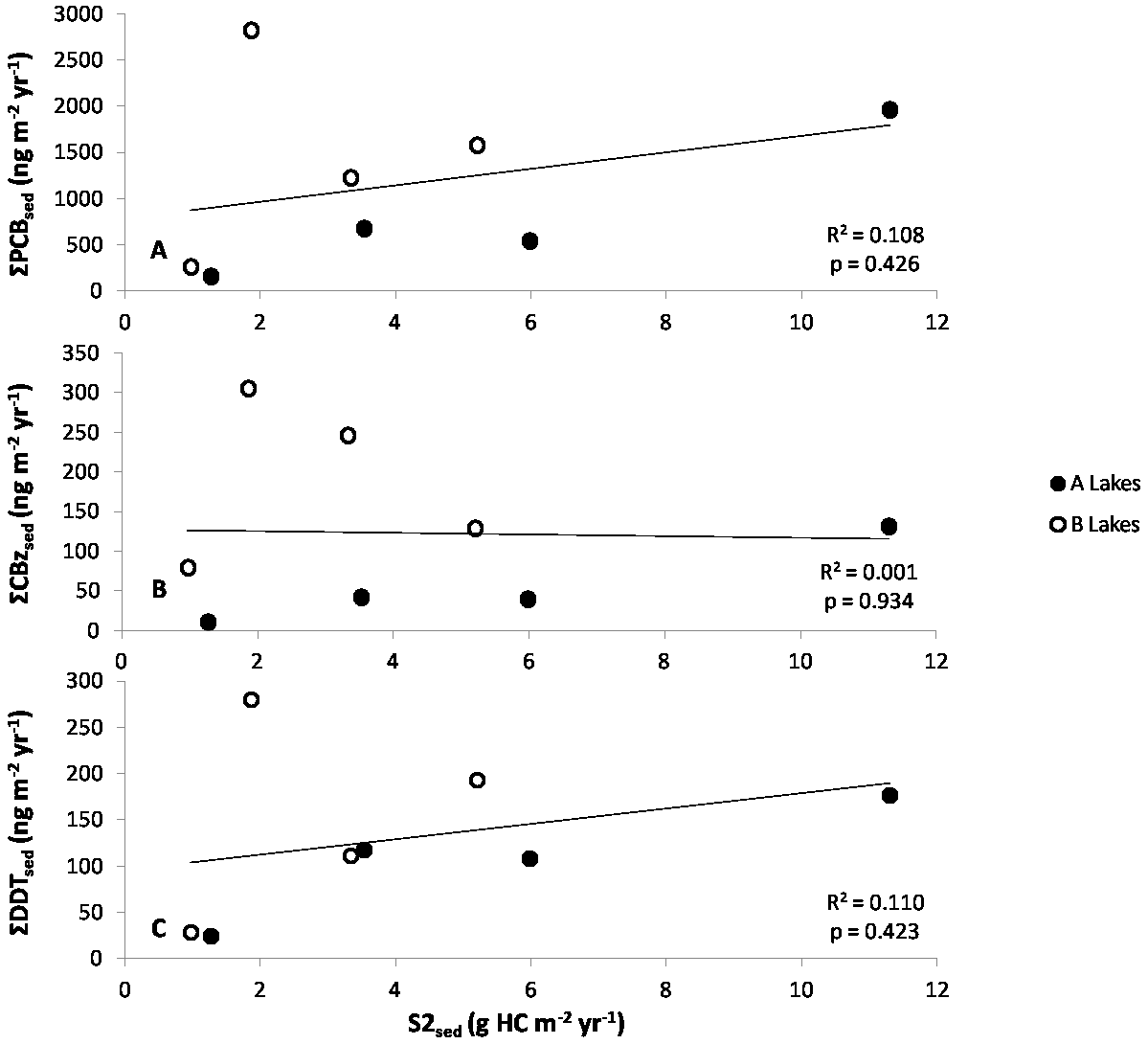
	MDL (ng g^{-1} TOC)	**Congeners**				
PCBs						
DiCBs	0.135	8-5	14			
TriCBs	0.118	18	19	31-28	29	32
TetraCBs	0.058	44	49	52		
PentaCBs	0.072	87	99	105	110	118
HexaCBs	0.070	128	132	138	146	149
		153	155	156	157	163
HeptaCBs	0.064	170	180	183	187	
OctaCBs	0.026	194	195	201	203	
NonaCBs	0.039	206				
DecaCBs	0.074	209				
CBzs	0.054	PentaCBz	HexaCBz			
DDTs	0.055	2, 4'-DDT	2, 4'-DDD	2,4'-DDE		
		4, 4'-DDT	4, 4'-DDD	4,4'-DDE		



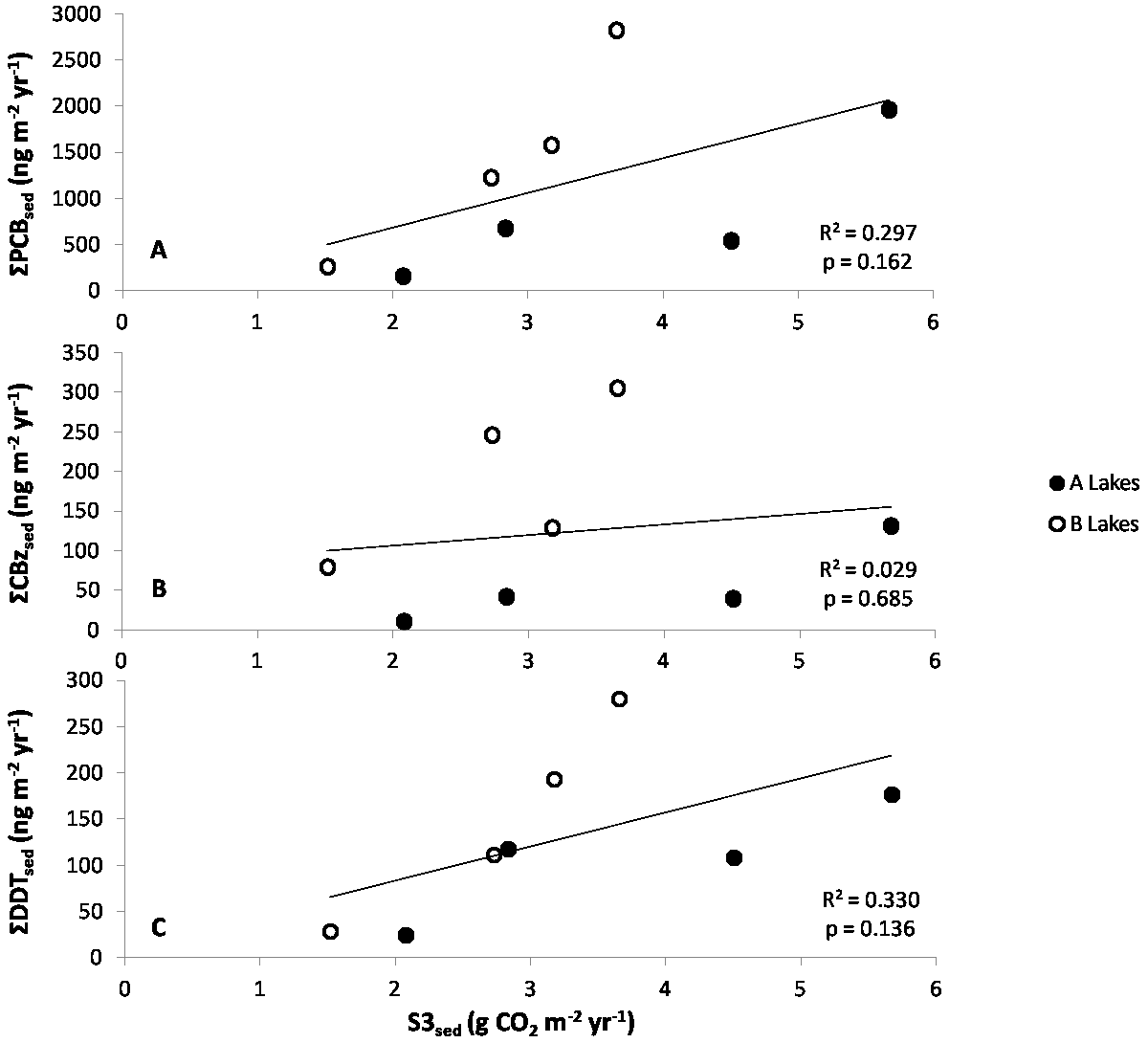
Supplemental Figure S2.1. Mean total, organic and inorganic sedimentation rates (g m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores (focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb) from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT concentrations (ng g^{-1} DW), panels A, B and C, respectively. Cumulative inventories of each contaminant were calculated over the top 5.5 cm of each core to determine concentration. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).



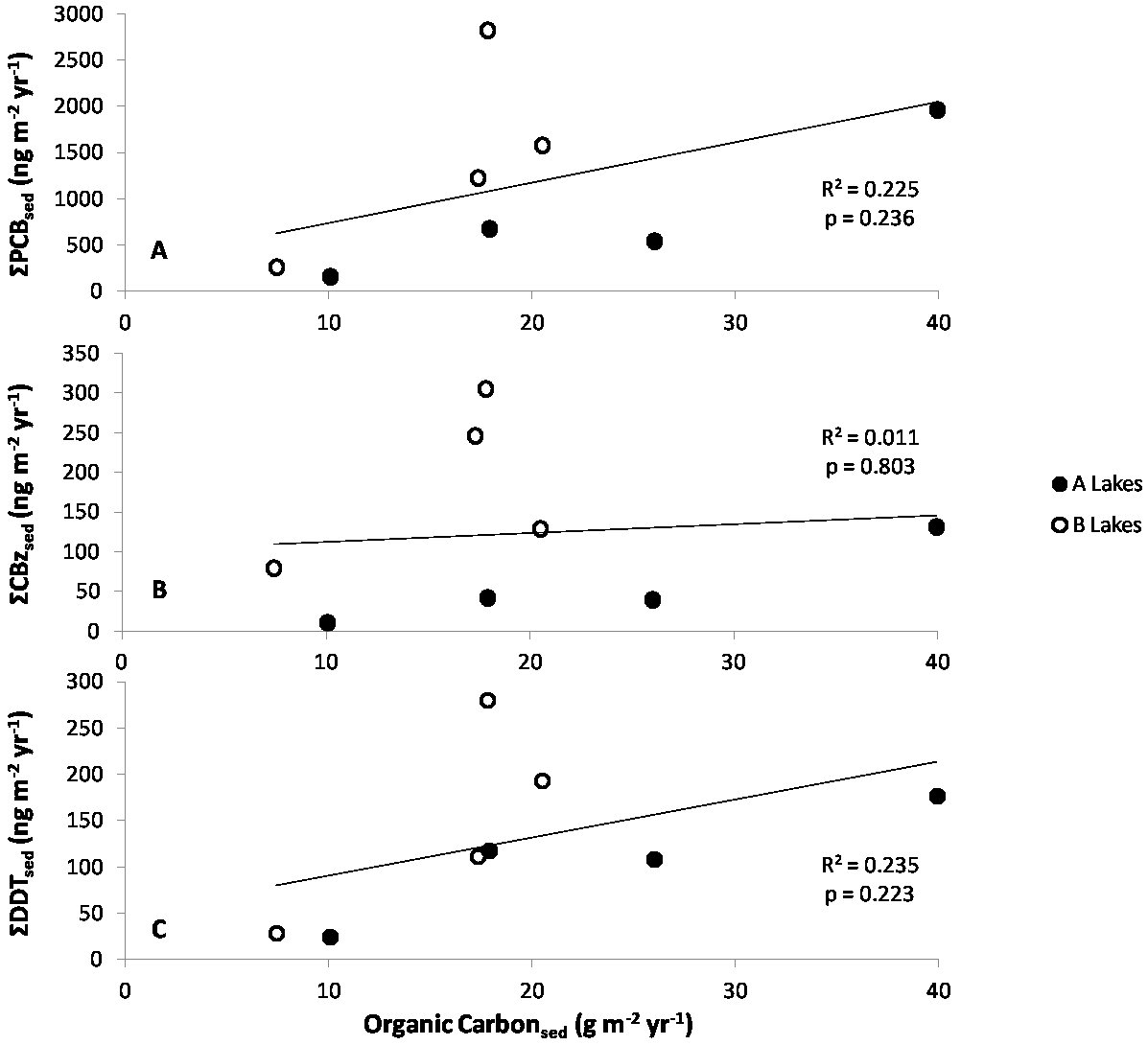
Supplemental Figure S2.2. Inferred chlorophyll *a* flux (mg m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores from 7 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}), panels A, B and C, respectively. Cumulative inventories of each contaminant and chlorophyll *a*, were calculated over the top 5.5 cm of each core and multiplied by focus-corrected sedimentation rate to determine fluxes. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 7).



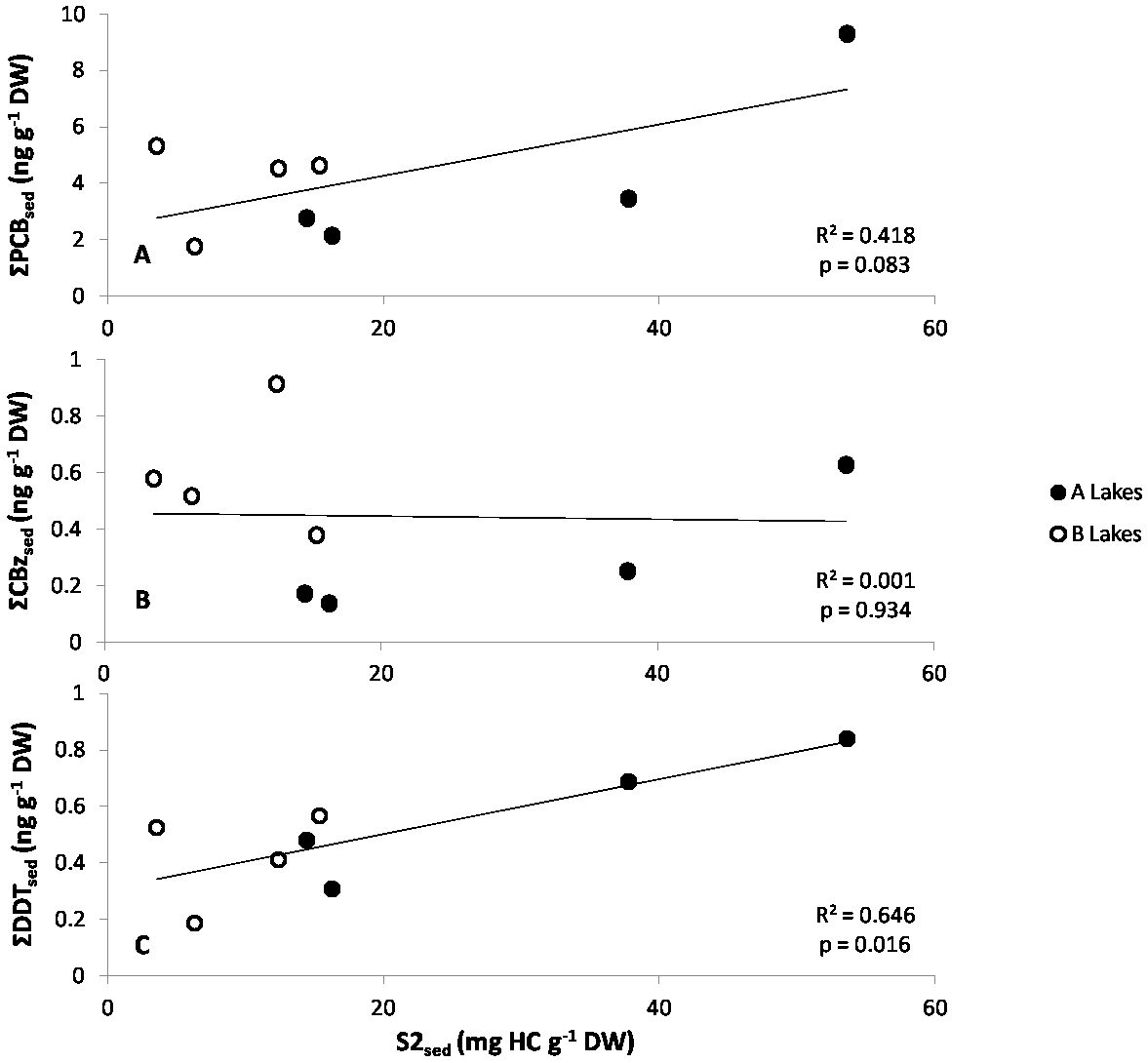
Supplemental Figure S2.3. S2 (algal-derived organic carbon) flux (g HC m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}), panels A, B and C, respectively. Cumulative inventories of each contaminant and S2 carbon were calculated over the top 5.5 cm of each core and multiplied by focus-corrected sedimentation rate to determine fluxes. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).



