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Use of pre-industrial baselines to assess sources and pathways of metals in surface sediment of floodplain lakes in the Peace-Athabasca Delta (Alberta, Canada)

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Use of pre-industrial baselines to assess sources and pathways of metals in surface sediment of floodplain lakes in the Peace-Athabasca Delta (Alberta, Canada)

by

Tanner Owca

Thesis

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Abstract

The effects of natural resources exploitation in northern Canada on downstream aquatic ecosystems is a concern. Assessing these effects requires comprehensive monitoring practices to better inform stakeholders and environmental stewardship decisions. Here, a monitoring approach is developed and applied to assess metals concentrations in lake surface sediments of the Peace-Athabasca Delta (PAD), northern Alberta, Canada. Since the ecological integrity of the PAD is strongly tied to river floodwaters that are critical for replenishing the delta, and the PAD is located downstream of the Alberta oil sands, concerns have been raised over the potential transport of metal contaminants to the PAD via the Athabasca River. To address this knowledge gap, surface sediment samples (top ~1-cm) were collected in September 2017 from 61 lakes across the delta, and again in July 2018 from a subset of 20 lakes that had received river flood sediment two months earlier, to provide a snapshot of metals (Be, Cd, Cr, Cu, Pb, Ni, V, Zn) concentrations that have recently accumulated in these lakes. To assess for contamination, metals concentrations were normalized to aluminum and then compared to baseline metal-aluminum relations for the Athabasca and Peace sectors developed from pre-1920 measurements in lake sediment cores. Also, river-bottom sediment collected by the Regional Aquatics Monitoring Program (RAMP) and Joint Oil Sands Monitoring (JOSM) program from 2000-2015 were re-assessed on the lake-derived baselines. Most surficial lake sediment metals concentrations collected in both 2017 and 2018 fall consistently within the range of natural variability (i.e., pre-1920), apart from a few lakes of the PAD that show a slight enrichment of Cd and Zn. Among the suite of metals analyzed by RAMP and JOSM, only Cr was enriched in river-bottom sediment. Interquartile ranges of the enrichment factors span a narrow range close to 1 for all metals in surficial lake sediment. Thus, results presented here show little to no evidence of recent oil sands-derived metals enrichment in sediment of lakes in the PAD and also demonstrates the usefulness of these methods as a monitoring framework.

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Chapter 1: Introduction

Background

With approximately 164 billion barrels of recoverable oil, the Alberta Oil Sands Region in northern Alberta, Canada, is the third largest oil reserve in the world (CAPP, 2018). In 2017, oil sands mined a total of 2.8 million barrels of oil a day, which is estimated to increase to 3.7 million barrels by 2025 (CAPP, 2018). Oil deposits in this region are found near the surface in a viscous petroleum substance known as bitumen, and may be extracted via surface mining (open-pit) or in situ techniques (Dowdeswell, 2010). Like most large-scale mining developments, these extraction processes have implications for the environment and local landscape. Surface mining causes major land disturbances (Timoney & Lee, 2009; Schindler, 2010), peatland loss (Rooney et al., 2012), and areal deposition of contaminants (Kelly et al., 2009; Kelly et al., 2010; Kirk et al., 2014), whereas bitumen extraction via in situ techniques causes aquifer dewatering near drilling locations (Hackbarth, 1980). Mining activities can have negative impacts on the local landscape and these effects may extend beyond the surrounding area influencing quality of the environment and health of persons living downstream of developments.

Concerns have been raised regarding the potential for oil sands operations to pollute the Athabasca River, which flows directly into the Peace-Athabasca Delta (PAD) ~200 km north and downstream of the mining area (MCFN, 2014). The PAD is one of the world's largest inland freshwater deltas, having cultural (providing resources for First Nations), national (~80% lies within Wood Buffalo National Park [WBNP]), and international significance (UNESCO World Heritage Site and Ramsar Wetland of International Importance). The abundant shallow lakes within this landscape are strongly influenced by periodic river flood events, occurring along the Peace and Athabasca rivers, which maintains lake water balances, but also supplies nutrients and influences habitat availability (PADPG, 1973; Prowse & Conly, 1998; Wolfe et al., 2007; Timoney, 2013; Remmer et al., 2018). While river floodwaters are critical in maintaining the ecological integrity of this deltaic landscape, the same floodwaters can deliver inorganic sediments that may include metals contaminants from upstream geological or anthropogenic sources.

Overwhelming concern for pollution (among other stressors) and the lack of monitoring in this region has culminated in a petition filed by the Mikisew Cree First Nations in 2014 to classify WBNP as World Heritage in Danger (MCFN, 2014). This petition resulted in an investigation and a report by the World Heritage Committee (WHC) and the International Union for the Conservation of Nature (IUCN) on the status of WBNP, where it was recommended that the scope of monitoring be extended to understand the cumulative impacts of stressors on the PAD (WHC/IUCN, 2017). Since the release of this report, Parks Canada replied with an Action Plan to address the recommendations proposed by WHC/IUCN (Parks Canada, 2019). In the Action Plan, Parks Canada states the need for ongoing monitoring of lakes in the PAD particularly to assess impacts from oil sands operations (Parks Canada, 2019). But before these recommendations can be addressed, an adequate monitoring framework utilizing baseline (reference) conditions must be established.

To address the lack of baseline knowledge, the use of paleolimnological techniques has been proposed to assess the degree of metals enrichment in lake sediments downstream of mining operations (Dowedeswell et al., 2010; Wrona & di Cenzo, 2011). Floodplain lakes in the PAD serve as excellent archives for such investigation because lakes are sometimes located in the down-wind direction of mining operations and are also found near the terminus of the Athabasca River. Therefore, these lakes have the ability to accrete metals contaminants from both aerial deposition and river floodwaters. Analysis of sediment cores from these lakes can define the natural range of metals concentrations conveyed by the atmosphere or Athabasca River, and determine if concentrations have changed since the onset of oil sands developments.

Wiklund et al. (2012, 2014) utilized these methods to evaluate river- and atmosphere-derived contamination in the PAD. However, these studies were limited to a few lakes and did not investigate the spatial extent and hydrological spectrum of lakes located in the PAD. Wiklund at al. (2012) examined the atmospherically-sourced metal depositional history of one lake located above the Peace River’s floodplain. Wiklund et al. (2014) used lake sediment cores from two flood-prone lakes in the Athabasca Delta to establish baseline (reference) conditions, to evaluate metals concentrations in surficial river-bottom sediment of the Athabasca River and its distributaries. However, assessment of river-bottom sediments is difficult because the nature of fluvial environments provides challenges in determining when these river sediments were deposited. Lakes, on the other hand, accrete sediment vertically, and provide opportunity to evaluate metals concentrations in recently deposited sediment across the delta.

Environmental Monitoring

Environmental monitoring and its shortcomings

Environmental monitoring is a systematic process of measurements that aims to characterize and monitor certain target proxies enabling one to assess the health of the environment (Dowdeswell, 2010). This is accomplished by collecting long-term measurements of air, water, soil and biota to define baseline conditions representative of the range of natural variation (Dowdeswell, 2010). Knowledge of these baseline conditions becomes instrumental in detecting environmental change, which can then be used to inform environmental stewardship decisions, environmental impact assessments and policy. Therefore, well-designed programs are important to inform strategic management of natural resources enabling the protection of the environment against anthropogenic effects (Lindenmayer & Likens, 2009). However, these programs are often unsuccessful and have acquired poor reputations (Lovett et al., 2007; Lindenmayer & Likens, 2010).