Supplemental Figure 2.4. S3 (terrestrially-derived organic carbon) flux (g CO_2 m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}), panels A, B and C, respectively. Cumulative inventories of each contaminant and S3 carbon were calculated over the top 5.5 cm of each core and multiplied by focus-corrected sedimentation rate to determine fluxes. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).



Supplemental Figure S2.5. Organic carbon flux (g m^{-2} yr^{-1}) over the top 5.5 cm of sediment cores from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}), panels A, B and C, respectively. Cumulative inventories of each contaminant and organic carbon were calculated over the top 5.5 cm of each core and multiplied by focus-corrected sedimentation rate to determine fluxes. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).



Supplemental Figure S2.6. S2 (algal-derived organic carbon) concentration (mg HC g^{-1} DW) over the top 5.5 cm of sediment cores from 8 study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT concentrations (ng g^{-1} DW), panels A, B and C, respectively. Cumulative inventories of each contaminant and S2 carbon were calculated over the top 5.5 cm of each core to determine concentration. "A Lakes" denote reference lakes and "B Lakes" denote lakes affected by slumps. R^2 and *p*-values of individual linear regressions noted above (n = 8).

3.0 Temporal assessment of the interactions of polychlorinated biphenyls and organochlorine pesticides with the organic matter in sediment of retrogressive thaw slump-affected lakes of the Mackenzie River Delta uplands, NT, Canada

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3.1 – Abstract

Using a comparative temporal analysis on sediment core profiles from 8 lakes in the Mackenzie River Delta uplands, NT, we examined how the presence of retrogressive thaw slumps on lake shores have historically affected persistent organic pollutants (POPs, including polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides) depositing to lake sediments. Sediment core profiles from affected lakes had higher and more variable POP fluxes compared with reference lakes. Fluctuations in contaminant profiles generally did not coincide with changes in inferred chlorophyll *a*, S2 (mostly algal-derived carbon) and S3 (mostly terrestrially-derived carbon) deposition, with correlations neither consistent nor often significant. Thus, the temporal relationships observed in this study do not support the contention that algal-derived organic carbon increases the delivery of organic pollutants to sediments (the algal-scavenging hypothesis), as previously proposed for mercury.

3.2 – Introduction

The anthropogenic production and use of various persistent organic pollutants (POPs) during the past century has resulted in the global distribution of polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides, even in areas of low direct human impact such as the Arctic (Muir *et al*., 1996; ACIA, 2005). Their persistence, bioaccumulative nature and toxicity at low concentrations make them priority concerns for both ecosystems and indigenous communities that experience some of the highest exposures to POPs in Canada (Stockholm Convention, 2001; El-Shahawi *et al*., 2010; Rigét *et al*., 2010; Donaldson *et al*., 2010). The historical atmospheric transport and deposition of POPs into remote Arctic regions is well recorded in sediment archives of lake ecosystems (Evenset *et al*., 2007; Gustafsson *et al*., 2001; ACIA, 2005).

Approximately 24% of the exposed land in the Northern Hemisphere is underlain by permafrost (Zhang *et al*., 2000). With Arctic air temperatures rising by as much as 5 °C during the 20th century (Anisimov *et al*., 2001), and consequent increases in shallow permafrost temperatures (Smith *et al*., 2005), both incidences of retrogressive thaw slump development and slump expansion rates have increased along tundra lake shorelines in the Mackenzie River Delta uplands, NT (Kokelj *et al*., 2009a; Lantz and Kokelj, 2008). The delivery of material from the thaw slump into the lake results in elevated water ionic concentrations, pH, conductivity and total sedimentation rates, and reduced dissolved organic carbon (DOC), colour, turbidity and sediment total organic carbon (TOC) content (Kokelj *et al*., 2005; Deison *et al*., 2012). Noted declines in lake ionic concentration, hardness and alkalinity relative to thaw slump age suggest that water chemistry of affected lakes may gradually revert to pristine conditions subsequent to slump stabilization (Kokelj *et al*., 2009b). However, due to the polycyclic nature of thaw slump development, reinitiation events are anticipated with continued global warming (Kokelj *et al*., 2009a).

Continuously changing limnological conditions, increased light penetration and higher temperatures lengthening growing seasons impact autochthonous primary productivity (APP) in Arctic lakes (Macdonald *et al*., 2005; ACIA, 2005; Smol *et al*., 2005), which becomes archived in the sediment. Considering that hydrophobic POPs are associated with organic matter in sediments (Gustafsson *et al*., 2001), historical fluctuations of APP could impact the delivery of contaminants to the lake bed from the water column, providing the basis of the algal-scavenging hypothesis (Stern *et al*., 2005). If temporal changes in algal productivity are affecting sedimentary deposition of POPs, implications for environmental monitoring of contaminant concentrations will have to be assessed.

Many previous temporal studies of algal-scavenging have focussed solely on the relationships between profiles of mercury (Hg) and organic carbon proxies of APP in single sediment cores of Arctic lakes (Stern *et al*., 2009; Outridge *et al*., 2007; Jiang *et al*., 2011). Other multi-site studies in the Canadian Arctic and Subarctic only found correlations between Hg and APP profiles in a subset of study lakes (Kirk *et al*., 2011; Deison *et al*., 2012), suggesting other factors besides algal scavenging is contributing to Hg deposition. Work by Stern *et al*. (2005) and Outridge *et al*. (2009) each compared flux profiles of various POPs and algal productivity in one Arctic lake sediment core, however some POP flux profiles were minimally associated with APP (Outridge *et al*., 2009). To the best of our knowledge, a multisite temporal analysis of algal-scavenging of halogenated organic contaminants in Arctic lakes has not yet been conducted.

The objectives of this study were: (1) to determine the historical effects of thaw slump development on POP deposition in lakes; and (2) to test the algal-scavenging hypothesis by determining whether sedimentary fluxes of POPs are correlated with algal-derived organic matter. This study used various characterized organic matter proxies and focussed on contamination by atmospherically-

deposited PCBs, hexa- and pentachlorobenzenes (CBzs), and dichlorodiphenyltrichloroethane and metabolites (DDTs).

3.3 – Methods

3.3.1 – Study Area

Sediment cores were examined from eight lakes chosen along a transect of the uplands east of the Mackenzie River Delta between Inuvik and Richard Islands, NT, Canada (Figure 3.1). Four lakes with thermokarst activity along their shorelines were paired with four lakes without slumping as reference lakes, based on similarities in location and physical characteristics in previous work by Lantz and Kokelj (2008). For each pair, lakes with thaw slumps, referred to as slump-affected lakes, are labelled "b" lakes and undisturbed (reference) lakes are labelled "a" lakes. Physical characteristics and lake locations are detailed in Table 3.1.

3.3.2 – Sample Collection

A sediment core was collected from the deepest basin of each lake in the summers of 2007 and 2008 using a Glew gravity corer, and subsectioned into 0.25 cm intervals from 0 – 15 cm, then 0.5 cm intervals for the remainder (Glew *et al.*, 2001). Sediment samples were stored in Whirl-Pak bags and frozen. Subsamples of sediment were freeze-dried for radiometric dating, organic carbon determination and inferred chlorophyll *a* analysis (Deison *et al.*, 2012).

3.3.3 – Sediment Dating

Sediment cores were radiometrically dated via gamma (γ) spectroscopy by determining unsupported ^{210}Pb activity profiles, as described in Appleby (2001) to establish sediment age and sedimentation rate. In brief, homogenized samples from 12 – 15 interval depths per core were freeze-dried and packed into centrifuge tubes to a height of 2 cm. Tubes were then sealed in epoxy resin and

allowed to sit for a minimum of 21 days to allow radioisotopes to reach secular equilibrium. Samples were then counted for 23 hours (82,800 seconds) on a digital high purity germanium well detector (DSPec Model # GWL-120230, Ortec, Oak Ridge, TN, USA) using Maestro Version 6.08 (Advanced Measurement Technology Inc., Oak Ridge, TN, USA) to determine activities of ^{210}Pb and ^{137}Cs, following the methods of Appleby (2001). ^{226}Ra activity was determined by measuring the emissions of its daughter isotope ^{214}Pb.

Sedimentation rates and age were determined using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978) as calculated by ScienTissiMe (Scheer Software Solutions, Barry's Bay, ON, Canada). ^{137}Cs activity was used to validate ^{210}Pb dating profiles, due to its peak maximum in 1963 from atmospheric fallout caused by nuclear weapon-testing detonations (Appleby, 2008). Focus factors (FF) were calculated by dividing the deposition rate of unsupported ^{210}Pb in surface intervals of each sediment core by the estimated atmospheric unsupported ^{210}Pb deposition rate at this latitude (50 Bq m^{-2} yr^{-1}, Omelchenko *et al.*, 1995):

$$FF = \frac{unsupported\ ^{210}Pb\ inventory\ (Bq\ m^{-2}) \times\ ^{210}Pb\ decay\ constant\ (0.03114\ yr^{-1})}{50\ Bq\ m^{-2}\ yr^{-1}}$$

FF and geometric mean sedimentation rates for each core are detailed in Table 3.1.

3.3.4 – Organic Geochemistry Analysis

Rock-Eval®6 (Vinci Technologies, France) pyrolysis analysis was performed on interval depths of each sediment core by the Geological Survey of Canada in Calgary, AB to determine quantities and qualitative sources of organic matter based on thermal degradation. Analysis was performed following the method outlined in Lafargue *et al*. (1998) and specified by Sanei *et al*. (2005). An internal shale standard (9107, Geological Survey of Canada – Calgary) was used for quality control.

Sediment samples (30 – 50 mg) were placed in a pyrolysis oven, under inert atmosphere (N_2), and heated from 100 – 650 °C at a programmed rate of 25 °C per minute. Hydrocarbons (HC) released were measured using flame ionization detection (FID). CO and CO_2 released by oxygen-bearing organic compounds were measured by online infrared (IR) detectors. Samples were then transferred to an oxidation oven and heated from 400 – 850 °C in air, incinerating any residual organic carbon. CO and CO_2 released were again measured by IR detection. TOC (% DW) of the sediment was determined by the total amount of organic carbon released during both pyrolysis and oxidation.

HC released over 300 °C during pyrolysis is referred to as the S2 fraction, consisting of the kerogen remaining after labile hydrocarbons volatilized off (Lafargue *et al*., 1998). The S2 fraction is released due to the thermal cracking of high-molecular weight, hydrogen-rich macromolecules forming the structure of algal cell walls (Carrie *et al*., 2012; Sanei *et al*., 2005). S2 is referred to as 'algal-derived' carbon, and thus can be used as a proxy of historical autochthonous primary productivity (Brazeau *et al*., 2013; Kirk *et al*., 2011; Outridge *et al*., 2007).

The S3 fraction consists of the CO and CO_2 produced during the pyrolysis of oxygen-bearing organic compounds in the kerogen (Lafargue *et al*., 1998). This organic matter is composed of carbohydrates and lignins from terrigenous sources (Carrie *et al*., 2012; Carrie *et al*., 2009), and thus can be used for a proxy of allochthonous carbon inputs or 'terrestrially-derived' organic matter in the sediment.

3.3.5 – Organic Contaminant Extraction and Analysis

PCBs and OCs were extracted from sediment samples using accelerated solvent extraction (ASE), isolated using gel permeation chromatography (GPC) and silica gel fractionation, and analysed using gas chromatography – micro electron capture detection (GC-μECD). Briefly, sequential core interval samples were combined to create a pooled sample with approximately 0.25 g of TOC. Samples were

homogenized with Hydromatrix™ diatomaceous earth (Varian Inc., Palo Alto, CA, USA), spiked with a PCB/OC recovery standard and extracted by ASE (ASE-200, Dionex Corporation, Sunnyvale, CA, USA) using a solution of 1:1 hexane:dichloromethane (DCM) followed by 1:1 acetone:DCM. Samples then underwent liquid-liquid extraction with DCM to remove contaminants in co-extracted water, followed by passing through a sodium sulphate bed to remove remaining water.

Following a slightly modified US Environmental Protection Agency (EPA) Method 3640 A, sulfur and other matrix materials were removed by running samples on Envirogel™ GPC columns (Waters Corporation, MA, USA) with DCM as the mobile phase delivered by an Agilent 1100 Series preparative HPLC system (Agilent Technologies, Santa Clara, CA, USA). Samples were then eluted through 8 g activated silica gel columns (Grade 635, 60 – 100 mesh, 60 Å) with hexane followed by 1:1 hexane:DCM to separate the PCBs from most OCs in different fractions. Each sample fraction was evaporated to a final volume of 0.5 ml in 2,2',4-trimethylpentane and spiked with octachloronaphthalene (OCN) as an internal standard.

Aliquots of the final extracted samples were analysed on a Hewlett Packard (HP) 6890 GC and an HP G2397A ^{63}Ni µECD detector (Agilent Technologies) following US EPA Method 508.1. Separation was completed on a DB5-MS+DG column (Agilent Technologies) with H_2 as the carrier gas. OC standards for GC-µECD calibration were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Recovery spike OC standards, OCN and all PCB standards were purchased from Ultra Scientific (North Kingstown, RI, USA). The congeners and compounds monitored for ΣPCBs, ΣCBzs and ΣDDTs are detailed in Supplemental Table S3.1, along with detection limits. Method limits of quantification were based on a signal to noise ratio of 3, and were below 0.15 ng g^{-1} TOC.

Samples were blank corrected to remove effects of background contamination. Recovery spikes reflected a mean recovery of 91.1 – 112.7% for PCBs and 63.6 – 84.9% for OCs (n = 56) and thus were

not recovery-corrected. Due to the limited amount of sample, replicate extractions (n = 11) were performed on Standard Reference Material® (SRM) 1944 (organic contaminants in New York/New Jersey waterway sediment) from the National Institute of Standards and Technology (Gaithersburg, MD, U.S.A.). Mean recovery (± 1 SD) of ΣPCBs for replicates was 90.4 ± 12.7% of certified SRM values.

3.3.6 – Inferred Chlorophyll a in Sediment

Visible reflectance spectroscopy (VRS) was used to infer chlorophyll *a* content in sediment by the Paleoecological Environmental Assessment and Research Laboratory (PEARL, Queen's University, Kingston, ON, Canada), following methods outlined in Michelutti *et al.* (2010). In brief, sediment samples were freeze-dried (0.2 – 1.0 g DW), sieved (125 µm mesh) and analyzed on a FOSS NIRSystems Model 6500 rapid content analyzer. Examination of the distinct reflectance peaks between 650 and 700 nm on the spectra allowed for the determination of both chlorophyll *a* and its diagenetic derivatives (pheophytin *a* and pheophorbide *a*), thus allowing for an inferred total chlorophyll *a* content and accounting for degradation (Michelutti *et al*., 2010; Wolfe *et al.*, 2006).

3.3.7 – Flux Calculations and Statistical Analysis

Fluxes of each contaminant, inferred chlorophyll *a*, S2 and S3 carbon fractions were calculated by multiplying DW-normalized concentrations by the sample focus-corrected sedimentation rate. Data were analysed using SPSS 16.0 (IBM Corporation, Armonk, NY, U.S.A.). Pearson correlations were used to assess the relationships in each sediment core between fluxes of each contaminant, inferred chlorophyll *a*, S2 and S3 carbon fractions.