There are various reasons as to why environmental monitoring programs may be ineffective. Monitoring programs are often implemented only after environmental concerns have been raised (Blais et al., 2015). Therefore, the lack of long-term monitoring prior to an environmental disturbance creates a lack of knowledge regarding the natural range of conditions. Without knowledge of pre-disturbance conditions, it is difficult to detect the impacts or gauge the severity of an event (Smol, 2008; Blais et al., 2015).

Once a monitoring program has been implemented, they are generally driven by short-term funding opportunities or political directives (Lindenmayer & Likens, 2009). Therefore, these transient programs require quick turnarounds to produce data, which is often related to the lack of funding (Caughlan & Oakley, 2001). With short-term goals as the driving factor, these programs will likely be poorly designed and operate without a well-established framework (Bernhardt et al., 2005; Conrad & Daoust, 2008). When monitoring programs do not have clearly defined objectives, they often operate by collecting data first and thinking later (Roberts, 1991), resulting in monitoring too many things poorly rather than a few things well (Zeide, 1994). Consequently, large datasets are produced that provide little information to answer probing scientific questions (Ward et al., 1986). To effectively monitor environmental related issues, programs should be based on carefully posed questions and objectives (Lindenmayer & Likens, 2009). Although these programs sometimes fall short in meeting their objectives, they are critical tools needed by stakeholders and policy-makers to properly identify emerging anthropogenic stresses on natural resources.

To ensure monitoring programs are successful, authors have listed a few important components, which should be incorporated into all monitoring programs when being designed. Some of the common recommendations that have been addressed in the literature are that: 1) above all, monitoring programs require good, clear scientific questions; 2) the data should be frequently used and interpreted; 3) collaboration is key; and 4) data should be transparent and publicly available (Lovett et al., 2007; Lindenmayer & Likens, 2010; Dowdeswell, 2010). Well-designed monitoring programs can therefore produce valuable information for natural resource managers, stakeholders and research scientists alike.

The lack of long-term data in the PAD has made it difficult to assess its current state and the cumulative impacts of oil sands operations. Despite several different monitoring programs (Regional Aquatics Monitoring Program, Joint-Oil Sands Monitoring/Oil Sands Monitoring) that have been implemented in this region, there is still a need for a robust, comprehensive and sustainable aquatic ecosystem monitoring program (WHC/IUCN, 2017).

Linking scientific research and environmental monitoring

While research and monitoring have slightly different objectives, they share similar activities that are tightly linked (Franklin et al., 1999). The fundamental basis of scientific research is to establish facts and draw conclusions from well-developed research questions, whereas monitoring programs aim to evaluate the state of the environment and report findings based on long-term standardized measurements and systematic observations (Dowdeswell, 2010). Despite these slight differences, collaborative efforts between scientific research and monitoring programs is required to establish best practices.

Ecologists and natural resources managers recognize the importance of long-term research, which often includes monitoring, for the establishment of baseline conditions that better informs environmental stewardship decisions (Lindenmayer & Likens, 2009). Traditionally, scientists have distanced themselves from monitoring because they have viewed it as a routine collection of data for non-scientific purposes (Franklin et al., 1999). However, recently scientists have begun to see the value of long-term databases for their own research. Long-term monitoring data provides several benefits for ecologists, because ecosystem dynamics change slowly over time and systematic observations and measurements enable more accurate detection of regime shifts (Lovett, 2007). Thus, monitoring data are slowly becoming an integral component of environmental science (Lovett, 2007). Likewise, scientific research approaches are inherent in establishing effective environmental monitoring programs. Research practices help develop and sustain monitoring programs by: 1) guiding the monitoring design; 2) providing quality control; 3) assisting in the interpretation of results; and 4) providing periodic assessments of the effectiveness of these program (Franklin et al., 1999). Therefore, these approaches may have slightly different objectives, but nonetheless, collaboration is required by both parties to create the most effective monitoring framework possible.

Using lake sediment to develop a monitoring framework

Sediment monitoring has become an integral part of aquatic monitoring programs (Reuther, 2009). This aspect of aquatic monitoring is important because contaminants within the sediment can influence the overlying waters' composition and quality before becoming part of the sedimentary record (Reuther, 2009). Effective use of aquatic sediment monitoring can provide an understanding of the spatial and temporal trends of contaminants in sediment to better manage and protect freshwater resources. Objectives for these programs are to measure, map and document the distribution of contaminants (Reuther, 2009). Before users can undertake analyses and interpretation of sampled sediment data, an understanding of the physical properties and characteristics of sediment for a given location is required.

In the absence of long-term monitoring data, paleolimnological approaches can be used to provide baseline conditions that are indicative of the natural variation in sediment. An understanding of this range of natural variation is required to accurately differentiate natural shifts in the environment versus changes caused by anthropogenic activities (Loring, 1991; Kersten & Smedes, 2002; Dowdeswell, 2010). Lakes serve as natural archives, accumulating deposition from natural and anthropogenic sources (e.g. river floodwaters), and provide knowledge of the historical development of sedimentary pollution (Smol, 1992; Reuther, 2009; Wiklund et al., 2014). However, differing energy gradients created from floodwaters will affect sedimentation differently in lakes, which is especially the case for lakes located in hydrologically-dynamic environments such as floodplains. Therefore, to accurately assess for pollution, geochemical normalizing techniques are required (Kersten & Smedes, 2002). Metals preferentially bind to clay-size particles and since river floodwaters enter lakes of the PAD carrying these finer grains, variations in metals concentrations can be observed independent of any additional supply of metals from anthropogenic sources. To compensate for this issue, lithogenic normalizers can be used to account for the grain size effect. Typically, lithium (Li) and aluminum (Al) are used as the normalizing agents because these elements are incorporated into the sediment particle matrix of silicates and are conservative lithogenic elements (Loring, 1991; Wiklund et al., 2014; MacDonald et al., 2016; Lintern et al., 2016). Using normalizing agents, linear relationship can be developed between metals contaminants and the normalizer (Kersten & Smedes, 2002; Wiklund et al., 2014; MacDonald et al., 2016). The natural variation can then be defined by constructing 95% Prediction Intervals about the linear normalizer-metal regression. This is deemed to be the natural variation of metals concentrations in lake sediments. Values plotting above the upper limits of this range may be considered as being derived from pollution. To quantify the potential magnitude of pollution, enrichment factors (EFs) can then be used, which measure the level of enrichment above the defined baseline relationship. Enrichment factors are a ratio, where EFs that are equal to 1indicates no enrichment but an EF of 2 would be considered a doubling.

Research objectives

The main objective of this study is to assess metals concentrations in recently deposited sediment in lakes from across the PAD using baseline metals concentrations established from the analysis of pre-1920 sediments in a suite of lake sediment cores. To accomplish this, surface sediment from a spatially comprehensive dataset of 61 lakes was sampled in September 2017, which covers the hydrological spectrum of lakes in the PAD. Opportunistic sampling in July 2018, following flooding occurring along the Peace and Athabasca rivers between the months of April- and May 2018, provided an opportunity to sample freshly deposited river-derived sediment in a suite of 20 lakes, which offered a snapshot of metals concentrations transported by the rivers during the 2018 spring freshet. Additionally, using aluminum as the normalizing agent, rather than lithium as conducted by Wiklund et al. (2014) to develop baseline metal conditions, enabled the assessment of additional RAMP/JOSM river bottom sediment samples that was not previously possible. It is envisioned that this framework lays a monitoring foundation that can be used to detect future potential impacts of oil sands operations on lake sediments in the PAD, a recommendation expressed by the WHC/IUCN and acknowledged by Parks Canada (WHC/IUCN, 2017; Parks Canada, 2019).