3.4 – Results and Discussion

3.4.1 – Persistent Organic Pollutant Fluxes in Sediment Profile

ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}) in three reference lakes displayed similar sedimentary profiles, with small sub-surface maxima, but relatively little fluctuation overall (Figure 3.2). Lake 9a demonstrated greater variability in POP flux than other reference lakes; however, contaminants still presented historic maxima (depth 4 – 5cm) and then declined towards the sediment surface. POP deposition generally did not increase at the sediment surface. Instances when it did occur (e.g. ΣDDT flux in Lake 9a) reflected one data point in profile, providing a weak basis for inferring amplified contaminant deposition. When considering concentration (ng g^{-1} TOC) profiles, again surface fluctuations were not generally apparent (Supplemental Figure S3.1).

Contaminant fluxes in thaw slump affected lakes demonstrated greater variability in sediment profiles and were often higher than their reference lake counter-parts (Figure 3.3). Lake 14b profiles and ΣCBz flux in Lake 9b reveal multiple sub-surface maxima rather than a single peak like other sediment profiles. POP fluxes tended to increase towards the surface, however this may be a consequence of factoring in the variable sedimentation rates as the concentration profiles generally do not reflect this increase (Supplemental Figure S3.2).

Sediment contaminant concentration profiles in both reference and slump-affected lakes were similar to findings of multiple study sites around the Arctic (AMAP, 2004; Muir *et al.*, 1996; Muir *et al*., 1995; Malmquist *et al*., 1998; Stern *et al*., 2005; Gubala *et al*., 1995; Evenset *et al*., 2007). Concentrations at surface and maxima were similar to those observed in remote Yukon, Alaska and High Arctic lakes (AMAP, 2004; Gubala *et al*., 1995; Outridge *et al*., 2009). POP flux ranges of surface sediments in profile were also similar to other Canadian subarctic lakes (Muir *et al*., 1996; Muir *et al*., 1995), but greater than those reported for remote Alaska and Greenland lakes (Gubala *et al*., 1995; Malmquist *et al*., 1998).

3.4.2 – Relationships between Persistent Organic Pollutants and Organic Carbon Proxies

Similarities in sediment core profiles were generally not apparent between POP fluxes and inferred chlorophyll *a*, S2 (mostly algal-derived carbon) and S3 (mostly terrestrially-derived carbon) fluxes in both reference and slump-affected lakes (Figures 3.2 and 3.3). Sub-surface maxima in POP fluxes were not often reflected in the various organic carbon fluxes (e.g. lakes 2a, 2b and 14b). Similarly, instances of surface enrichment of inferred chlorophyll *a*, S2 and S3 carbon fractions often did not correspond to increases in contaminant deposition (e.g. 14a and 9b) and vice versa (e.g. 14b and 36b).

Correlation analysis of each contaminant vs. inferred chlorophyll *a*, S2 and S3 carbon fluxes did not provide consistent trends and seldom reflected significant relationships (Supplemental Figures S3.3 – S3.8). Comparison between elements of individual sediment core profiles carries inherent risks of autocorrelation due to historical artefacts which is demonstrated in our findings.

Previous work by Outridge *et al*. (2009) failed to observe significant relationships between S2 carbon and both ΣPCB and ΣDDT fluxes, suggesting the contaminant profiles more closely followed historic global production similar to Stern *et al*. (2005). Despite some studies in the High Arctic reporting significant correlations between Hg and S2 carbon in sediment profiles (Stern *et al*., 2009; Outridge *et al*., 2007; Jiang *et al*., 2011), this study corresponds with findings of other multi-site studies that determined greater variation in Hg concentrations and fluxes was explained by lake-specific variables, such as sedimentation rate and catchment inputs than S2 carbon (Kirk *et al*., 2011; Deison *et al*., 2012). These data do not lend support to the algal-scavenging hypothesis.

3.5 – Conclusions

This study demonstrates the historical influences of thaw slump development along lake shores in the Arctic. Sediment profiles of slump-affected lakes generally demonstrated higher and more variable fluxes of organic contaminants than neighbouring reference lakes. Correlations between temporal fluxes of POPs and organic matter proxies to lake sediment were inconsistent and seldom

reflected significant relationships. Deposition rates of POPs and autochthonous organic matter proxies did not support the algal-scavenging hypothesis.

3.6 – Acknowledgements

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Table 3.1. Location and physical characteristics of 8 study lakes in the Mackenzie River Delta uplands, NT. Thaw slump activity and morphometric data were determined via aerial photograph analysis and ground surveys during 2001 – 2005 (Kokelj *et al*., 2005).

Lake	Latitude (°N)	Longitude (°W)	A_o[1] (ha)	CA[2] (ha)	DA[3] (ha)	Thaw Slump Status	Z_m[4] (m)	FF[5]	Sed Rate[6] (g m^{-2} yr^{-1})
	I. Reference Lakes								
2a	68°30'09.6"	133°39'55.8"	2.0	17.2	—	—	6.1	0.50	244.5
9a	68°58'05.8"	133°53'53.0"	3.1	29.3	—	—	2.7	0.35	236.4
14a	68°31'02.7"	133°44'55.4"	3.4	33.5	—	—	7.5	0.63	121.2
36a	68°30'10.4"	133°42'02.2"	0.8	6.6	—	—	9.5	1.13	78.4
	II. Slump-Affected Lakes								
2b	68°30'26.6"	133°40'08.3"	4.9	15.9	1.0	Stable	3.4	0.87	247.3
9b	68°58'14.1"	133°53'59.2"	3.6	7.2	2.5	Active	3.0	0.64	346.9
14b	68°31'45.4"	133°44'14.8"	9.2	45.1	2.3	Active	10.5	0.91	575.7
36b	68°30'37.6"	133°43'34.9"	3.9	24.4	4.9	Stable	7.4	1.00	153.6

[1] A_o = lake surface area

[2] CA = catchment area

[3] DA = disturbance area of slump

[4] Z_m = maximum lake depth

[5] FF = focusing factor

[6] Focus corrected geometric mean sedimentation rate was calculated using the CRS model (Appleby and Oldfield, 1978)

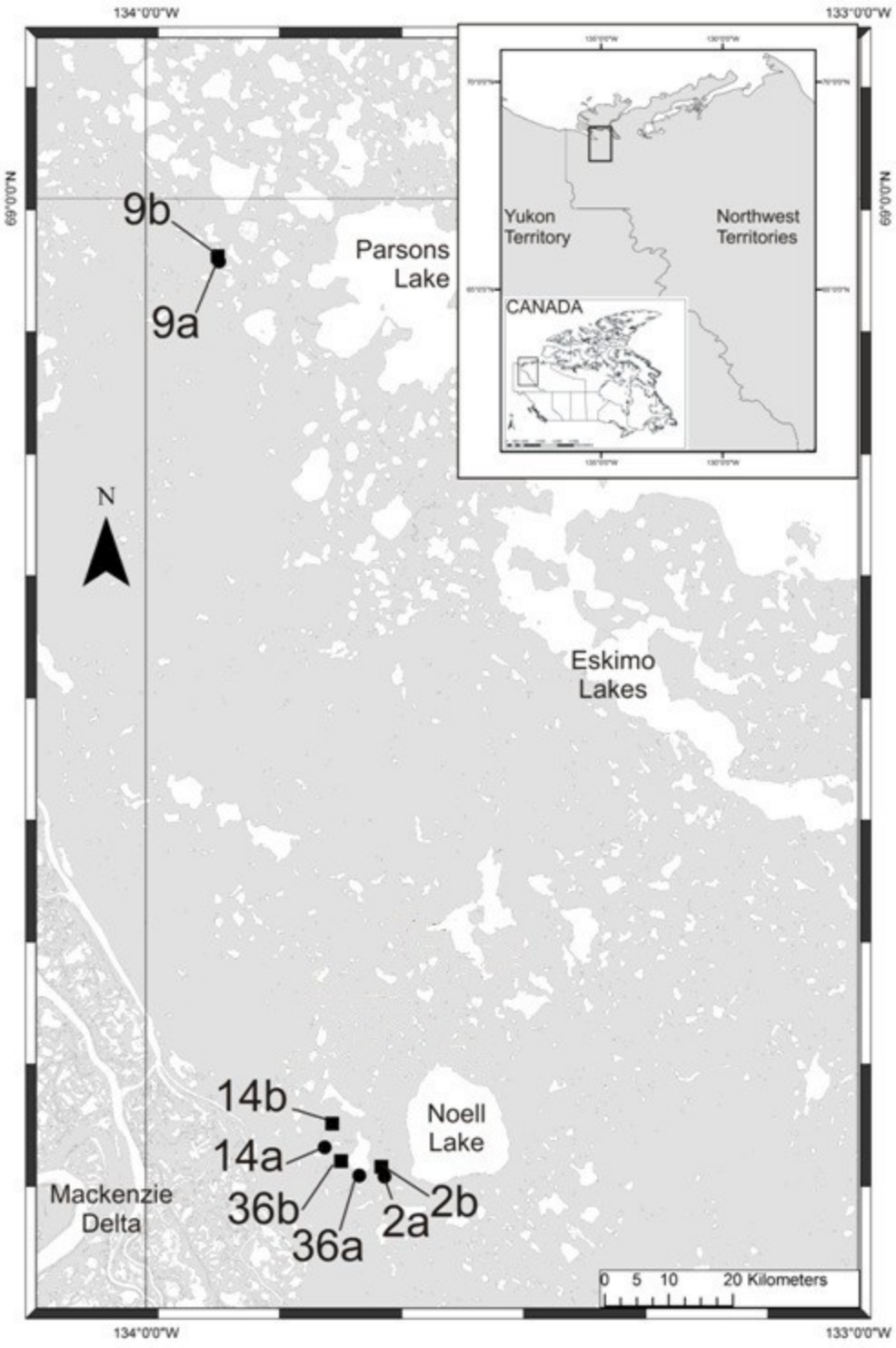


Figure 3.1. Location of the 8 study lakes in the Mackenzie Delta uplands, NT. “a” denotes reference lakes and “b” denotes slump-affected lakes.

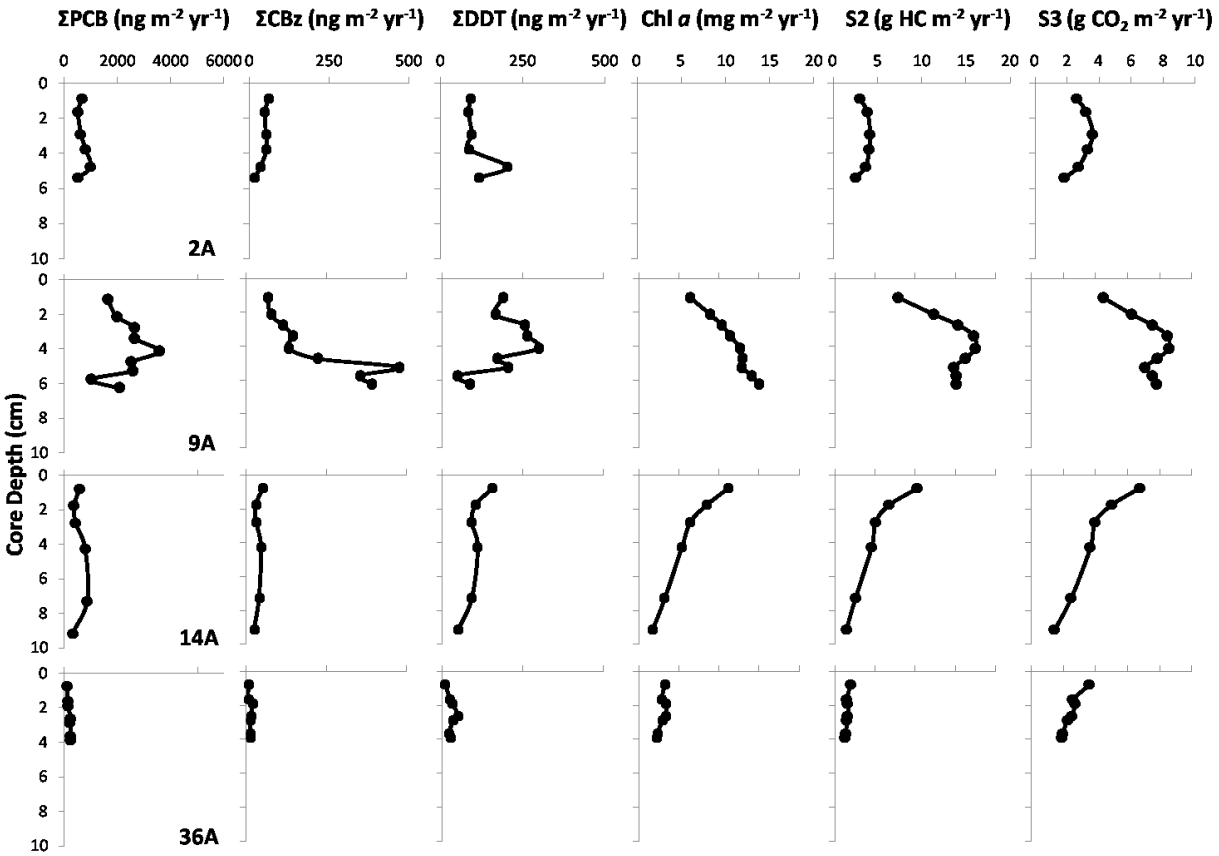


Figure 3.2. Temporal distributions of ΣPCB, ΣCBz, ΣDDT fluxes (ng m^{-2} yr^{-1}), inferred chlorophyll *a* flux (mg m^{-2} yr^{-1}), S2 (algal-derived) carbon flux (g HC m^{-2} yr^{-1}) and S3 (terrestrially-derived) carbon flux (g CO_2 m^{-2} yr^{-1}), all focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb, in sediment core depth profiles from 4 reference lakes in the Mackenzie River Delta uplands, NT. Chlorophyll *a* data not available for Lake 2a.