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Chapter 2: Research Manuscript for Submission

Title

Use of pre-industrial baselines to assess sources and pathways of metals in surface sediment of floodplain lakes in the Peace-Athabasca Delta (Alberta, Canada)

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Introduction

As large-scale mining operations continue to grow across northern Canada, so do concerns about releases of contaminants and their effects on the ecological integrity of downstream aquatic ecosystems (Schindler & Smol, 2006; Smol, 2008; Schindler, 2010). Comprehensive monitoring programs are needed to protect downstream natural resources from harmful effects of industrial pollution, inform stakeholders, ensure industrial compliance, and guide environmental stewardship decisions. These programs may vary depending on the industry or project type, but they all share a common objective to identify anthropogenic effects on the environment (Roach & Walker, 2017). However, monitoring efforts are often initiated only after concerns have been raised (Blais et al., 2015). This presents challenges for formulation of evidence-based recommendations by policy-makers, because an absence of sufficient long-term, pre-development data impairs the ability to discern the role of anthropogenic activities from natural processes occurring in the landscape (Smol, 2008; Blais et al., 2015). Thus, effectiveness of monitoring programs is greatly improved when they include long-term or pre-disturbance data to define baseline conditions and the range of natural variation (Smol, 1992; Lindenmayer & Likens, 2009; Dowdeswell et al., 2010).

In northern Alberta (Canada), local, national, and international concerns have been raised about the environmental consequences of contaminant releases from oil sands mining activities to the Athabasca River and, at its terminus, the Peace-Athabasca Delta (PAD). The PAD is one of the world’s largest inland freshwater deltas, and its abundant shallow lakes provide habitat for a variety of biota and resources that support indigenous communities based in Fort Chipewyan. Mostly protected within the boundaries of Wood Buffalo National Park (WBNP), the PAD has gained recognition as a Ramsar Wetland of International Importance and contributed to the listing of WBNP as a UNESCO World Heritage Site for its historical, ecological, and cultural significance. Shallow lakes dominate this landscape and are largely dependent on periodic ice-jam flood events that occur along the Peace and Athabasca rivers to maintain lake-water balances (PADPG, 1973; Prowse & Conly, 1998; Wolfe et al., 2007; Timoney, 2013; Remmer et al., 2018). Although river floodwaters play an integral part in lake hydrological and ecological conditions, they also convey sediment and associated contaminants (e.g., metals) from upstream sources. Bitumen deposits in the Alberta oil sands region, ~200 km upstream of the PAD, are the largest and shallowest among Canada's reserves (Dowdeswell et al., 2010). Here, the Athabasca River and some of its major tributaries flow through the deposits situated along the river banks and naturally erode bitumen exposures and associated contaminants. It is therefore essential to identify the natural range of contaminant concentrations in the Athabasca River to accurately evaluate the extent of river pollution contributed by oil sands operations to the PAD.

It has remained challenging to assess the extent of metals enrichment at the PAD because systematic monitoring in the Lower Athabasca Oil Sands Region, by the industry-funded Regional Aquatics Monitoring Program (RAMP), was not initiated until 1997 - three decades after the start of oil sands production (Cronmiller & Noble, 2018). The lack of pre-industrial data has impeded ability of RAMP and other monitoring programs to detect and quantify the extent to which the industry has increased supply of contaminants to the Athabasca River and downstream delta. Indeed, these programs have been criticized for their study design and inability to detect trends of contaminant concentration since industrial development (Schindler, 2010; Dowdeswell et al., 2010; Gosselin et al., 2010; Dillon et al., 2011). This has resulted in calls for better monitoring practices for nearly a decade and the emergence of a petition in 2014, led by the Mikisew Cree First Nation (MCFN), to World Heritage Committee (WHC) and International Union for the Conservation of Nature (IUCN) to add WBNP to the List of World Heritage in Danger. Among several concerns, this petition cited oil sands development as an immediate threat to the integrity of WBNP (MCFN, 2014). In response, WHC/IUCN (2017) outlined 17 recommendations for WBNP to address in their Reactive Monitoring Mission Report. Recommendation #9 states the need to "expand the scope of monitoring and project assessments to encompass possible individual and cumulative impacts on the Outstanding Universal Value of the property and in particular the PAD" (WHC/IUCN, 2017, p. 4). In reply, Parks Canada (2019) stated in the Action Report that the Oil Sands Monitoring (OSM) program (previously known as JOSM), led by the federal and provincial governments, is currently assessing the cumulative impacts of oil sands operations on the PAD. In the OSM's 2017-2018 annual report, their first listed objective was to obtain data on baseline conditions (OSM, 2018). Knowledge of these pre-industrial baseline conditions has remained a key and fundamental knowledge gap for monitoring programs, lingering since the 2011 Integrated Oil Sands Environment Monitoring Plan, which was intended to provide guidance to the Joint-Oil Sands Monitoring (JOSM) program (Wrona et al., 2011).

For nearly a decade, paleolimnological analysis of sediment cores from floodplain lakes has been proposed as a promising source to establish pre-industrial baseline concentrations of contaminants conveyed by the Athabasca River (Dowedeswell et al., 2010; Wrona & di Cenzo, 2011). Sediment accumulated by floodplain lakes provides an archive of materials supplied via multiple pathways, including from river floodwaters and the atmosphere, and stratigraphic analyses enable detection of changes in contaminant concentrations from natural and anthropogenic sources (Smol, 1992; Wiklund et al., 2012, 2014; MacDonald et al., 2016). This approach was applied by Wiklund et al. (2012, 2014) in the PAD to quantify sediment metals concentrations before onset of oil sands industrial development, which were otherwise unattainable. They represent the first assessments of temporal changes in metals concentrations, via atmospheric and river pathways, at the PAD using baseline reference conditions established from analyses of radiometrically-dated sediment cores.

Studies have demonstrated that emissive dust, created as a consequence of bitumen mining and upgrading activities, can be detected on the landscape adjacent to the oil sands operations (Landis et al., 2012). Concentrations of metals of concern have been shown to decline with distance from the centre of the oil sands operations in snow, lichen and Athabasca River water (Kelly et al., 2010; Landis et al., 2012; Kirk et al., 2014). Analysis of a sediment core from a lake elevated above the PAD floodplain reveals that oil-sands operations have not yet elevated atmospheric supply of metals to this region, located some 200 km to the north (Wiklund et al., 2012). However, mining operations continue to encroach towards the delta. The newly completed Fort Hills open-pit mine and the proposed Teck Frontier project are reducing the distance of mining activities to the PAD to less than 100 km, which increases the potential for mid-field atmospheric deposition of metals contaminants.

Mining-related contaminants may also enter lakes of the PAD via river floodwaters. Using pre-industrial (pre-1920) baselines derived from analyses of sediment cores from two floodplain lakes, Wiklund et al. (2014) assessed metals concentrations in samples of surficial river-bottom sediment collected by RAMP in the Athabasca Delta. This study demonstrated that the metals concentrations remain within the range of natural variability. The knowledge of baseline metals concentrations provided useful insight and enabled evaluation of RAMP-collected river sediment for the first time for evidence of industry-caused enrichment. While Wiklund et al. (2014)

demonstrated that such approaches could be utilized to interpret metal concentrations in surficial sediment in the Athabasca River and its distributaries, the study was localized to the Athabasca Delta and due to the dynamic nature of fluvial environments, it remains uncertain if recently *collected* surface sediment in the Athabasca River and its distributaries represents recently *deposited* sediment. Lakes, on the other hand, tend to accrete sediment vertically and likely serve as a more informative monitor of recently deposited sediment metals concentrations.

The objective of this study is to assess metals concentrations in recently deposited sediment in lakes from across the PAD using baseline metals concentrations established from the analysis of pre-1920 sediments in a suite of lake sediment cores. To accomplish this, surface sediment was sampled in 2017 from 61 lakes which span the hydrological spectrum of lake water balance conditions across the Peace and Athabasca sectors of the PAD. In the following year, timely re-sampling of a subset of these lakes that flooded in spring 2018 provided opportunity to assess metal concentrations in newly deposited river-supplied sediment from the Peace and Athabasca rivers. RAMP and JOSM river sediment metals concentrations were also assessed using baseline information derived from lake sediment cores. Metals reported in this study include seven priority pollutants listed under the US Environmental Protection Agency`s Clean Water Act (beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn)) and vanadium (V). These metals were chosen since a study by Kelly et al. (2010) showed they possess higher concentrations within snowpack near oil sands developments and in river waters downstream of oil sands development, and were also the suite of metals reported in Wiklund et al. (2014). It is envisioned that the methods used and the framework developed in this study can be adopted by agencies and stakeholders implementing Wood Buffalo National Park’s Action Plan (Parks Canada, 2019) for ongoing monitoring of metals deposition in lakes of the PAD.

Methods

Study area

Water balance of the abundant, shallow lakes in the PAD is influenced by precipitation and runoff, evaporation, and inflow from rivers, which ranges from continuous to episodic (Wolfe et al., 2007). Magnitude and frequency of river flooding to lakes varies with elevation and proximity to the river channel network, which cause lakes in the PAD to span a broad hydrological gradient. Based on these varying factors, lakes have been previously designated into three main hydrological categories (PADPG, 1973; Pietroniro et al., 1999; Wolfe et al., 2007). Lakes receiving (near-)continuous river through-flow are categorized as open-drainage, those periodically receiving river floodwaters during open-water and ice-jam flooding are distinguished as restricted-drainage, and lakes that episodically receive river inputs during ice-jam flooding are deemed closed-drainage. Lakes located in the northern Peace sector, which are mostly closed-drainage, occasionally receive river inputs from the Peace River during ice-jam events, while lakes in the southern Athabasca sector, which are predominantly restricted-drainage with few open- and closed-drainage lakes, receive more frequent floodwaters from the Athabasca River during both the spring melt and open-water seasons.

River floodwaters convey suspended sediments that are predominantly minerogenic, but which vary spatially and temporally in amounts of organic and inorganic material and in grain size (Wiklund et al., 2012). River sediment supplied to floodplain lakes in the Peace and Athabasca sectors of the PAD likely differ in metals signatures, because the Peace and Athabasca rivers flow through different geology. The Peace River naturally flows through sedimentary exhalative deposits (containing Ag, Cu, Pb and Zn) and black shale polymetallic deposits (containing Mo, Ni and Zn) near the town of Peace River, Alberta (Rukhlov, 2011). The Peace River also flows through Devonian carbonate outcrops rich in Zn near Vermilion Chutes, Alberta (Rice, 2003; Pana, 2003; Rukhlov, 2011). North of Fort McMurray, the Athabasca River flows through bitumen deposits containing relatively high concentrations of Ni and V (Speight, 2005). The Athabasca River also flows through several Mississippi Valley-Type and Prairie-Type deposits (containing Au, Ag, platinum group elements and Cu) between Fort McMurray and the PAD (Rukhlov, 2011). The study design outlined in this paper encompasses the spatial extent required to include lakes in the PAD that span the entirety of the hydrologic gradient and their potential metal sources.

Lake sediment core locations

To establish the natural variability of metals concentrations in sediment, cores were retrieved from six floodplain lakes (Figure 1). The lakes were chosen based on proximity to the Peace and Athabasca rivers because they are capable of capturing a natural archive of sediment supplied by river floodwaters. Lakes cored in the Peace sector include PAD 65, which is ~2 km from the Peace River, and PAD 67, which is north of the Peace sector and ~1 km from the Slave River. Because the Peace River contributes the majority of the water to the Slave River (English et al., 1997) and channels conveying outflow from the Athabasca sector experience flow reversals during ice-jams events that flood PAD 67 (e.g., Jasek, 2019), the Peace River is likely the sole source of river water and suspended sediment entering PAD 67, despite its location downstream of the confluence with Lake Athabasca outflow. Sediment cores were collected from four flood-prone lakes in the Athabasca sector, including M7 (located ~1 km from the Athabasca River), PAD 32 (~6.5 km from the Embarras River, a distributary of the Athabasca River), PAD 30 and PAD 31, which are ~0.07 km and ~0.2 km, respectively, from Mamawi Creek, a distributary that conveys Athabasca and Embarras river flow.

Lake surface sediment sampling locations in 2017 & 2018

In September 2017, surface sediment samples were collected from 61 lakes that span the hydrological gradients of the Peace and Athabasca sectors of the PAD (Figure 1). This dataset includes 38 lakes originally sampled by Wolfe et al. (2007). Twenty-seven of the lakes are located in the Peace sector and 34 lakes are in the Athabasca sector. Lakes were categorized into sectors based on their geographic location. Lakes located north of PAD 37 (Jemis Lake - N58˚39’53.7”, W111˚27’12.4”; Figure 1) were considered part of the Peace sector and lakes to the south, including PAD 37, were grouped into the Athabasca sector.

Ice-jam flooding occurred in the Peace and Athabasca sectors in late April and early May of 2018 (Jasek, 2019), which provided excellent opportunity to acquire in July 2018 recently-deposited river-supplied flood sediment from 20 flooded lakes (of the 61 lake set; Figure 1) where it is known the flood-layer of sediment was supplied from one of the Peace or Athabasca rivers. Mapping of floodwater extent in spring 2018 was determined from measurements of lake and river water isotope composition, specific conductivity and observations of sampling personnel (Remmer et al., in review). Collection of surface-sediment from the 20 flooded lakes (8 in the Peace sector, 12 in the Athabasca sector) carefully obtained only the clearly visible surficial flood layer of light grey inorganic sediment at the tops of the cores.

Sediment core and surface sediment collection

Lake sediment cores analyzed in this study were collected from an inflatable kayak or the floats of a helicopter using a Glew (1989) gravity corer (GC) from PAD 31 (GC-4, 38 cm) in September 2010 and a hammer-driven gravity corer (HC) from PAD 32 (HC-3, 46 cm) in June 2015, PAD 65 (HC-1, 54 cm) and PAD 67 (HC-2, 56 cm) in June 2016, and PAD 30 (HC-1, 40 cm) and M2 (HC-1, 40 cm) in July 2016. Lake sediment cores were transported to a field station, sectioned into 1-cm intervals using a vertical extruder (Glew, 1989) and sealed in Whirl-Pak bags. Surface sediment samples were collected in September 2017 and July 2018 using a Mini-Glew gravity corer (Glew, 1991) deployed from a helicopter with floats. In 2017, the top ~1 cm of sediment was immediately removed upon retrieval and sealed into Whirl-Pak bags. In 2018, the uppermost flood layer of distinctive light grey inorganic-rich sediment was immediately removed upon retrieval and sealed into Whirl-Pak bags. All sediment samples were shipped on ice to the University of Waterloo and stored in a dark cold room (4˚C) until analysis.