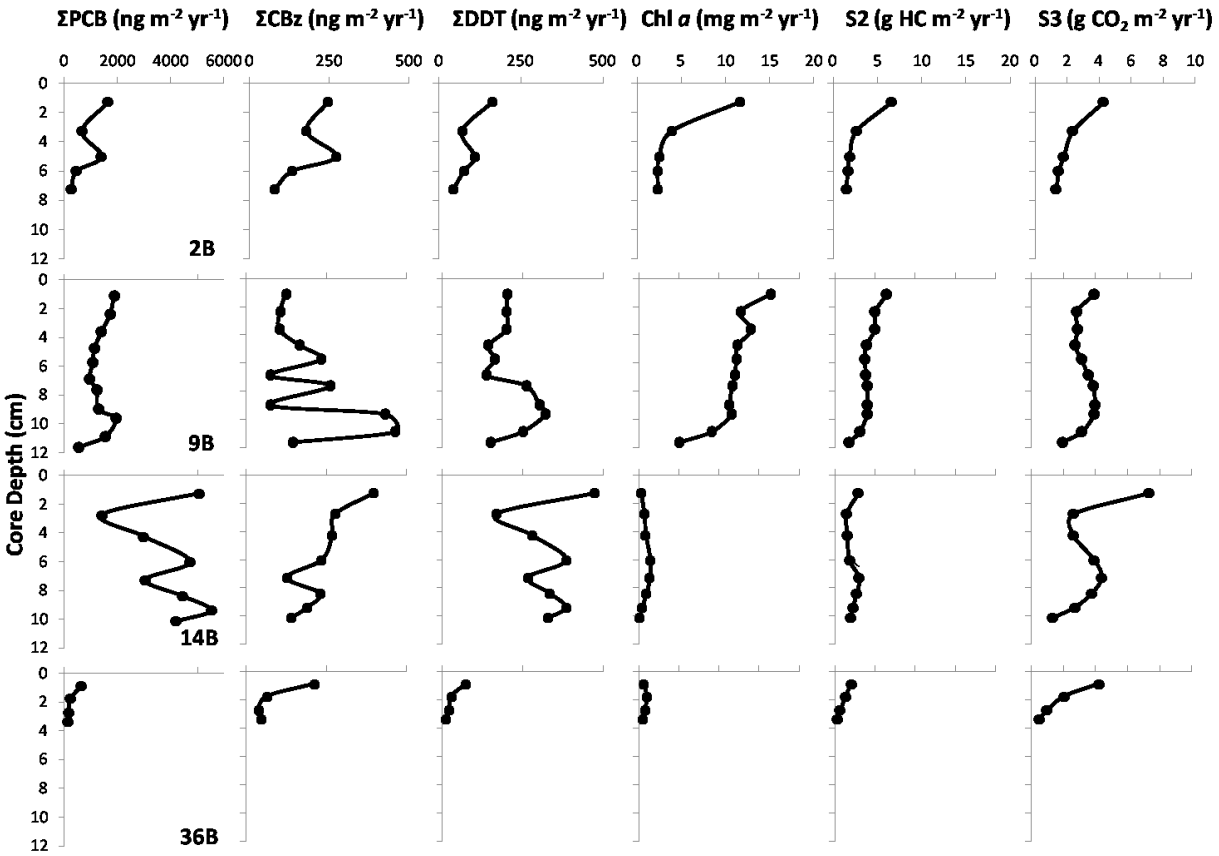
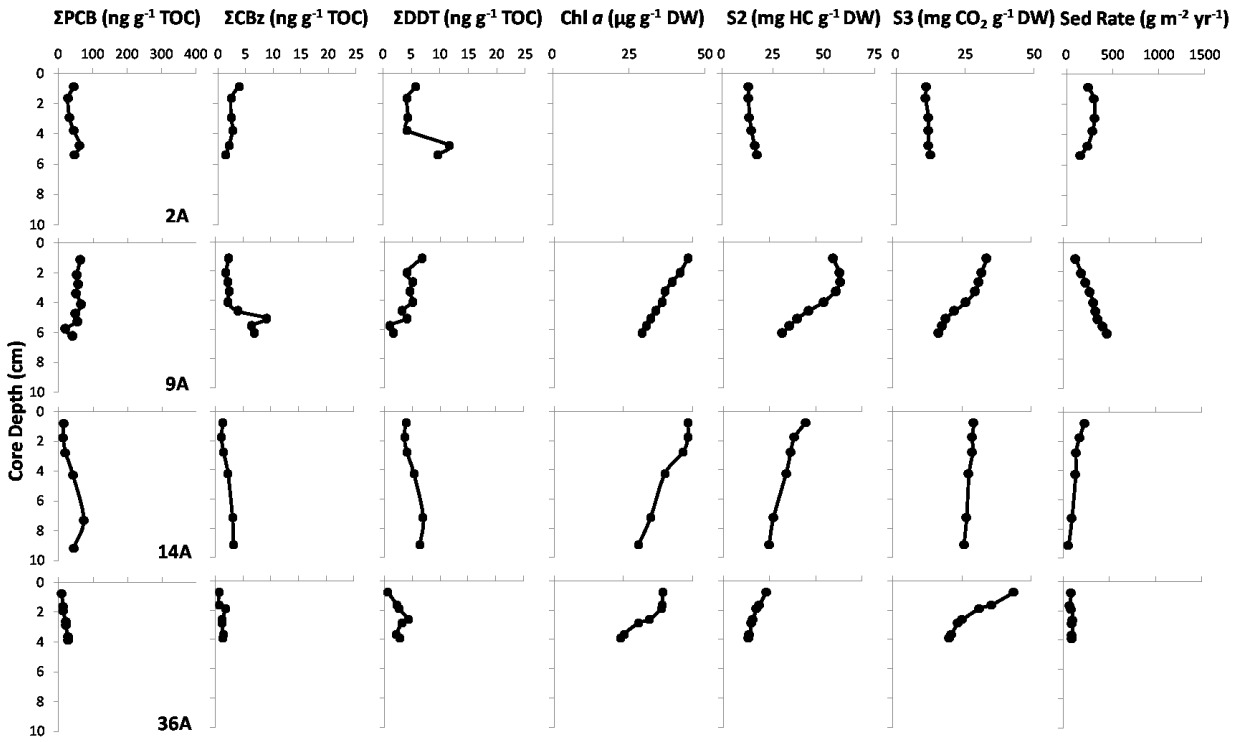


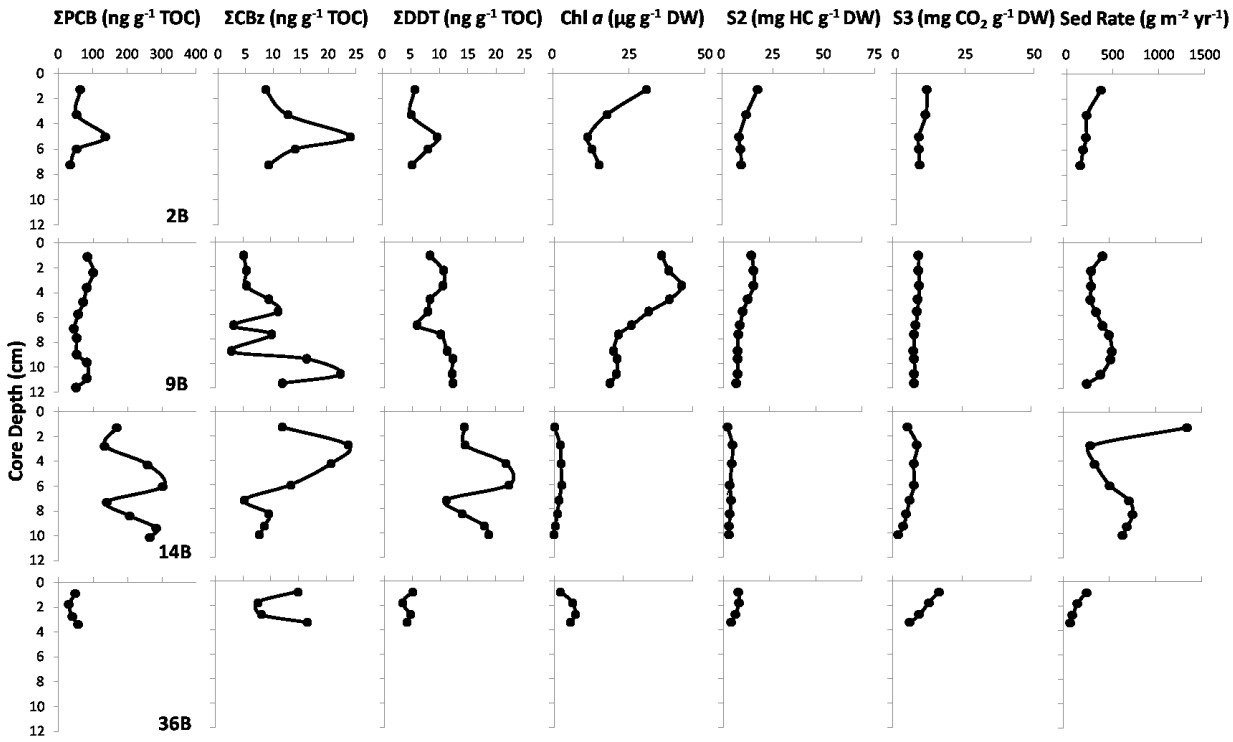
Figure 3.3. Temporal distributions of ΣPCB, ΣCBz, ΣDDT fluxes (ng m^{-2} yr^{-1}), inferred chlorophyll *a* flux (mg m^{-2} yr^{-1}), S2 (algal-derived) carbon flux (g HC m^{-2} yr^{-1}) and S3 (terrestrially-derived) carbon flux (g CO_2 m^{-2} yr^{-1}), all focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb, in sediment core depth profiles from 4 lakes affected by thaw slump activity in the Mackenzie River Delta uplands, NT.

Supplemental Table S3.1. Mean method detection limits (MDL) (ng g^{-1} TOC) and congeners monitored for polychlorinated biphenyls (ΣPCBs), chlorobenzenes (ΣCBzs) and dichlorodiphenyltrichloroethane (ΣDDTs) and metabolites.

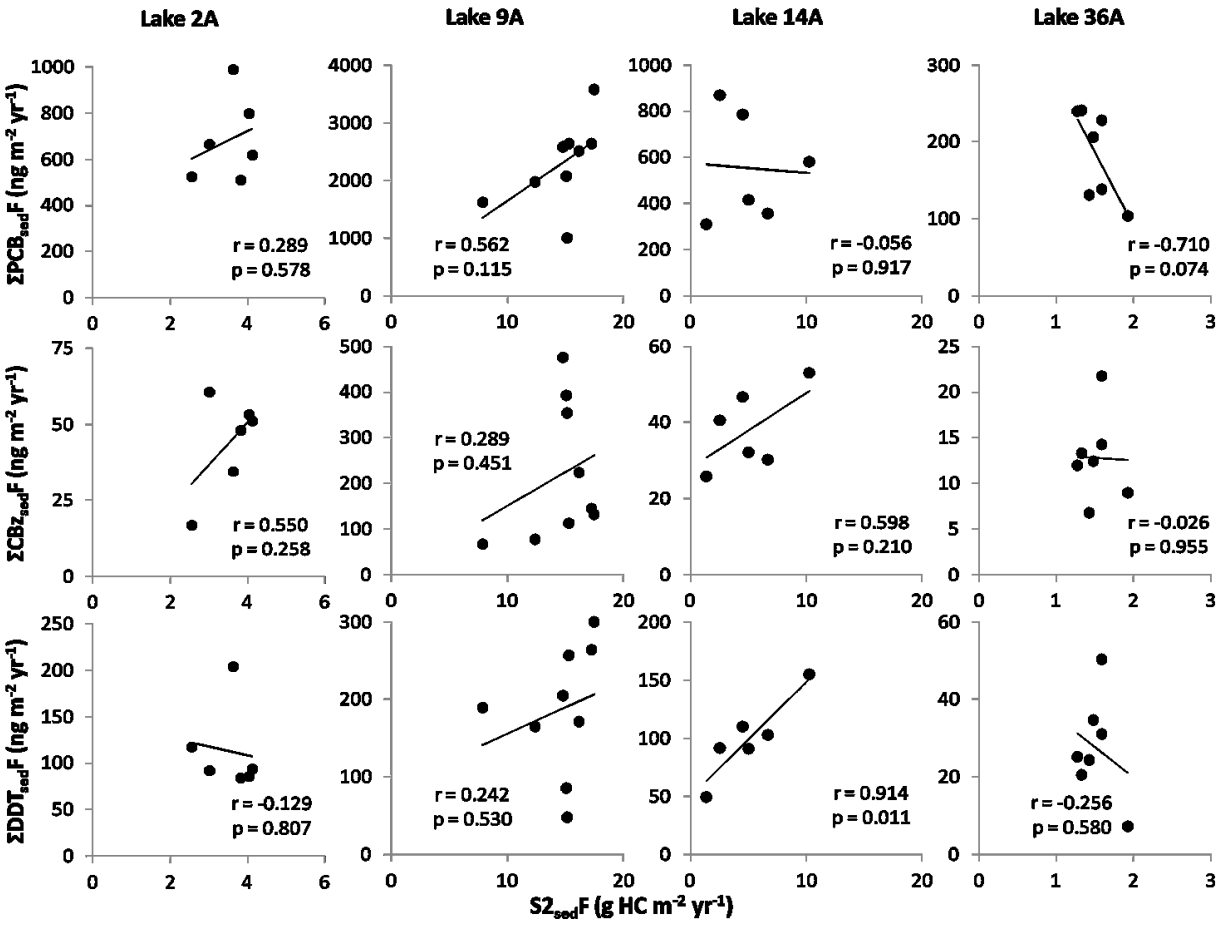
	MDL (ng g^{-1} TOC)	**Congeners**				
PCBs						
DiCBs	0.135	8-5	14			
TriCBs	0.118	18	19	31-28	29	32
TetraCBs	0.058	44	49	52		
PentaCBs	0.072	87	99	105	110	118
HexaCBs	0.070	128	132	138	146	149
		153	155	156	157	163
HeptaCBs	0.064	170	180	183	187	
OctaCBs	0.026	194	195	201	203	
NonaCBs	0.039	206				
DecaCBs	0.074	209				
CBzs	0.054	PentaCBz	HexaCBz			
DDTs	0.055	2, 4'-DDT	2, 4'-DDD	2,4'-DDE		
		4, 4'-DDT	4, 4'-DDD	4,4'-DDE		



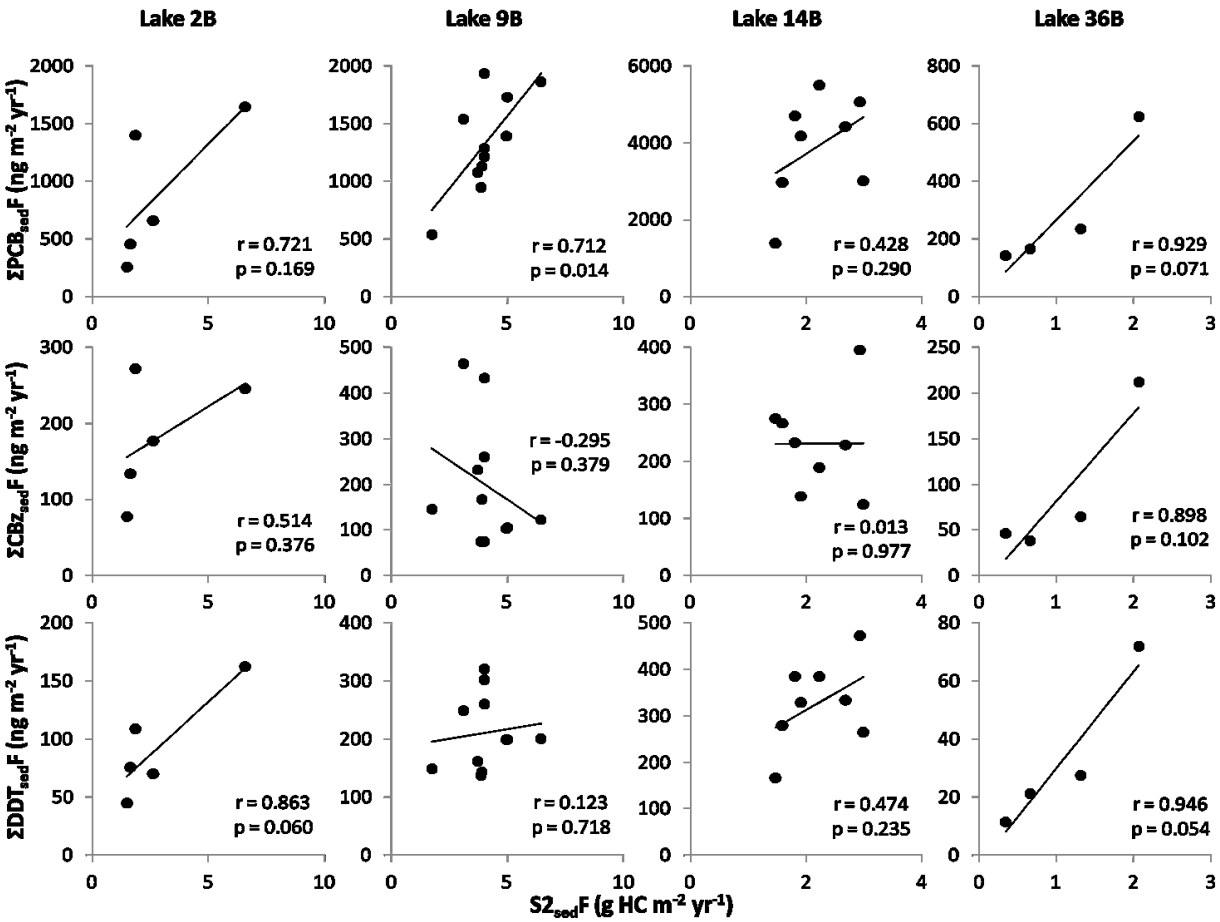
Supplemental Figure S3.1. Temporal distributions of ΣPCB, ΣCBz, ΣDDT concentrations (ng g^{-1}TOC), inferred chlorophyll *a* concentration (µg g^{-1} DW), S2 (algal-derived) carbon concentration (mg HC g^{-1} DW), S3 (terrestrially-derived) carbon concentration (mg CO_2 g^{-1} DW), and sedimentation rate (g m^{-2} yr^{-1}, focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb) in sediment core depth profiles from 4 reference lakes in the Mackenzie River Delta uplands, NT. Chlorophyll *a* data not available for Lake 2a.



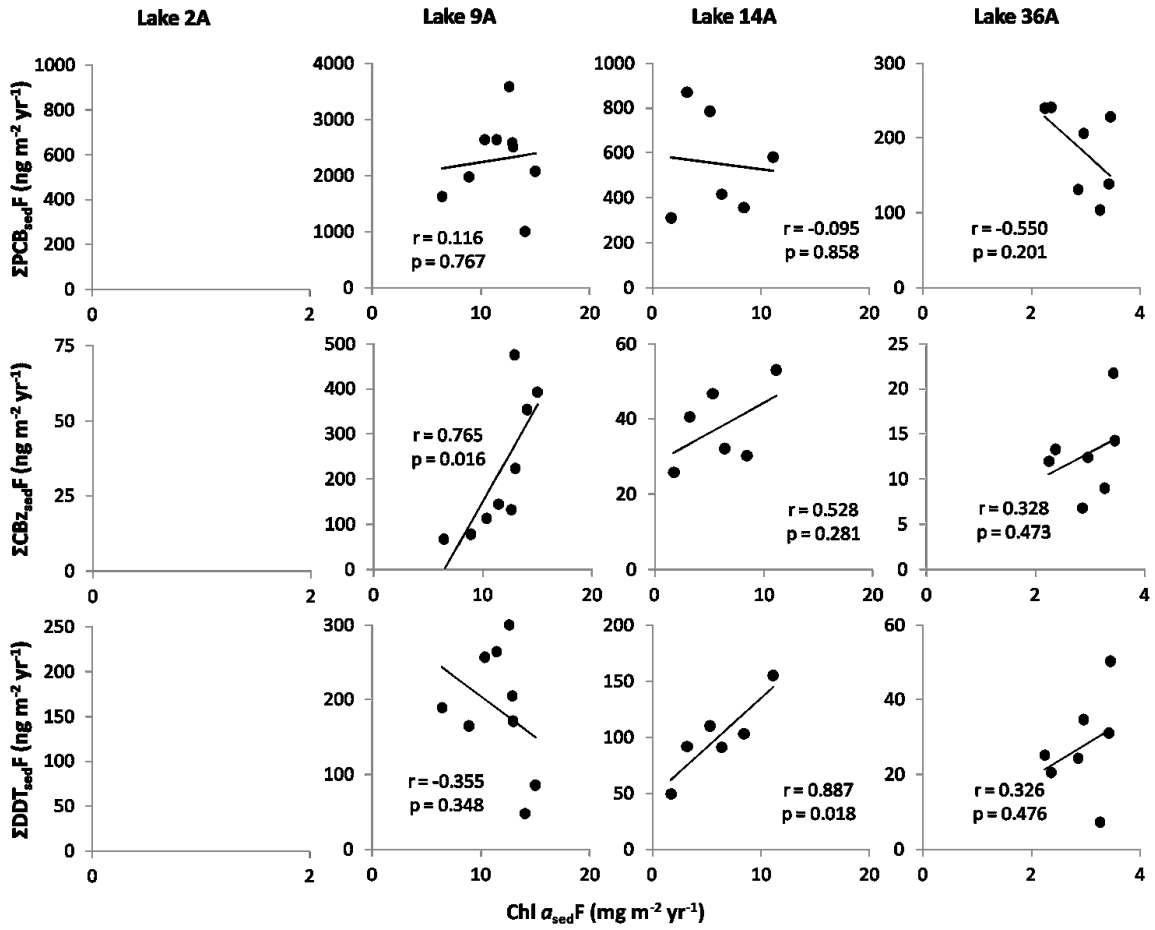
Supplemental Figure S3.2. Temporal distributions of ΣPCB, ΣCBz, ΣDDT concentrations (ng g^{-1}TOC), inferred chlorophyll *a* concentration (µg g^{-1} DW), S2 (algal-derived) carbon concentration (mg HC g^{-1} DW), S3 (terrestrially-derived) carbon concentration (mg CO_2 g^{-1} DW), and sedimentation rate (g m^{-2} yr^{-1}, focus corrected to 50 Bq m^{-2} yr^{-1} excess ^{210}Pb) in sediment core depth profiles from 4 thaw slump affected lakes in the Mackenzie River Delta uplands, NT.



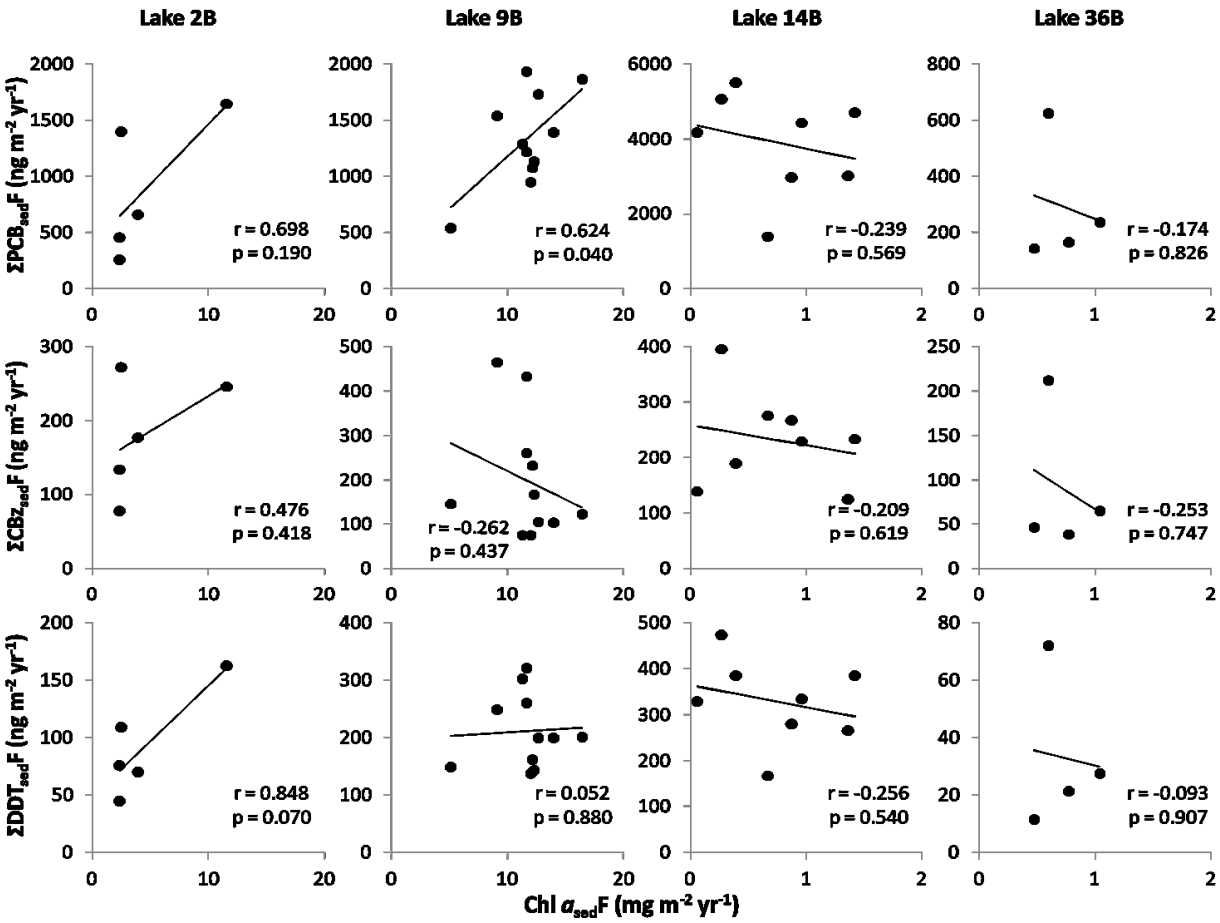
Supplemental Figure S3.3. S2 (algal-derived organic carbon) flux (g HC m^{-2} yr^{-1}) of sediment cores from 4 reference study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (n = 6, 9, 6 and 7 respectively).



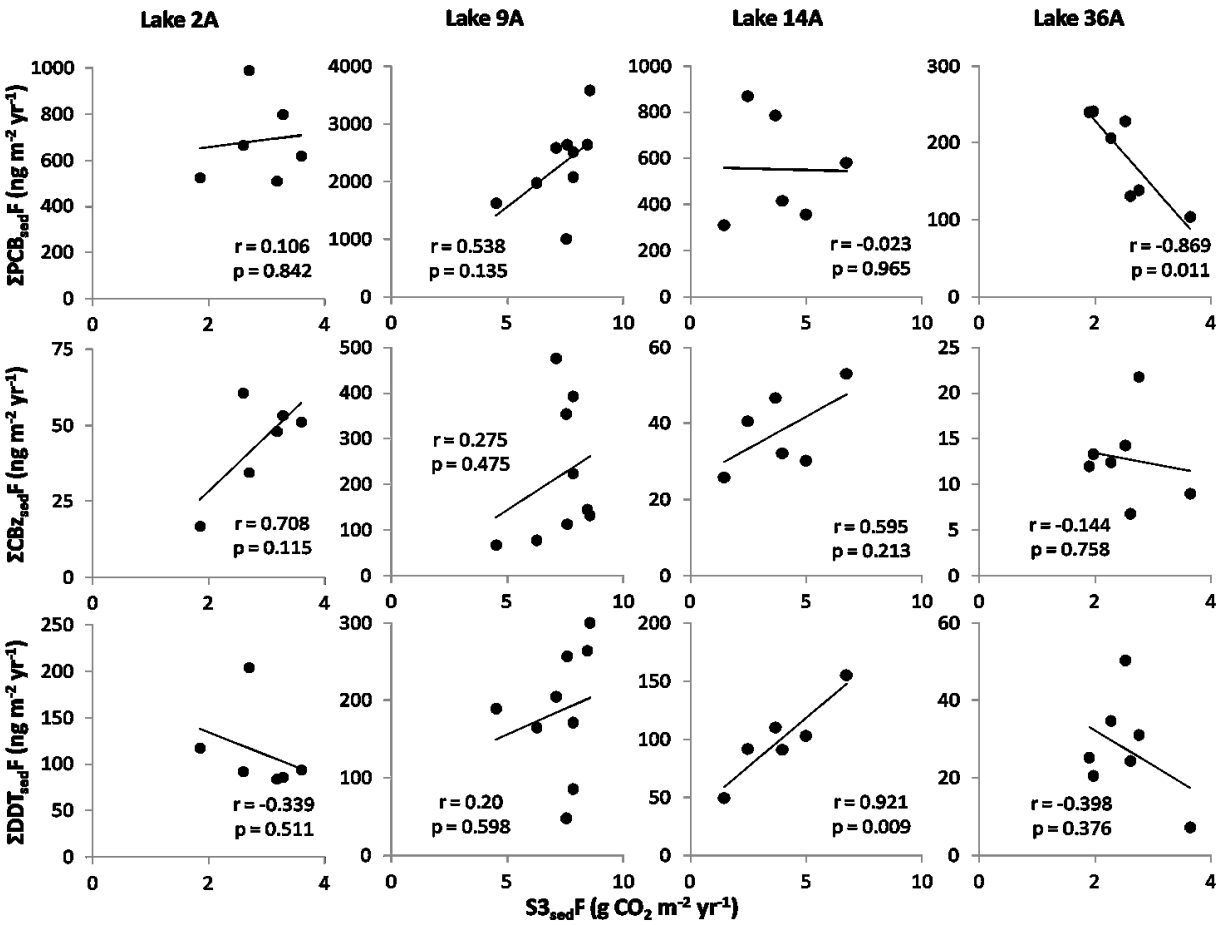
Supplemental Figure S3.4. S2 (algal-derived organic carbon) flux (g HC m^{-2} yr^{-1}) of sediment cores from 4 study lakes affected by thaw slump activity in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (n = 5, 11, 8 and 4 respectively).



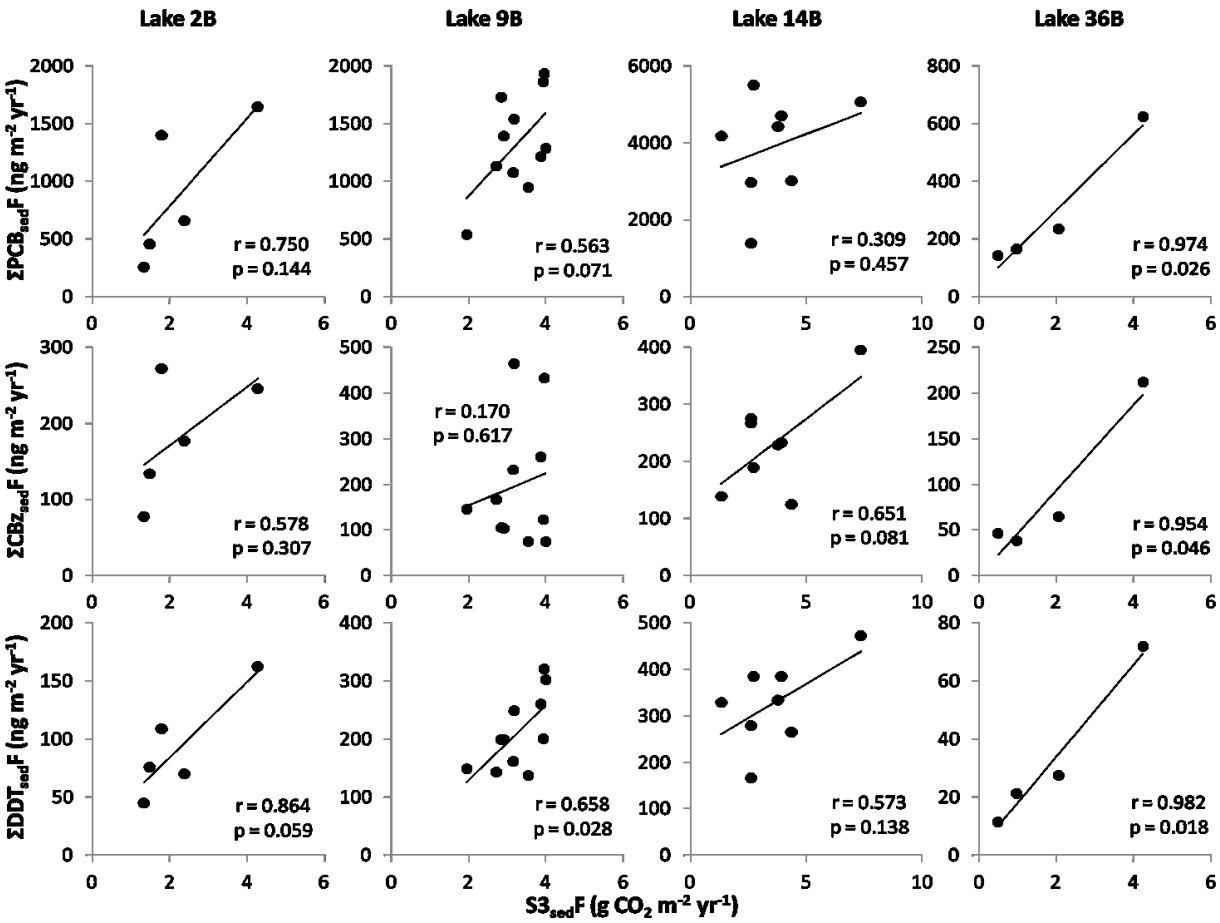
Supplemental Figure S3.5. Inferred chlorophyll *a* flux (mg m^{-2} yr^{-1}) of sediment cores from 4 reference study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (data not available for Lake 2A, n = 9, 6 and 7 respectively for remainder).