Radiometric dating of sediment cores

Radiometric dating of sediment cores was conducted at the University of Waterloo Environmental Research (WATER) Laboratory with the use of an Ortec co-axial HPGe Digital Gamma Ray Spectrometer (Ortec #GWL-120-15). Select 1-cm sediment intervals were freeze-dried and loaded into pre-weighed SARSTEDT polypropylene tubes to a height of 3.5 cm. The tubes were capped with a silicone disc, epoxy resin, and left for a minimum of 21 days, allowing ^{222}Rn and its decay products to equilibrate with ^{226}Ra prior to measuring activity of ^{210}Pb, ^{214}Bi, and ^{214}Pb. Chronologies were developed using a Constant of Rate Supply (CRS; Appleby, 2001) model, where the weighted mean of ^{214}Pb and ^{214}Bi activities were used to estimate supported ^{210}Pb activities. Ages were calculated when unsupported ^{210}Pb activity was present in the sample and a linear extrapolation using the calculated sedimentation rate from these measurements were applied to all depths below the presence of any unsupported ^{210}Pb activity.

Analysis of metal concentrations

Freeze-dried sediment from 1-cm intervals of the sediment cores and the lake surface sediment samples were disaggregated and homogenized using a mortar and pestle. Subsamples (~1-g) were submitted to ALS Canada Ltd. (Waterloo, ON) for metals analysis following the method EPA 200.2/6020A, a partial digestion (using HNO_3 and HCl) which liberates metals that may be environmentally available (US EPA, 1998).

RAMP/JOSM river surficial sediment metals data

River-bottom sediment metals concentration data collected by RAMP and JOSM from 2000-2015 were obtained from the RAMP database for seven sampling locations within the Athabasca sector of the PAD (ATR-ER, BPC-1, BPC-2, EMR-1, EMR-2, FLC-1, GIC-1; Figure 1; RAMP, 2018). River-bottom sediment was analysed for metals concentrations following methods SW6010 (2000-2002), EPA 200.3/200.8-ICPMS (2003-2009) and EPA 200.2/6020A (2010-2015), as listed in RAMP and JOSM annual reports (RAMP, 2019).

Numerical analyses

Pre-industrial baselines for sediment metals concentrations were established for the Peace River and the Athabasca River using the pre-1920 strata in the lake sediment cores as a framework to detect enrichment since onset of oil sands mining and production, following methods presented by Wiklund et al. (2012, 2014). Metals were normalized to account for mineralogical and granular variability in lake sediment. Metals preferentially adsorb to fine clay-sized grains (Loring, 1991; Kersten & Smedes, 2002) and since many lakes in the PAD are subject to varying energy conditions, this can lead to variations in metals concentrations independent of any additional supply of metals due to anthropogenic activities. Therefore, positive correlations are expected between metals and normalizing agents, as metal concentrations should be proportionally linked to changes in grain size or mineralogy (Loring, 1991). Using R (R Core Team, 2018) and RStudio (RStudio Team, 2016), Akaike information criterion with a correction for small sample size (AICc) was calculated to determine the best linear model for pre-1920 lake sediment metal concentrations and possible geochemical normalizers (Al, Li, Ti, Zr). Baselines were developed by constructing 95% Prediction Intervals (PI) around linear relations for pre-1920 metals concentrations relative to Al concentrations (as a result of the AICc analysis – see below). Additionally, Al was utilized as the normalizing agent, rather than lithium (Li) as reported in Wiklund et al. (2010, 2014), to maximize the number of river sediment samples collected by RAMP and JOSM that could be assessed on the pre-1920 baselines, as Li has only been reported by RAMP and JOSM since 2010. Lakes used to form the baselines include PAD 65 and PAD 67 for the Peace River and PAD 30, PAD 31, PAD 32, and M7 for the Athabasca River.

For each metal, we ran a heterogeneity of slopes test to determine whether metal-Al linear relations differ for pre-1920 Peace versus Athabasca sector baselines. Heterogeneity of slopes tests were performed using R “car” package (Fox & Weisberg, 2019) in RStudio and α was set to 0.05.

Lake surface sediment (2017, 2018) and RAMP/JOSM (2000-2015) metals concentrations were plotted on sector-specific pre-1920 baselines, along with Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQG) (CCME, 2001), to evaluate the extent of anthropogenic enrichment. If metal concentrations plot within the bounds of the 95% PI, this was used to indicate a common source between recently deposited metals and metals deposited prior to 1920.

Enrichment factors (EF) were used to quantify the degree of enrichment of metals in surface sediment of lakes in the PAD collected in September 2017 and July 2018, relative to pre-1920 baseline metals concentrations. EFs are expressed as a ratio of the measured Al-normalized metal concentrations to the metal concentration that is expected based on its pre-1920 relationship with the normalizing agent (Al). Boxplots were used to present the EFs graphically.

Using R and RStudio, two-sample t-tests ($\alpha = 0.05$) were used to determine if means of the 2017 and 2018 EF values differed significantly. The variance was calculated for each population set to determine whether an equal or unequal (Welch) variance t-test was required.

Results

Sediment core chronologies

Radiometric data were utilized to develop sediment core chronologies for the six lakes that defined pre-1920 metal concentrations (Figure 2). ^{210}Pb activity profiles in lake sediment cores from four lakes (PAD 32, M7, PAD 65 and PAD 67) show a consistent decline of activity with depth. Background (i.e., supported) ^{210}Pb activity for these four lakes was reached between 16-33 cm indicating variable sedimentation rates among lakes. For these lakes, pre-1920 sediments occur below 19, 32, 27 and 21 cm for PAD 32, M7, PAD 65 and PAD 67, respectively. Lakes PAD 30 and PAD 31 display different ^{210}Pb activity profiles with low activity at the bottom of the core, a rise in activity at mid-depth, and a decline in the upper sections of the cores (Figure 2). The decline in the top section of these cores correspond with increasing deposition of inorganic sediment related to the Embarras Breakthrough in 1982, an avulsion which conveyed Athabasca and Embarras river flows into Cree and Mamawi creeks and increased flooding at PAD 30 and PAD 31 (Kay et al., in review). In the cores from PAD 30 and PAD 31, pre-1920 sediments occur below 24 and 26 cm, respectively.

Developing pre-1920 baselines for sector-specific lakes

Baseline linear relations, including 95% prediction intervals (PI), between the metals of interest (Be, Cd, Cr, Cu, Ni, Pb, V, Zn) and Al were established from measurements of the metal concentrations in pre-1920 sediment for the Peace and Athabasca sectors (Figure 3). Akaike information criterion with a correction for small sample sizes (AICc) demonstrated that Al was the best normalizing agent for V in the Peace and Athabasca sectors (Table 1). Aluminum was also deemed the best normalizing agent for five other metals, of the eight studied here, in both the Peace and Athabasca sectors (see Table E1). Positive linear relationships between metals (Peace sector: Be, Cd, Cr, Cu, Ni, Pb, V and Zn; Athabasca sector: Be, Cr, Cu, Ni, Pb, V and Zn) and Al indicated that these metals may be normalized using Al concentrations (Kersten & Smedes, 2002; Table 2). Cadmium was the only metal that did not normalize in the Athabasca sector due to negative relationship with Al, which does not fit the criteria for normalization and was therefore removed from all other analyses.

Based on heterogeneity of slopes tests, slopes of pre-1920 metal-Al regressions differ significantly between the Peace and Athabasca sectors (Table 3). The slopes of all metal-Al relations were steeper for the pre-1920 Peace sector regressions than those for the Athabasca sector (Table 2; Figure 3). Consequently, at higher Al concentrations metals concentrations were elevated in the pre-1920 Peace sector baselines relative to those in the Athabasca sector baselines (Table 2; Figure 3).

Several of the pre-1920 sediment samples from lakes in the Peace sector plot above the Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guideline~~s~~ (ISQG) (Figure 3). Measured concentrations of Cd (48% of samples), Cu (13%) and Zn (38%) plotted above the guidelines. However, no measured metal concentrations in pre-1920 sediment samples from lakes of the Athabasca sector exceeded ISQG.