Supplemental Figure S3.6. Inferred chlorophyll *a* flux (mg m^{-2} yr^{-1}) of sediment cores from 4 study lakes affected by thaw slump activity in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (n = 5, 11, 8 and 4 respectively).



Supplemental Figure S3.7. S3 (terrestrially-derived organic carbon) flux (g CO_2 m^{-2} yr^{-1}) of sediment cores from 4 reference study lakes in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (n = 6, 9, 6 and 7 respectively).



Supplemental Figure S3.8. S3 (terrestrially-derived organic carbon) flux (g CO_2 m^{-2} yr^{-1}) of sediment cores from 4 study lakes affected by thaw slump activity in the Mackenzie River Delta uplands, NT, plotted against ΣPCB, ΣCBz and ΣDDT fluxes (ng m^{-2} yr^{-1}). r and *p*-values of individual Pearson correlations noted above (n = 5, 11, 8 and 4 respectively).

4.0 – General Conclusions and Perspectives on Future Research

Although persistent organic pollutants (POPs) have been widely studied and monitored in the circumpolar Arctic, this study is one of the first to investigate the effects climate warming-induced alterations in physical landscapes are having on POP deposition and partitioning, specifically in tundra lake ecosystems experiencing retrogressive thaw slump development in the Mackenzie River Delta uplands, NT. Surface sedimentary organic matter in slump-affected lakes had higher POP concentrations than neighbouring pristine reference lakes, despite similar contaminant deposition rates. This difference is likely explained by the reduced availability of organic matter for adsorption in the water column, a consequence of inorganic material delivered by the thaw slump accelerating flocculation and deposition (Thompson *et al.*, 2008). Considering that thaw slump development would not be expected to influence atmospheric deposition processes, as corroborated in the similar contaminant fluxes between lake types, contaminants newly delivered into slump-affected lakes experience more efficient scavenging by the remaining organic carbon in a simple solvent switching process.

Both spatial and temporal analyses revealed that autochthonous primary productivity fluxes are poor predictors of POP sedimentary deposition in reference and slump-affected lakes. Historical fluctuations in contaminant delivery in sediment cores of all 8 lakes did not coincide with deposition of either inferred chlorophyll *a* or predominantly algal-derived organic carbon fractions, as identified using Rock-Eval® analysis. Surface sediment deposition rates of POPs and these primary productivity proxies were not significantly correlated, thus not providing support for algal-scavenging as an explanation for POP concentrations.

The prediction that climate warming in the Arctic will lead to stimulated primary productivity within lake ecosystems is partially predicated on increased input of organic matter and inorganic

nutrients, mobilized by accelerated microbial activity of surrounding soil catchments (Karlsson *et al*., 2005; ACIA, 2005). Although this may be a reasonable assumption, warming-induced landscape disturbances may have greater relative impacts, as demonstrated by thaw slump-affected lake water having reduced available nutrient concentrations and primary productivity as a function of the proportion of the surrounding catchment disturbed (Adam Houben, *unpublished data*). The subsidence of considerable portions of surrounding land, as much as 33% of the catchment area of lakes included in this study, effectively removes this soil as a source of nutrients and terrestrial organic carbon for the lake until the thaw slump has stabilized and been recolonized by vegetation.

The algal-scavenging hypothesis also assumes that contaminant availability is not a limiting resource in this process. If atmospheric deposition and air-water exchange of POPs is sufficient to ensure an adequate contaminant supply in the water, then increased lake primary productivity may result in higher POP fluxes to sediment as demonstrated in eutrophic vs. oligotrophic lakes of the Experimental Lakes Area (Jeremiason *et al*., 1999). However, if input of POPs into the lake water is not sufficient and the pool of available contaminants to be scavenged is depleted, further primary productivity would cause a biodilution effect of contaminant concentrations across a greater phytoplankton biomass (Jeremiason *et al*., 1999). Consequently, when examining sedimentary concentrations of contaminants and proxies for primary productivity, as previously has been done for mercury for this proposed hypothesis, relationships may not accurately reflect the complexities and dynamics of these changing systems.

The amplification of POP concentrations on sedimentary organic matter in slump-affected lakes has coincided with contaminant accumulation in benthic organisms. Invertebrate communities of these lakes had lower densities and biomass, and consequently higher POP concentrations, than neighbouring reference lakes (Rebecca D'Onofrio, *unpublished data*). The larger available organic carbon pool in

water of reference lakes effectively dilutes POP concentrations delivered to the sediment, where subsequent consumption by benthic invertebrate results in decreased initial contaminant loads to transfer up the food chains of these small tundra lakes. Higher invertebrate biomass of reference lakes would also effectively dilute dissolved contaminants across a larger pool of organisms than that of slump-affected lakes, again by a simple solvent switching process and causing further biodilution.

Understanding the complexities of physical and chemical limnological changes that tundra lakes are experiencing as a consequence of climate warming will clarify dominant factors influencing POPs in these dynamic ecosystems. Although the predicted pulse of mobilized organic matter and nutrients from catchment soils, combined with extended growing seasons and warmer water, would potentially increase autochthonous primary productivity, the effects on POP fate may ultimately be mitigated by the impact of permafrost thawing in the Arctic.

4.1 – References

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Jeremiason, J.D., S.J. Eisenreich, M.J. Paterson, K.G. Beaty, R. Hecky and J.J. Elser. 1999. Biogeochemical cycling of PCBs in lakes of variable trophic status: A paired-lake experiment. *Limnol Oceanogr*. 44: 889 – 902.

Karlsson, J., A. Jonsson, and M. Jansson. 2005. Productivity of high-latitude lakes: climate effect inferred from altitude gradient. *Glob Change Biol*. 11: 710 – 715.

Thompson, M.S., S.V. Kokelj, F.J. Wrona and T.D. Prowse. 2008. The impact of sediments derived from thawing permafrost on tundra lake water chemistry: An experimental approach. In *Proceedings of the Ninth International Conference on Permafrost*, Kane, D.L., K.M. Hinkel (eds.). Fairbanks Alaska. Institute of Northern Engineering, University of Alaska Fairbanks (Vol 2): 1763 – 1768.

Appendix A – Abbreviations and Glossary

A.1 – Abbreviations

ACIA	Arctic Climate Impact Assessment
AMAP	Arctic Monitoring and Assessment Programme
APP	Autochthonous primary productivity
ASE	Accelerated solvent extraction
CBz(s)	PeCBz and HCB
Chl *a*	Chlorophyll *a*
CO	Carbon monoxide
CO_2	Carbon dioxide
CRS	Constant rate of supply model
Cs	Cesium
DCM	Dichloromethane
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DDTs	DDT, DDD and DDE
DOC	Dissolved organic carbon
DW	Dry weight
EPA	Environmental Protection Agency
FF	Focus factor
FID	Flame ionization detection
GC-µECD	Gas chromatography – micro electron capture detection
GPC	Gel permeation chromatography
H_2	Hydrogen gas

HC	Hydrocarbon
HCB	Hexachlorobenzene
Hg	Mercury
IPCS	International Programme on Chemical Safety
IR	Infrared
kt	Kiloton
MDL	Method detection limit
MeHg	Methylmercury, CH_3Hg
N_2	Nitrogen gas
Ni	Nickel
NLET	National Laboratory for Environmental Testing
OC(s)	Organochlorine pesticide(s)
OCN	Octachloronaphthalene
Pb	Lead
PCB(s)	Polychlorinated biphenyl(s)
PeCBz	Pentachlorobenzene
POC	Particulate organic carbon
POP(s)	Persistent organic pollutant(s)
Ra	Radium
SD	Standard deviation
SRM	Standard reference material
THg	Total mercury
TOC	Total organic carbon
UNEP	United Nations Environment Programme
VRS	Visible reflectance spectroscopy

A.2 – Glossary

Active layer	Upper layer of permafrost that thaws during summer
Aerosol	Suspension of fine solid particles or liquid droplets in a gas
Allochthonous	Derived from outside the lake or water body
Anthropogenic	An effect or object resulting from human activity
Autochthonous	Derived from inside the lake or water body
Bioaccumulation	The build-up of substances in the tissues of organisms over time from all exposure routes
Biodilution	Decrease in contaminant concentration with an increase in biomass or trophic level
Biomagnification	The non-linear increase in concentration of a bioaccumulating substance as trophic levels are ascended
Catchment	Area of land where water from rain or snowmelt converges into a common body of water
Compartment	Part of an ecosystem considered an independent system for purposes of assessment of uptake, distribution, and dissipation of a substance
Congener	An individual PCB, or other group of contaminants
Deposition, sediment	Transport of material to the lake bed
Diagenesis	The physical, chemical, and biological changes undergone by sediment after it is deposited
Dry deposition	Delivery of airborne contaminants to the surface by particle fallout, diffusion and air movements
Eutrophic lake	A nutrient-rich, highly productive lake
Flocculation	Formation of a light, loose precipitate from a solution
Flux	Rate of compound mass flow across a unit area
Kerogen	Insoluble organic matter in sediment or sedimentary rock
Limnological	Relating to limnology, the study of inland waters

Mineralization	The release of recalcitrant compounds during microbial decomposition of organic materials in sediment; the conversion of organic substances to inorganic derivatives
Oligotrophic lake	A lake with low levels of nutrients and primary production
Partitioning	Distribution of a solute between two immiscible solvents
Permafrost	Perennially frozen ground; material that stays at or below 0 °C for at least two consecutive summers
Recalcitrant	Resistance to biodegradation
Retrogressive thaw slump	A form of thermokarst, develop due to thawing of ice-rich permafrost on a slope that recedes and expands away from point of original subsidence
S2	The Rock-Eval® fraction of insoluble organic matter kerogen which corresponds to the hydrogen-rich aliphatic biomacromolecules, commonly associated with cell walls of algal matter and referred to as 'algal-derived'
S3	The Rock-Eval® fraction of insoluble organic matter kerogen which corresponds to the oxygen-rich carbohydrate and lignin biomacromolecules, commonly associated with terrigenous plant sources and referred to as 'terrestrially-derived'
Siliciclastic	A term pertaining to clastic sediment composed of silicon-bearing and clay minerals
Solvent depletion	Concentration amplification of an analyte in a solvent by depletion or consumption of the solvent
Solvent switching	Concentration amplification of an analyte in a solvent by transfer due to high partition coefficient between two phases
Supported ^{210}Pb	^{210}Pb that is derived from *in situ* decay of the parent radionuclide ^{226}Ra
Themorkarst	Land surface characterized by irregular terrain due to a subsidence and deformation caused by ice-rich permafrost thaw
Unsupported ^{210}Pb	^{210}Pb that is derived from atmospheric flux
Volatilization	Process by which a substance is transformed into vapour/gas
Wet deposition	Delivery of airborne contaminants to the surface as a result of their incorporation into rain or snow which subsequently falls to the ground

Appendix B – Persistent Organic Pollutants in Sediment Profiles

Table B.1 – Persistent organic pollutant concentrations and fluxes in sediment core profiles.

Lake	Concentration (ng g^{-1} TOC)			Concentration (ng g^{-1} DW)			Flux (ng m^{-2} yr^{-1})		
Depth (cm)	ΣPCB	ΣCBz	ΣDDT	ΣPCB	ΣCBz	ΣDDT	ΣPCB	ΣCBz	ΣDDT
2a									
0.875	41.23	3.76	5.73	2.84	0.26	0.39	664.55	60.64	92.38
1.625	25.49	2.40	4.21	1.71	0.16	0.28	509.30	47.92	84.09
2.875	28.69	2.37	4.38	2.02	0.17	0.31	618.60	51.12	94.33
3.75	39.56	2.64	4.26	2.85	0.19	0.31	798.94	53.28	85.98
4.75	56.27	1.96	11.60	4.36	0.15	0.90	988.46	34.53	203.77
5.375	42.55	1.37	9.57	3.55	0.11	0.80	524.63	16.86	118.00
2b									
1.25	57.24	8.55	5.66	4.38	0.65	0.43	1647.08	246.13	162.74
3.25	47.00	12.59	4.99	3.01	0.81	0.32	663.22	177.64	70.46
5.0	123.78	23.99	9.63	6.46	1.25	0.50	1403.31	271.99	109.18
6.0	47.65	13.93	7.95	2.55	0.75	0.43	457.27	133.64	76.30
7.25	30.16	9.13	5.20	1.69	0.51	0.29	259.40	78.56	44.69
9a									
1.125	57.42	2.37	6.69	12.25	0.50	1.43	1623.86	66.92	189.14
2.125	47.37	1.85	3.96	10.04	0.39	0.84	1969.35	77.06	164.51
2.75	51.45	2.20	5.02	10.84	0.46	1.06	2635.76	112.93	257.03
3.375	45.20	2.48	4.53	9.26	0.51	0.93	2632.11	144.66	263.97
4.125	59.66	2.20	5.01	11.05	0.41	0.93	3571.70	131.46	300.00
4.75	44.69	3.96	3.04	7.12	0.63	0.48	2508.17	222.57	170.87
5.25	49.66	9.17	3.95	6.97	1.29	0.55	2575.77	475.67	204.67
5.75	18.33	6.46	0.86	2.37	0.84	0.11	1003.38	353.95	47.17
6.25	36.66	6.96	1.51	4.38	0.83	0.18	2064.29	391.69	85.05
9b									
1.125	75.67	5.00	8.14	4.40	0.29	0.47	1866.33	123.22	200.83
2.375	91.67	5.61	10.60	5.64	0.34	0.65	1728.70	105.85	200.00
3.625	73.69	5.50	10.54	4.58	0.34	0.65	1396.74	104.25	199.72
4.75	65.14	9.55	8.19	3.83	0.56	0.48	1136.51	166.57	142.95
5.75	51.77	11.20	7.81	3.02	0.65	0.46	1073.75	232.27	162.04
6.875	40.19	3.18	5.81	2.22	0.18	0.32	952.71	75.51	137.79
7.625	46.89	10.05	10.08	2.44	0.52	0.52	1214.44	260.26	260.96
9.0	48.08	2.79	11.29	2.43	0.14	0.57	1287.43	74.79	302.36
9.625	73.75	16.45	12.23	3.80	0.85	0.63	1937.62	432.26	321.28
10.875	74.96	22.56	12.14	3.79	1.14	0.61	1541.64	463.96	249.79
11.625	45.03	12.08	12.33	2.14	0.57	0.58	543.24	145.79	148.78

Lake	Concentration (ng g^{-1} TOC)			Concentration (ng g^{-1} DW)			Flux (ng m^{-2} yr^{-1})		
Depth (cm)	ΣPCB	ΣCBz	ΣDDT	ΣPCB	ΣCBz	ΣDDT	ΣPCB	ΣCBz	ΣDDT
14a									
0.75	14.37	1.31	3.83	2.52	0.23	0.67	580.88	52.97	154.78
1.75	12.55	1.06	3.62	2.04	0.17	0.59	356.82	30.23	102.84
2.75	18.46	1.42	4.03	3.02	0.23	0.66	416.56	32.18	91.00
4.25	37.75	2.25	5.28	5.86	0.35	0.82	783.44	46.75	109.59
7.25	65.85	3.07	6.92	9.34	0.44	0.98	869.42	40.58	91.31
9.125	39.64	3.28	6.31	5.51	0.46	0.88	310.52	25.70	49.42
14b									
1.25	153.20	11.98	14.33	3.77	0.30	0.35	5061.14	395.79	473.45
2.75	121.59	23.90	14.54	4.73	0.93	0.56	1401.91	275.51	167.66
4.25	232.92	20.86	21.83	8.66	0.78	0.81	2985.54	267.35	279.80
6.0	273.74	13.58	22.39	9.35	0.46	0.76	4715.37	234.00	385.70
7.25	126.00	5.23	11.07	4.25	0.18	0.37	3024.79	125.56	265.76
8.375	185.81	9.60	14.01	5.88	0.30	0.44	4438.94	229.39	334.60
9.375	256.53	8.82	17.91	7.97	0.27	0.56	5509.92	189.57	384.72
10.125	238.48	7.92	18.76	6.52	0.22	0.51	4185.24	138.95	329.27
36a									
0.75	7.40	0.64	0.51	1.24	0.11	0.08	103.22	8.96	7.13
1.625	11.79	0.61	2.19	1.79	0.09	0.33	130.93	6.81	24.34
1.875	11.34	1.78	2.53	1.57	0.25	0.35	138.64	21.72	30.95
2.625	19.04	1.19	4.20	2.28	0.14	0.50	227.76	14.23	50.30
2.875	18.70	1.13	3.15	2.13	0.13	0.36	205.80	12.45	34.64
3.625	24.65	1.36	2.10	2.58	0.14	0.22	240.57	13.30	20.46
3.875	25.37	1.27	2.66	2.58	0.13	0.27	239.51	11.97	25.08
36b									
0.875	43.95	14.90	5.08	2.47	0.84	0.28	624.68	211.76	72.14
1.75	27.85	7.60	3.25	1.52	0.42	0.18	236.83	64.67	27.61
2.75	35.55	8.28	4.60	1.65	0.38	0.21	165.85	38.64	21.48
3.375	50.66	16.50	4.03	1.82	0.59	0.14	144.14	46.94	11.46

Table B.2 – Lake 2a sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	0.875	1.625	2.875	3.75	4.75	5.375
Congeners						
8-5	5.52	3.40	3.06	3.38	4.05	2.88
14	-	-	-	-	-	-
19	-	-	-	-	-	-
18	5.51	3.52	3.72	5.83	7.58	5.18
32	-	-	1.24	-	-	-
29	0.98	-	-	-	-	-
31-28	5.04	3.04	3.51	5.30	7.40	6.30
52	8.71	5.20	6.54	9.66	15.42	11.01
49	3.50	2.10	2.61	3.80	5.83	4.42
44	3.71	1.91	2.46	4.28	7.92	5.84
155	-	-	-	-	-	-
99	1.16	0.97	0.80	1.13	1.23	1.06
87	1.46	1.10	0.96	1.47	1.65	1.41
110	1.29	0.93	0.80	1.41	1.97	1.47
149	0.91	0.70	0.59	0.73	0.70	0.65
118	1.04	0.80	0.66	0.93	0.86	0.86
146	-	-	-	-	-	-
153	0.31	0.26	0.16	0.20	0.19	0.19
132	0.36	0.30	0.27	0.36	0.36	0.33
105	0.33	0.28	0.25	0.31	0.32	0.29
138	0.41	0.31	0.29	0.27	0.25	0.17
163	0.33	0.26	0.22	0.25	0.25	0.23
187	-	-	-	-	-	0.07
183	-	-	-	-	-	-
128	-	-	-	-	-	-
156	-	-	-	-	-	-
201	-	-	-	-	-	-
157	-	-	-	-	-	-
180	0.35	0.20	0.28	0.22	0.10	0.05
170	0.14	0.05	0.07	0.04	0.04	0.03
203	0.18	0.15	0.21	-	0.13	0.11
195	-	-	-	-	-	-
194	-	-	-	-	-	-
206	-	-	-	-	-	-
209	-	-	-	-	-	-

Table B.3 – Lake 2b sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	1.25	3.25	5.0	6.0	7.25
Congeners					
8-5	12.53	18.35	36.28	18.56	12.25
14	-	-	-	-	-
19	3.44	2.12	3.85	1.75	1.58
18	5.02	4.63	11.85	4.62	3.24
32	-	-	-	-	-
29	5.08	1.44	2.66	3.43	2.96
31-28	5.52	4.33	13.59	3.74	2.43
52	9.52	6.02	18.89	5.06	2.77
49	3.60	2.40	7.57	1.83	1.30
44	4.06	2.05	9.45	1.54	0.34
155	-	-	-	-	-
99	1.35	0.70	2.09	0.58	0.31
87	1.76	0.73	2.72	0.80	0.52
110	1.95	0.37	3.51	0.54	-
149	0.75	0.65	1.91	0.83	0.64
118	1.25	1.05	2.81	1.31	0.73
146	-	-	0.24	-	-
153	0.44	0.60	1.44	0.79	0.35
132	0.32	0.30	0.72	0.34	0.23
105	0.34	0.33	0.94	0.42	0.26
138	0.02	0.11	0.37	0.12	-
163	0.27	0.41	1.02	0.56	0.25
187	-	0.23	0.48	0.25	-
183	-	-	0.32	0.16	-
128	-	-	-	-	-
156	-	-	-	-	-
201	-	-	-	-	-
157	-	-	-	-	-
180	0.03	0.16	0.53	0.20	0.02
170	-	-	0.11	-	-
203	-	-	0.45	0.21	-
195	-	-	-	-	-
194	-	-	-	-	-
206	-	-	-	-	-
209	-	-	-	-	-

Table B.4 – Lake 9a sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	1.125	2.125	2.75	3.375	4.125	4.75	5.25	5.75	6.25
Congeners									
8-5	4.02	2.96	3.35	2.40	3.16	2.79	4.43	2.08	4.56
14	-	-	-	-	-	-	-	-	-
19	3.38	-	-	-	2.87	2.19	3.13	1.21	-
18	5.81	3.87	5.12	4.58	6.07	5.29	6.33	3.08	5.08
32	2.26	1.73	2.03	1.72	2.37	1.96	2.47	-	1.97
29	2.00	1.72	2.43	2.77	3.01	2.25	3.95	2.32	4.07
31-28	5.14	4.64	5.32	4.31	5.61	4.30	5.17	2.36	4.34
52	7.13	7.08	7.78	5.86	7.23	6.05	6.68	2.49	4.61
49	2.62	2.72	3.03	2.40	2.91	2.36	2.61	1.05	2.16
44	2.50	2.42	2.79	1.88	2.59	1.97	2.00	0.11	1.03
155	-	0.42	0.56	0.44	0.46	0.47	0.42	0.27	0.42
99	1.69	2.18	1.95	1.73	1.94	1.50	1.69	0.64	1.28
87	2.43	2.53	2.42	2.16	2.48	1.88	1.87	0.69	1.34
110	3.83	3.46	3.18	2.76	3.50	2.34	2.13	0.27	1.24
149	4.44	3.79	3.74	4.00	4.27	2.86	2.13	0.59	1.37
118	2.06	1.71	1.48	1.70	1.53	1.31	1.20	0.49	1.01
146	0.33	0.21	0.27	-	0.22	-	-	-	-
153	1.72	1.46	1.62	1.48	4.08	1.08	0.70	0.10	0.45
132	1.65	1.40	1.46	1.45	1.94	1.06	0.86	0.23	0.53
105	0.59	0.49	0.50	0.52	0.54	0.33	0.37	-	0.27
138	0.88	0.74	0.79	0.70	0.73	0.63	0.56	0.14	0.37
163	1.33	1.00	1.05	1.01	1.02	0.86	0.67	0.18	0.41
187	0.44	0.26	-	0.42	0.36	0.37	-	-	-
183	0.24	-	-	0.21	0.19	0.23	-	-	-
128	0.19	-	-	-	-	-	-	-	-
156	-	-	-	-	-	-	-	-	-
201	-	-	-	-	-	-	-	-	-
157	-	-	-	-	-	-	-	-	-
180	0.38	0.31	0.45	0.36	0.32	0.33	0.30	0.03	0.16
170	0.11	0.09	0.14	0.10	0.07	0.06	-	-	-
203	0.24	0.18	-	0.22	0.18	0.24	-	-	-
195	-	-	-	-	-	-	-	-	-
194	-	-	-	-	-	-	-	-	-
206	-	-	-	-	-	-	-	-	-
209	-	-	-	-	-	-	-	-	-

Table B.5 – Lake 9b sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	1.125	2.375	3.625	4.75	5.75	6.875	7.625	9.0	9.625	10.875	11.625
Congeners											
8-5	5.86	6.92	6.58	7.52	4.22	4.94	5.29	4.32	6.05	7.07	4.97
14	-	-	-	-	-	-	-	-	-	-	-
19	3.68	3.54	3.46	4.25	-	2.78	3.34	2.79	3.97	4.36	3.27
18	5.65	5.04	5.12	6.31	5.99	4.59	5.53	4.18	6.40	7.26	5.13
32	-	-	-	-	-	-	-	-	-	-	-
29	1.36	1.23	1.19	1.72	4.41	3.75	3.08	2.46	2.92	4.92	4.16
31-28	7.51	7.08	6.67	7.87	4.43	5.38	5.62	4.88	7.44	8.04	5.00
52	8.82	8.44	9.02	8.36	7.09	4.85	5.77	5.28	9.06	8.11	4.86
49	3.47	3.31	3.62	3.40	3.88	2.25	2.88	2.64	4.09	3.62	2.37
44	3.34	3.57	3.55	3.39	3.30	1.60	2.55	1.77	4.29	3.63	1.58
155	-	-	-	-	-	-	0.89	0.53	-	-	-
99	2.23	2.65	2.56	2.17	1.50	0.97	1.32	1.45	2.49	2.87	1.36
87	3.29	3.55	3.17	2.62	2.13	1.37	1.71	2.06	3.40	3.73	1.86
110	5.32	6.47	5.31	4.30	3.05	1.55	2.29	3.23	6.00	5.39	2.12
149	5.57	8.18	5.72	4.35	4.99	1.85	2.15	3.70	5.55	4.78	2.41
118	3.81	5.19	3.74	2.79	1.37	1.25	1.41	2.21	3.10	2.89	1.69
146	0.49	0.98	0.55	0.27	0.26	0.10	0.13	0.28	0.43	0.33	-
153	4.45	6.07	3.62	1.37	1.66	0.72	0.79	1.85	2.38	2.87	1.83
132	2.16	3.21	2.01	1.21	1.56	0.61	0.71	1.27	1.97	1.87	0.90
105	1.15	1.72	1.21	0.78	0.45	0.38	0.44	0.68	0.95	0.90	0.50
138	1.39	2.46	1.14	0.55	0.52	0.20	0.31	0.59	0.84	0.72	0.27
163	2.33	4.01	2.03	0.93	-	0.48	0.58	1.10	1.49	1.37	0.59
187	0.97	1.89	0.85	0.28	0.41	-	-	0.45	0.45	-	-
183	0.48	0.96	0.42	-	0.22	-	-	0.23	0.24	-	-
128	0.34	0.66	0.32	-	-	-	-	-	-	-	-
156	0.22	0.47	0.20	-	-	-	-	-	-	-	-
201	-	-	-	-	-	-	-	-	-	-	-
157	-	0.30	-	-	-	-	-	-	-	-	-
180	1.07	2.22	0.90	0.25	0.03	0.19	0.09	0.14	0.25	0.22	0.01
170	0.43	0.99	0.31	0.05	-	0.03	-	-	-	-	-
203	0.27	0.54	0.29	0.20	-	0.19	-	-	-	-	-
195	-	-	0.13	-	-	-	-	-	-	-	-
194	-	-	-	-	-	-	-	-	-	-	-
206	-	-	-	0.19	0.29	0.15	-	-	-	-	0.17
209	-	-	-	-	-	-	-	-	-	-	-

Table B.6 – Lake 14a sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	0.75	1.75	2.75	4.25	7.25	9.125
Congeners						
8-5	2.60	2.18	2.82	4.84	5.26	5.32
14	-	-	-	-	-	-
19	-	-	-	-	-	-
18	1.79	1.75	2.83	5.27	7.45	6.32
32	-	2.39	3.29	1.83	-	-
29	-	-	-	-	5.49	-
31-28	1.12	0.93	1.48	3.82	5.51	4.27
52	2.51	1.72	2.55	4.40	8.83	6.60
49	1.18	0.71	1.00	2.04	4.83	3.56
44	-	-	-	1.19	4.11	2.08
155	-	-	-	-	-	-
99	0.50	0.33	0.39	0.83	1.87	0.94
87	0.48	0.34	0.48	1.35	2.66	1.60
110	-	-	-	1.56	3.80	1.67
149	1.04	0.64	1.05	3.13	6.21	3.17
118	0.50	0.34	0.58	1.24	1.70	1.03
146	-	-	-	0.17	0.33	-
153	0.80	0.20	0.35	1.39	2.07	0.79
132	0.50	0.25	0.39	1.10	1.94	0.95
105	0.19	0.14	0.19	0.39	0.56	0.32
138	0.26	0.04	0.09	0.47	0.65	0.25
163	0.35	0.22	0.36	1.03	1.41	0.69
187	0.17	0.12	0.20	0.48	0.51	-
183	-	-	-	0.27	0.27	-
128	-	-	-	0.18	-	-
156	-	-	-	-	-	-
201	-	-	-	-	-	-
157	-	-	-	-	-	-
180	0.29	0.06	0.13	0.22	0.03	0.08
170	0.09	0.02	0.05	0.07	-	-
203	-	0.15	0.23	0.25	-	-
195	-	-	-	-	-	-
194	-	-	-	-	-	-
206	-	-	-	0.26	0.36	-
209	-	-	-	-	-	-

Table B.7 – Lake 14b sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	1.25	2.75	4.25	6.0	7.25	8.375	9.375	10.125
Congeners								
8-5	17.30	28.21	42.19	20.00	10.31	14.01	14.83	15.22
14	-	-	-	-	-	-	-	-
19	6.50	5.04	6.33	6.86	5.17	6.54	6.43	12.12
18	12.00	11.49	16.16	15.49	12.35	19.57	23.24	22.44
32	4.32	-	-	5.78	4.81	7.55	8.83	8.63
29	15.74	-	14.15	10.38	10.68	10.73	6.42	6.63
31-28	20.27	15.58	21.49	23.31	21.34	34.16	44.29	38.02
52	17.80	15.21	17.93	18.25	11.24	17.11	22.76	19.64
49	7.68	7.15	9.37	8.94	5.89	9.78	13.55	11.98
44	7.30	6.26	9.93	10.29	6.06	11.01	16.35	14.45
155	-	-	-	-	-	-	-	-
99	3.53	2.55	5.23	7.14	2.73	4.40	6.24	5.49
87	5.03	3.86	8.75	11.38	4.36	6.29	9.60	8.36
110	9.14	6.68	17.64	25.32	8.11	13.03	21.96	17.55
149	5.94	4.89	15.01	24.20	5.73	7.87	14.65	13.17
118	6.79	6.34	12.21	15.23	4.63	6.61	11.97	10.29
146	0.66	0.35	1.75	3.10	0.66	1.11	2.32	1.75
153	3.18	1.72	8.29	16.45	2.94	4.40	8.78	8.62
132	2.05	1.53	5.49	9.76	2.16	2.89	5.45	4.76
105	1.78	0.99	3.32	5.05	1.50	2.31	4.48	3.64
138	1.20	0.68	3.66	6.83	1.20	1.53	3.32	3.43
163	2.37	1.39	6.33	12.20	2.08	2.64	6.16	6.11
187	0.67	0.34	2.18	4.19	0.58	0.68	1.62	1.94
183	0.39	0.18	1.08	2.10	0.32	0.39	0.81	0.97
128	0.53	0.20	1.08	1.93	0.42	0.56	1.11	1.05
156	-	-	-	3.23	-	-	-	-
201	-	-	-	-	-	-	-	-
157	-	-	-	-	-	-	-	-
180	0.56	0.34	2.04	3.79	0.40	0.43	1.01	1.65
170	0.24	0.15	0.89	1.57	0.21	0.19	0.35	0.56
203	-	-	-	0.97	-	-	-	-
195	-	-	-	-	-	-	-	-
194	-	-	-	-	-	-	-	-
206	-	-	-	-	-	-	-	-
209	0.23	0.45	0.41	-	0.13	-	-	-

Table B.8 – Lake 36a sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	0.75	1.625	1.875	2.625	2.875	3.625	3.875
Congeners							
8-5	0.96	1.02	1.48	2.13	2.02	2.43	2.65
14	-	-	-	-	-	-	-
19	-	-	0.72	0.97	0.96	1.27	1.34
18	0.91	1.33	1.51	2.34	2.38	3.11	3.33
32	-	-	-	-	-	-	-
29	0.77	0.88	0.93	1.40	2.01	2.34	2.53
31-28	0.62	0.65	1.23	2.05	2.22	2.90	3.16
52	1.16	1.25	1.39	2.02	2.21	3.13	2.98
49	0.41	0.83	0.50	0.82	0.94	1.30	1.33
44	-	-	-	-	-	0.37	0.33
155	-	-	-	-	-	-	-
99	0.28	2.19	0.37	0.58	0.53	0.64	0.61
87	0.40	0.35	0.43	0.88	0.83	0.98	1.08
110	-	-	0.08	0.82	0.66	0.92	1.06
149	0.42	0.46	0.47	1.10	1.11	1.28	1.36
118	0.65	1.60	0.69	1.27	0.91	0.96	1.05
146	-	-	-	0.09	0.05	0.04	0.05
153	0.17	-	0.46	0.71	0.54	1.59	1.32
132	0.17	-	0.17	0.42	0.37	0.44	0.46
105	0.23	0.34	0.23	0.42	0.29	0.30	0.32
138	-	-	-	0.10	0.04	0.06	0.06
163	0.14	0.33	0.29	0.52	0.34	0.31	0.35
187	-	0.24	0.16	0.17	0.16	0.15	-
183	0.12	0.17	0.11	0.14	0.13	0.14	-
128	-	-	-	0.10	-	-	-
156	-	-	-	-	-	-	-
201	-	-	-	-	-	-	-
157	-	-	-	-	-	-	-
180	-	0.01	-	-	-	-	-
170	-	0.02	-	-	-	-	-
203	-	0.14	0.11	-	-	-	-
195	-	-	-	-	-	-	-
194	-	-	-	-	-	-	-
206	-	-	-	-	-	-	-
209	-	-	-	-	-	-	-

Table B.9 – Lake 36b sediment core profile PCB congener concentrations (ng g^{-1} TOC).