Assessment of surface sediment metals concentrations from 2017 and 2018 relative to pre-1920 baselines

Surficial lake sediment metals concentrations from September 2017 (Figure 4) and July 2018 (Figure 5) were assessed for evidence of enrichment based on pre-1920 baselines for the Peace and Athabasca sectors. Most metals concentrations from the 2017 dataset plot below the upper 95% PI. This is entirely the case for Be, Cr, Ni, Pb and V. For other metals, concentrations for some samples plot above the upper 95% PI. For the lakes in the Peace sector, this includes Cd (4 of 27 samples; 14.8%), Cu (1 of 27 samples; 3.7%) and Zn (5 of 27 samples; 18.5%). In the Athabasca sector, this includes Be (6 of 34 samples; 17.6%), Cr (1 of 34; 2.9%), Cu (3 of 34 samples; 8.8%), Pb (1 of 34 samples; 2.9%), V (3 of 34 samples; 8.8%) and Zn (11 of 34 samples; 32.4%). Some measurements of Cd (14 of 27 samples; 51.9%), Cu (1 of 27 samples; 3.7%), and Zn (8 of 27 samples; 29.6%) exceed the CCME ISQG in the Peace sector, whereas one measurement of Zn (1 of 34 samples; 2.9%) exceeds the CCME ISQG in the Athabasca sector.

Similar patterns are evident for the metal concentrations in the 2018 flood-supplied surface-sediment samples (Figure 5). All measurements of Be, Cr, Ni, Pb and V plot within the 95% PIs of the pre-1920 baselines, whereas concentrations of Cd, Cu and Zn exceed the 95% PIs in a few samples. In the Peace sector, Cd (2 of 8 samples; 25%) and Zn (1 of 8 samples; 12.5%) plot above the upper 95% PIs. In the Athabasca sector, Cu (1 of 12 samples; 8.3%) and Zn (2 of 12 samples; 16.7%) exceed the upper 95% PIs. Some metal concentrations in the 2018 surface-sediment in the Peace sector also plot above the CCME ISQG, including Cd (7 of 8 samples; 87.5%), Cu (1 of 8 samples; 12.5%) and Zn (5 of 8 samples; 62.5%).

Assessment of RAMP/JOSM river-bottom sediment metals concentrations on pre-1920 baselines

River-bottom sediment metals concentrations collected in the Athabasca Delta by RAMP and JOSM were assessed on pre-1920 baseline metals concentrations defined from Athabasca sector lake sediment cores (Figure 6). The majority of RAMP/JOSM river-bottom sediment samples plot closely along the pre-1920 baselines for Be, Ni, Pb, V and Zn and within their 95% PIs. Some of the RAMP/JOSM surficial river-bottom sediment metals concentrations are enriched relative to the upper limit of the pre-1920 lake-derived 95% PI for Be (1 of 51 samples; 2%), Cr (19 of 51 samples; 37.3%), Cu (1 of 51 samples; 2%), Ni (2 of 51 samples; 3.9%), Pb (2 of 51 samples; 3.9%) and V (1 of 51 samples; 2%). For some metals, particularly Cu, but also Pb and Zn, metals concentrations at low Al values plot below pre-1920 baselines. No RAMP/JOSM metal concentrations plot above the CCME ISQG.

Enrichment factor analysis

Enrichment factors (EF) were calculated as a means of quantifying and summarizing metals concentrations in recently deposited lake sediments relative to the natural range in pre-1920 baseline samples (Figure 7). Note that EFs are not shown for the RAMP/JOSM data because baseline metals concentrations at lower Al values (~4,000-10,000 μg/g) are not adequately characterized for river-bottom sediment. Since many metals concentrations plot below the pre-1920 regression lines, most of the EF interquartiles (25-75th percentile) are below 1 – the implications of which are discussed further below.

For most surficial lake sediment metals, median EF values were close to 1.0, and interquartile (25-75th percentile) ranges were typically narrow and centered near 1.0. However, there were few exceptions. For example, interquartile ranges fall above EF of 1 for Be in the Peace sector 2017 samples, Ni in the Athabasca sector 2017 and 2018 samples, Pb in the Athabasca sector 2018 samples, and Zn in the Athabasca sector 2017 and 2018 samples. Overall, this analysis demonstrated that no metals exceeded an EF of 1.6 and most EF values were ≤1.3. The highest EFs were measured for Cd (1.5) in 2018 within the Peace sector and Zn (1.6) in the Athabasca sector.

For most metals, independent-sample t-tests demonstrated that mean EF values did not differ significantly between samples collected in 2017 and 2018 (Table 6). Exceptions include Be and Pb. For both sectors of the PAD, mean EFs for Be were significantly lower in the 2018 flood-derived sediments than the 2017 surface sediments, and mean EFs for Pb were significantly higher in the 2018 flood-derived sediments (Figure 7).

Discussion

Use of floodplain lake sediment cores to establish sector-specific pre-1920 baseline metals concentrations in the PAD

Lack of knowledge of the natural range of variation in sediment metals concentrations has long hampered ability to accurately assess for evidence of metals pollution in the Athabasca River from oil sands operations (Schindler, 2010). To address this, paleolimnological approaches were used in this study to establish pre-industrial (defined as pre-1920; see Wiklund et al., 2012, 2014) baseline sediment metals concentrations from flood-prone lakes in both the Peace and Athabasca sectors of the PAD.

Comparison of baselines established from Al-normalized metals concentrations in sediments deposited before 1920 demonstrates that Peace River-sourced sediment possessed significantly different and steeper metal-normalizer relations, resulting in some elevated metals concentrations relative to the Athabasca sector, especially for Cu and Zn, but also V – a key metal of concern related to oil sands development (Table 2, 3; Figure 3). This can likely be attributed to the geological differences of their respective drainage basins. For example, the Peace River flows over and alongside several fault lines, near the town of Peace River, Alberta (Rukhlov, 2011). Faults act as pathways for upwelling of mineralized fluids and as a result, several sedimentary exhalative deposits (containing Cu, Pb and Zn) and black shale polymetallic deposits (containing Ni and Zn) have been reported (Rukhlov, 2011). These deposits are likely eroded by the Peace River and incorporated into the natural river sediment load, increasing concentrations of Cu, Ni, Pb and Zn. Additionally, the Peace River flows through ~10 km of Devonian carbonate outcrops, which are located along the riverbank between the upper and lower Vermilion Chutes. Alberta Geological Survey reports have identified that these carbonate outcrops contain high concentrations of Zn (Rice, 2003; Pana, 2003). It has been reported that Cd is often an element or impurity associated with Zn ores (Schwartz, 2000). Therefore, the Zn-rich Vermilion Chutes outcrop may explain why natural concentrations of Cd and Zn plot above CCME ISQG in lakes of the Peace sector (Figure 3). Notably, concentrations of Ni and V are higher in the pre-1920 Peace sector baselines compared to the Athabasca sector baselines despite the Athabasca River flowing through the McMurray Formation, which contains high concentrations of Ni and V (Speight, 2005).

Failure to account for these distinct differences in sediment metals concentrations supplied via the Peace River versus the Athabasca River can lead to erroneous conclusions about pollution from oil sands development. For example, if sediment supplied by the Peace River to floodplain lakes in the PAD were evaluated on the pre-1920 baseline of the Athabasca sector lake sediment cores, many of the samples would be erroneously identified as being enriched. While some of these metals (Cd, Cu and Zn) in both the 2017 and 2018 datasets possess concentrations above

CCME ISQG, metals concentrations indeed fall within the range of natural variation defined for the sediment conveyed by the Peace River. Mineralogical deposits listed above provide just a few of the potential sources that may lead to differences in the observed metal concentrations in lake sediment supplied by the Peace and Athabasca rivers. Further analysis of source contribution of metals upstream is required to more fully explain the differing metal-Al relations observed in this study.

The six collective lake sediment cores used to establish baseline metals concentrations are deemed sufficient to characterize metal-Al relations in lake sediment. The range of most Al concentrations captured by the two lake sediment cores (PAD 65, PAD 67) in the Peace sector and the four lake sediment cores (M7, PAD 30, PAD 31, PAD 32) in the Athabasca sector span ~10,000-18,000 μg/g (Figure 3). This range is adequate to capture the Al concentrations sampled from surficial sediments collected in 2017 from lakes spanning the hydrological gradient in the PAD and the 2018 flood-derived deposits. For the Athabasca sector, however, metal-Al relations are poor to weak for Cd, Cu and Ni, which impairs the ability to detect enrichment of these metals (Table 2). Fortunately, relations are strong for V, a metal of concern with respect to oil sands development.

Assessment of 2017 versus 2018 surficial lake sediment datasets

Analysis of two surficial lake sediment datasets provided an effective approach to assess the degree of metals enrichment across the PAD. The 2017 dataset included ~1 cm thick surficial sediments obtained from 61 lakes that span the full spectrum of hydrological conditions (Wolfe et al., 2007). Sedimentation rates differ substantially across this hydrological gradient, thus, the time intervals captured by those samples vary among lakes, which may include flood and non-flood conditions. In contrast, the 2018 dataset captures a flood event and represents a snapshot of metals concentrations in spring floodwaters. As suggested by Kelly et al. (2010), metals accumulated within snowpack in the oil sands region (Kirk et al., 2014) become mobilized during the spring freshet and move from the landscape to the Athabasca River. Despite this, t-tests demonstrated that EFs were not significantly elevated in 2018 flood-derived sediment compared to EFs in the 2017 dataset, except for marginal (~7-8%) increases of Pb EFs. However, Pb EFs rose in *both* the Peace and Athabasca sectors and thus are likely not related to oil sands activities. Furthermore, the spatially comprehensive 2017 dataset along with the opportunistic sampling of the 2018 flood deposits provides strong evidence that oil sands have not yet caused significant enrichment in recently deposited lake sediment relative to the pre-1920 baselines.

Assessing vanadium concentrations in surficial lake sediments in the PAD

Vanadium was scrutinized because it has been identified as an oil sands indicator metal for contamination (Gosselin et al., 2010; Wiklund et al., 2014), and is elevated in aerial deposition surrounding mining and bitumen processing activities (Kirk et al., 2014; Cooke et al., 2017; Klemt, 2018). Cooke et al. (2017) demonstrated from analyses of lake sediment cores that despite technological improvements to reduce emissions, modern enrichment of V remains clearly detectable in near- (~8x background) and mid-field (~4x background) sediment of upland lakes, relative to pre-1900 concentrations. Atmospheric deposition of V (and other metals) may be a more important pathway to lakes within a 50 km radius of the oil sands development than transport by river floodwaters. Results reported by Klemt (2018) reinforced this notion, as analyses of sediment cores from floodplain lakes along the Athabasca River adjacent to oil sands mining and processing facilities demonstrated that enrichment of V was detected in weakly flood-influenced sediment indicative of aerial deposition, but was not enriched in river-supplied lake sediment. Similarly, river-supplied sediment to Athabasca sector lakes in 2018 demonstrated no enrichment (mean V EF of 1.0 ± 0.04, 1 SD; range 0.9-1.1) relative to pre-1920 concentrations (Figure 7). Although near- to mid-field (0-50 km) atmospheric-sourced contamination is clearly detectable (Cooke et al., 2017; Kirk et al., 2014; Klemt, 2018), there is accumulating evidence of no near or downstream river contamination of V (Wiklund et al., 2014; Klemt, 2018; *this study*).

It is postulated that a few factors may be inhibiting the detection of V enrichment in near and downstream floodplain lakes. The natural sediment load of V (and other metals) in the Athabasca River may be overwhelming and masking anthropogenic contributions. In the Athabasca River, 6,350,000 tonnes of suspended sediments are estimated to pass the Embarras gauging station annually (Conly et al., 2002). Given the mean V concentration (20.5 g/tonne) from the

RAMP/JOSM datasets (Figure 6), the total estimated annual transport of V by the Athabasca River is ~130 tonnes. Based on the estimated 1,594 kg (1.6 tonnes) of V emissions reported by Kirk et al. (2014) for winter 2012 (67 days), ~9 tonnes of V were emitted by oil sands operations to the landscape that year. Even if all emissive concentrations of V from oil sands operations were conveyed to the Athabasca River, this would only account for ~7% of total annual V in the sediment load of the river. It is, however, unlikely that all atmospherically-deposited V is delivered to the river.

Retention of atmospherically-sourced V in the catchment could also affect concentrations conveyed to the Athabasca River. A study calculated that terrestrial retention of V for a relatively small acidified catchment in Ontario was 86% (Landre et al., 2010). In non-acidic conditions and within a much larger catchment, retention of V (and other metals) would likely be higher. Therefore, if this conservative retention coefficient is applied to the Athabasca oil sands region, without accounting for direct deposit of V to the river, it is estimated that only ~1% of annual V load in the Athabasca River would be derived from oil sands operations. These rough calculations indicate that it is important to not overlook the substantial natural loads of metals carried by the Athabasca River and needs to be considered when assessing oil sands pollution within river sediment.

Assessing for metals pollution in river bottom sediments in the PAD

The establishment of pre-1920 baseline metals concentrations constructed from lake sediment cores enabled cursory assessment of 15 years of RAMP and JOSM river sediment samples (Figure 6). This included an additional 10 years that were not assessed by Wiklund et al. (2014) due to limitations of the selected normalizing agent. Analysis of these 15 years of data resulted in no significant elevated concentrations measured in most metals relative to pre-1920 concentrations, consistent with the findings reported by Wiklund et al. (2014). However, a substantial number of samples (36 of 51; 70.6%) were enriched in Cr relative to pre-1920 concentrations (Figure 6). A potential source of this enrichment may come from elevated concentrations of chromite that have been reported in an alluvial sand and gravel pit in Whitecourt (Alberta), which the Athabasca River flows adjacent to (Mudaliar et al., 2007). The sediment from this location may have been transported along the river bed and sampled by RAMP/JOSM.

Although our data indicate no enrichment of metals (except Cr) in the RAMP/JOSM samples (2000-2015), there are challenges to interpreting these results. Our assessments of enrichment of the RAMP/JOSM data are inhibited by what appears to be steeper metal-Al relations at the low Al concentrations typical of river-bottom sediment, which are outside the range of our lake-derived pre-1920 baseline concentrations. This would imply that our baselines for the lower Al concentrations may be over-estimating natural river-bottom metals concentrations (leading to apparent EF values below 1), which is most evident for Cu but also the case for many of the other metals. Clearly, these results demonstrate that baselines constructed from lake sediment in this study are best applied to lake sediment, which vertically accrete as opposed to the unknown time-frame represented by river-bottom sediment (Timoney & Lee, 2011). Therefore, we advocate that sampling the fine-grained fraction of flood sediment deposited in floodplain lakes is a more sensitive, real-time approach to assessing metals concentrations of river suspended sediment.