Depth (cm)	0.875	1.75	2.75	3.375
Congeners				
8-5	10.55	8.02	12.05	15.43
14	1.05	-	-	-
19	4.38	2.59	2.33	2.99
18	5.37	2.97	2.45	4.45
32	-	-	-	-
29	2.25	1.12	0.71	4.27
31-28	5.53	3.49	3.47	5.18
52	3.95	2.64	3.06	4.33
49	2.03	1.57	2.08	2.07
44	0.37	0.26	0.67	1.17
155	-	-	-	-
99	0.70	0.49	0.76	0.75
87	1.11	0.68	1.04	1.31
110	1.11	0.61	0.99	2.06
149	1.04	0.83	1.69	1.68
118	1.58	0.86	1.25	1.67
146	0.27	-	-	-
153	0.50	0.40	0.89	0.96
132	0.55	0.33	0.60	0.63
105	0.57	0.27	0.33	0.50
138	0.33	0.29	0.28	0.27
163	0.63	0.41	0.60	0.66
187	-	-	-	0.23
183	-	-	-	-
128	-	-	-	-
156	-	-	-	-
201	-	-	-	-
157	-	-	-	-
180	0.08	0.02	0.31	0.06
170	-	-	-	-
203	-	-	-	-
195	-	-	-	-
194	-	-	-	-
206	-	-	-	-
209	-	-	-	-

Table B.10 – Lake 2a and 2b sediment core profile pesticide concentrations (ng g^{-1} TOC).

2a Depth (cm)	0.875	1.625	2.875	3.75	4.75	5.375
PeCBz	1.21	0.77	0.92	1.01	-	-
HCB	2.55	1.63	1.46	1.63	1.97	1.37
2,4'-DDE	2.43	1.70	1.88	2.59	3.64	2.78
4,4'-DDE	0.93	0.71	0.67	0.79	0.96	0.80
2,4'-DDD	1.15	0.91	0.86	0.88	0.77	0.79
4,4' + 2,4'-DDT	-	-	-	-	6.24	5.21
4,4'-DDD	1.22	0.89	0.96	-	-	-

2b Depth (cm)	1.25	3.25	5.0	6.0	7.25
PeCBz	2.27	3.27	5.76	4.59	3.11
HCB	6.28	9.31	18.23	9.34	6.02
2,4'-DDE	2.73	1.47	4.78	1.44	1.82
4,4'-DDE	1.22	1.79	4.85	4.19	1.50
2,4'-DDD	1.70	1.73	-	2.32	1.89
4,4' + 2,4'-DDT	-	-	-	-	-
4,4'-DDD	-	-	-	-	-

Table B.11 – Lake 9a and 9b sediment core profile pesticide concentrations (ng g^{-1} TOC).

9a Depth (cm)	1.125	2.125	2.75	3.375	4.125	4.75	5.25	5.75	6.25
PeCBz	0.66	0.70	0.82	1.60	0.83	2.78	7.32	5.56	5.00
HCB	1.70	1.15	1.39	0.88	1.37	1.18	1.85	0.90	1.95
2,4'-DDE	3.09	2.87	2.86	2.27	2.82	2.18	2.11	0.86	1.51
4,4'-DDE	1.30	1.08	1.05	0.85	1.01	0.87	0.76	-	-
2,4'-DDD	1.22	-	1.10	1.40	1.18	-	1.07	-	-
4,4' + 2,4'-DDT	-	-	-	-	-	-	-	-	-
4,4'-DDD	1.08	-	-	-	-	-	-	-	-

9b Depth (cm)	1.125	2.375	3.625	4.75	5.75	6.875	7.625	9.0	9.625	10.875	11.625
PeCBz	2.01	2.18	2.26	5.76	7.72	0.78	7.47	0.77	13.61	19.06	9.78
HCB	2.99	3.43	3.24	3.79	3.48	2.40	2.58	2.02	2.84	3.49	2.30
2,4'-DDE	3.42	3.82	3.81	3.39	3.67	2.67	7.00	6.04	7.15	6.68	7.31
4,4'-DDE	1.65	2.00	2.41	2.30	1.59	0.78	0.78	0.96	1.10	1.24	0.84
2,4'-DDD	1.84	1.88	1.51	1.28	1.45	1.27	1.19	1.77	1.29	1.43	1.66
4,4' + 2,4'-DDT	-	1.55	1.37	-	-	-	-	1.37	1.42	1.50	1.32
4,4'-DDD	1.24	1.35	1.44	1.23	1.10	1.10	1.11	1.16	1.27	1.30	1.20

Table B.12 – Lake 14a and 14b sediment core profile pesticide concentrations (ng g^{-1} TOC).

14a Depth (cm)	0.75	1.75	2.75	4.25	7.25	9.125
PeCBz	-	-	-	-	0.63	0.69
HCB	1.31	1.06	1.43	2.25	2.44	2.59
2,4'-DDE	0.93	0.66	1.00	1.77	3.69	3.45
4,4'-DDE	1.67	1.64	1.74	2.15	1.59	1.39
2,4'-DDD	1.23	-	1.29	1.37	1.64	1.47
4,4' + 2,4'-DDT	-	-	-	-	-	-
4,4'-DDD	-	1.32	-	-	-	-

14b Depth (cm)	1.25	2.75	4.25	6.0	7.25	8.375	9.375	10.125
PeCBz	3.69	10.05	-	3.72	-	2.53	1.41	-
HCB	8.30	13.84	20.86	9.86	5.23	7.08	7.42	7.92
2,4'-DDE	4.34	4.25	7.34	8.49	3.69	5.45	7.81	10.08
4,4'-DDE	2.43	2.17	5.29	5.28	2.00	2.96	4.58	3.92
2,4'-DDD	6.42	4.83	4.97	4.32	3.67	2.78	2.02	1.39
4,4' + 2,4'-DDT	-	1.79	2.41	2.63	1.71	1.68	2.06	1.98
4,4'-DDD	1.14	1.51	1.82	1.68	-	1.14	1.44	1.39

Table B.13 – Lake 36a and 36b sediment core profile pesticide concentrations (ng g^{-1} TOC).

36a Depth (cm)	0.75	1.625	1.875	2.625	2.875	3.625	3.875
PeCBz	0.24	0.16	1.12	0.18	0.20	0.20	-
HCB	0.41	0.45	0.66	1.01	0.93	1.17	1.27
2,4'-DDE	-	-	-	0.84	0.88	1.19	1.13
4,4'-DDE	0.51	1.43	2.53	1.58	1.31	0.90	0.72
2,4'-DDD	-	0.77	-	0.81	-	-	0.81
4,4' + 2,4'-DDT	-	-	-	-	-	-	-
4,4'-DDD	-	-	-	0.97	0.96	-	-

36b Depth (cm)	0.875	1.75	2.75	3.375
PeCBz	9.64	3.68	2.37	8.84
HCB	5.26	3.93	5.91	7.66
2,4'-DDE	1.48	0.88	1.19	1.54
4,4'-DDE	1.06	0.69	0.90	1.03
2,4'-DDD	2.53	1.68	1.53	1.47
4,4' + 2,4'-DDT	-	-	-	-
4,4'-DDD	-	-	0.98	-

Appendix C – Organic Geochemistry in Sediment Profiles

Table C.1 – Organic geochemistry fraction concentrations and fluxes in sediment core profiles.

Lake Depth (cm)	S2 Conc mg HC g^{-1} DW	S2 Flux g HC m^{-2} yr^{-1}	S3 Conc mg CO_2 g^{-1} DW	S3 Flux g CO_2 m^{-2} yr^{-1}	TOC % DW	TOC Flux g C m^{-2} yr^{-1}
2a						
0.875	12.86	3.01	11.09	2.59	6.89	16.12
1.625	12.86	3.83	10.67	3.18	6.71	19.98
2.875	13.48	4.12	11.76	3.60	7.05	21.56
3.75	14.40	4.04	11.66	3.27	7.20	20.19
4.75	16.02	3.63	11.90	2.70	7.75	17.57
5.375	17.24	2.55	12.50	1.85	8.35	12.33
2b						
1.25	17.56	6.61	11.36	4.28	7.65	28.77
3.25	11.94	2.63	10.80	2.38	6.41	14.11
5.0	8.49	1.84	8.30	1.80	5.22	11.34
6.0	9.18	1.64	8.29	1.48	5.36	9.60
7.25	9.62	1.48	8.73	1.34	5.59	8.60
9a						
1.125	59.31	7.86	33.95	4.50	21.34	28.28
2.125	62.92	12.35	31.98	6.28	21.19	41.57
2.75	63.05	15.32	31.10	7.56	21.08	51.23
3.375	60.78	17.27	29.76	8.46	20.49	58.24
4.125	54.17	17.51	26.50	8.56	18.52	59.87
4.75	45.98	16.19	22.27	7.84	15.94	56.12
5.25	40.03	14.80	19.17	7.09	14.03	51.86
5.75	35.79	15.15	17.80	7.54	12.93	54.74
6.25	32.00	15.08	16.58	7.81	11.95	56.31
9b						
1.125	15.23	6.45	9.30	3.94	5.82	24.66
2.375	16.26	4.98	9.29	2.84	6.16	18.86
3.625	16.26	4.96	9.55	2.92	6.21	18.95
4.75	13.15	3.90	9.17	2.72	5.88	17.45
5.75	10.47	3.72	8.84	3.14	5.83	20.74
6.875	9.00	3.85	8.28	3.55	5.54	23.71
7.625	8.04	4.00	7.76	3.86	5.20	25.90
9.0	7.59	4.02	7.55	4.00	5.05	26.77
9.625	7.87	4.01	7.75	3.95	5.16	26.27
10.875	7.60	3.09	7.81	3.18	5.05	20.57
11.625	6.83	1.74	7.67	1.95	4.75	12.06

Lake Depth (cm)	S2 Conc mg HC g^{-1} DW	S2 Flux g HC m^{-2} yr^{-1}	S3 Conc mg CO_2 g^{-1} DW	S3 Flux g CO_2 m^{-2} yr^{-1}	TOC % DW	TOC Flux g C m^{-2} yr^{-1}
14a						
0.75	44.51	10.28	29.24	6.75	17.50	40.41
1.75	38.44	6.72	28.60	5.00	16.27	28.44
2.75	36.55	5.03	28.80	3.97	16.39	22.57
4.25	34.00	4.55	27.52	3.68	15.52	20.75
7.25	27.30	2.54	26.67	2.48	14.18	13.20
9.125	24.90	1.40	25.78	1.45	13.89	7.83
14b						
1.25	2.18	2.92	5.49	7.36	2.46	33.04
2.75	4.99	1.48	8.91	2.64	3.89	11.53
4.25	4.61	1.59	7.64	2.64	3.72	12.82
6.0	3.59	1.81	7.81	3.94	3.42	17.23
7.25	4.20	2.99	6.17	4.39	3.38	24.01
8.375	3.56	2.68	5.02	3.79	3.17	23.89
9.375	3.23	2.23	3.93	2.72	3.11	21.48
10.125	2.99	1.92	2.09	1.34	2.74	17.55
36a						
0.75	23.10	1.92	43.75	3.64	16.77	13.94
1.625	19.43	1.42	35.64	2.61	15.17	11.10
1.875	17.97	1.58	31.25	2.76	13.86	12.23
2.625	15.87	1.59	25.19	2.52	11.97	11.96
2.875	15.23	1.47	23.51	2.27	11.37	11.00
3.625	14.15	1.32	21.13	1.97	10.47	9.76
3.875	13.69	1.27	20.44	1.90	10.16	9.44
36b						
0.875	8.17	2.07	16.74	4.23	5.62	14.21
1.75	8.41	1.31	13.17	2.05	5.46	8.50
2.75	6.52	0.66	9.61	0.97	4.64	4.67
3.375	4.34	0.34	6.22	0.49	3.59	2.85

Appendix D – Inferred Chlorophyll *a* in Sediment Profiles

Table D.1 – Inferred chlorophyll *a* concentrations and fluxes in sediment core profiles.

Lake Depth (cm)	Chl *a* Conc (μg g^{-1} DW)	Chl *a* Flux (mg m^{-2} yr^{-1})	Lake Depth (cm)	Chl *a* Conc (μg g^{-1} DW)	Chl *a* Flux (mg m^{-2} yr^{-1})
2a			**2b**		
0.875	-	-	1.25	30.84	11.60
1.625	-	-	3.25	17.73	3.90
2.875	-	-	5.0	11.51	2.50
3.75	-	-	6.0	12.93	2.32
4.75	-	-	7.25	15.28	2.35
5.375	-	-			
9a			**9b**		
1.125	48.48	6.43	1.125	38.78	16.43
2.125	45.46	8.92	2.375	41.43	12.68
2.75	42.58	10.35	3.625	45.91	14.01
3.375	40.20	11.42	4.75	41.63	12.34
4.125	39.08	12.63	5.75	34.23	12.17
4.75	36.71	12.93	6.875	27.99	11.98
5.25	34.80	12.86	7.625	23.40	11.65
5.75	33.27	14.08	9.0	21.36	11.32
6.25	31.90	15.03	9.625	22.83	11.63
			10.875	22.46	9.14
			11.625	20.15	5.12
14a			**14b**		
0.75	48.30	11.15	1.25	0.20	0.27
1.75	48.39	8.46	2.75	2.27	0.67
2.75	46.60	6.42	4.25	2.54	0.88
4.25	40.02	5.35	6.0	2.82	1.42
7.25	34.84	3.24	7.25	1.92	1.36
9.125	30.51	1.72	8.375	1.27	0.96
			9.375	0.57	0.40
			10.125	0.10	0.06
36a			**36b**		
0.75	39.30	3.27	0.875	2.36	0.60
1.625	39.03	2.86	1.75	6.67	1.04
1.875	38.77	3.42	2.75	7.70	0.77
2.625	34.50	3.45	3.375	5.94	0.47
2.875	30.50	2.95			
3.625	25.30	2.36			
3.875	24.10	2.24			