Conclusions and Recommendations

Scientific research is needed to inform environmental monitoring, and here, clearly defined research objectives have provided direction for future aquatic monitoring efforts using sediment from floodplain lakes in the PAD. In the absence of long-term monitoring data, the use of paleolimnological approaches have demonstrated to be an effective method in characterizing natural concentrations of metals in lake sediments, which are required to assess contemporary metals concentrations. Results demonstrate little to no enrichment of metals concentrations derived from oil sands operations in recently-deposited sediment in lakes of the PAD (Figure 7). This includes samples collected in 2018, exclusively conveyed by river floodwaters, which did not differ in metals concentrations from surface sediment obtained in 2017 from a broader hydrological network of lakes. The lack of enrichment in these samples, including an oil sands indicator metal such as V, provides strong evidence that little to no oil sands-derived metals contamination is yet detectable in lake sediments of the PAD (Figure 7).

The foundation of a successful sediment monitoring program requires knowledge of baseline metals concentrations and natural variation to accurately detect environmental changes due to anthropogenic activities (Smol, 1992; Lindenmayer & Likens, 2009; Dowdeswell et al., 2010; Wrona & di Cenzo, 2011). The development of this framework using lake sediment cores to construct pre-1920 metals concentrations was intended to build the foundation for continued aquatic sediment monitoring in the PAD, as a contribution to implementing Wood Buffalo National Park's Action Plan (Parks Canada, 2019). An important discovery is the need for Peace and Athabasca sector-specific baselines due to different metal-normalizer relations. The full 61-lake dataset is spatially comprehensive, spans the range of hydrological conditions and might be considered to be re-sampled every 6 years to track ongoing changes as the oil sands industry expands closer to the PAD. Metals concentrations exceeded CCME ISQG for protection of aquatic life only in the Peace sector lakes, including in sediments deposited before 1920, a finding that implies future potential contamination of anthropogenic sources could have greatest effects in those lakes. Given that the main concern is contamination from the oil sands via the Athabasca River, it may be preferential to sample lakes in the Athabasca sector more frequently (e.g., every 3 years). If coupled with routine water isotope monitoring of hydrological conditions (see Remmer et al., in review), then opportunistic lake surface-sediment sampling should be conducted soon after flood events to capture freshly deposited river-derived sediment, as was done in July 2018, to provide a snapshot of spring river metals concentrations.

Table 1. Results of Aikaike information criterion with a correction for small sample size (AICc) to determine the best pre-1920 vanadium-normalizer model for the Peace and Athabasca sectors.

Sector	Normalizer	AICc coefficient	Delta AICc	AICc weight
Peace	Al	280.62	0	1
	Li	344.86	64.24	5.20×10^{-26}
	Zr	436.79	156.17	4.90×10^{-28}
	Ti	455.12	174.5	2.59×10^{-44}
Athabasca	Al	346.32	0	1
	Li	462.76	116.44	1.12×10^{-14}
	Ti	472.09	125.77	1.22×10^{-34}
	Zr	547.05	200.73	1.28×10^{-38}

Table 2. Regression equations, R-squared and P-values for pre-1920 baselines metal-Al linear regressions for the Peace and Athabasca sectors.

Sector	Metal	Regression equation	R-square	P-value
Peace	Be	$y = 4.985x10^{-5}x + 0.1244$	0.88	$< 2.2x10^{-16}$
	Cd	$y = 3.242x10^{-5}x + 0.187$	0.84	$< 2.2x10^{-16}$
	Cr	$y = 1.661x10^{-3}x + 1.4117$	0.99	$< 2.2x10^{-16}$
	Cu	$y = 1.579x10^{-3}x + 8.2416$	0.95	$< 2.2x10^{-16}$
	Ni	$y = 2.007x10^{-3}x + 9.1078$	0.87	$< 2.2x10^{-16}$
	Pb	$y = 6.66x10^{-4}x + 4.5405$	0.78	$< 2.2x10^{-16}$
	V	$y = 3.095x10^{-3}x + 2.9212$	0.95	$< 2.2x10^{-16}$
	Zn	$y = 6.823x10^{-3}x + 19.372$	0.93	$< 2.2x10^{-16}$
Athabasca	Be	$y = 3.485x10^{-5}x + 0.3024$	0.52	$< 1.8x10^{-11}$
	Cd	$y = -1x10^{-5}x + 0.5025$	0.04	$1.29x10^{-1}$
	Cr	$y = 1.387x10^{-3}x + 3.2223$	0.91	$< 2.2x10^{-16}$
	Cu	$y = 2.776x10^{-4}x + 21.013$	0.04	$1.29x10^{-1}$
	Ni	$y = 6.217x10^{-4}x + 16.903$	0.05	$7.1x10^{-2}$
	Pb	$y = 3.412x10^{-4}x + 7.6384$	0.28	$7.22x10^{-06}$
	V	$y = 2.352x10^{-3}x + 6.167$	0.84	$< 2.2x10^{-16}$
	Zn	$y = 2.194x10^{-3}x + 52.131$	0.2168	$1.06x10^{-4}$

Table 3. Summary of results of a series of tests for heterogeneity of slopes used to determine if the regression slopes differ significantly between pre-1920s relations for metals-aluminum concentrations in sediment cores of lakes from the Peace versus Athabasca sectors of the delta. The table presents type III sum of squares for the interaction term, degrees of freedom, F-test statistic and P-value for each metal investigated. The sum of squares and degrees of freedom are sectors, residuals.

Metal	Sum of Squares	Degrees of Freedom	F-value	P-value
Be	0.02767, 0.3855	1, 124	8.9	$3.44\text{x}10^{-3}$
Cd	0.2257, 0.5608	1, 124	49.91	$1.02\text{x}10^{-10}$
Cr	9.237, 52. 79	1, 124	21.7	$8.1\text{x}10^{-6}$
Cu	208.08, 383.55	1, 124	67.27	$< 2.54\text{x}10^{-13}$
Ni	236.1, 1461	1, 124	19.98	$1.74\text{x}10^{-5}$
Pb	12.97, 121.8	1, 124	13.21	$4.07\text{x}10^{-4}$
V	67.87, 429.2	1, 124	19.61	$2.06\text{x}10^{-5}$
Zn	2635, 4653	1, 124	70.21	$< 9.73\text{x}10^{-14}$

Table 4. Summary of results for a series of two-sample t-test to determine if enrichment factors differed significantly between 2017 and 2018 surficial sediment metal concentrations by sector. Table presents t-value, degrees of freedom (df), mean of 2017 and 2018 lake sediment samples, and p-value.

Sector	Metal	t-value	df	2017 mean	2018 mean	p-value
Peace	Be	5.51	17.8	1.04	0.926	$3.33*10^{-5}$
	Cd	-0.625	9.4	0.957	1.01	0.55
	Cr	-1.68	10.7	0.95	0.976	0.122
	Cu	0.36	33	0.973	0.962	0.721
	Ni	1.85	33	0.925	0.881	0.073
	Pb	-3.03	17.5	0.923	0.998	$7.32*10^{-3}$
	V	1.42	33	0.992	0.969	0.164
	Zn	2.01	15.7	1.03	0.953	0.062
Athabasca	Be	4.79	25.06	1.07	0.962	$6.33*10^{-5}$
	Cd					
	Cr	0.15	19.9	0.98	0.977	0.882
	Cu	-1.06	26.2	0.976	1.02	0.298
	Ni	1.16	23.5	1.11	1.07	0.259
	Pb	-3.10	31.2	0.98	1.05	$4.07*10^{-3}$
	V	$-3.86*10^{-3}$	25.8	1.01	1.01	0.9997
	Zn	1.68	33.8	1.13	1.08	0.102

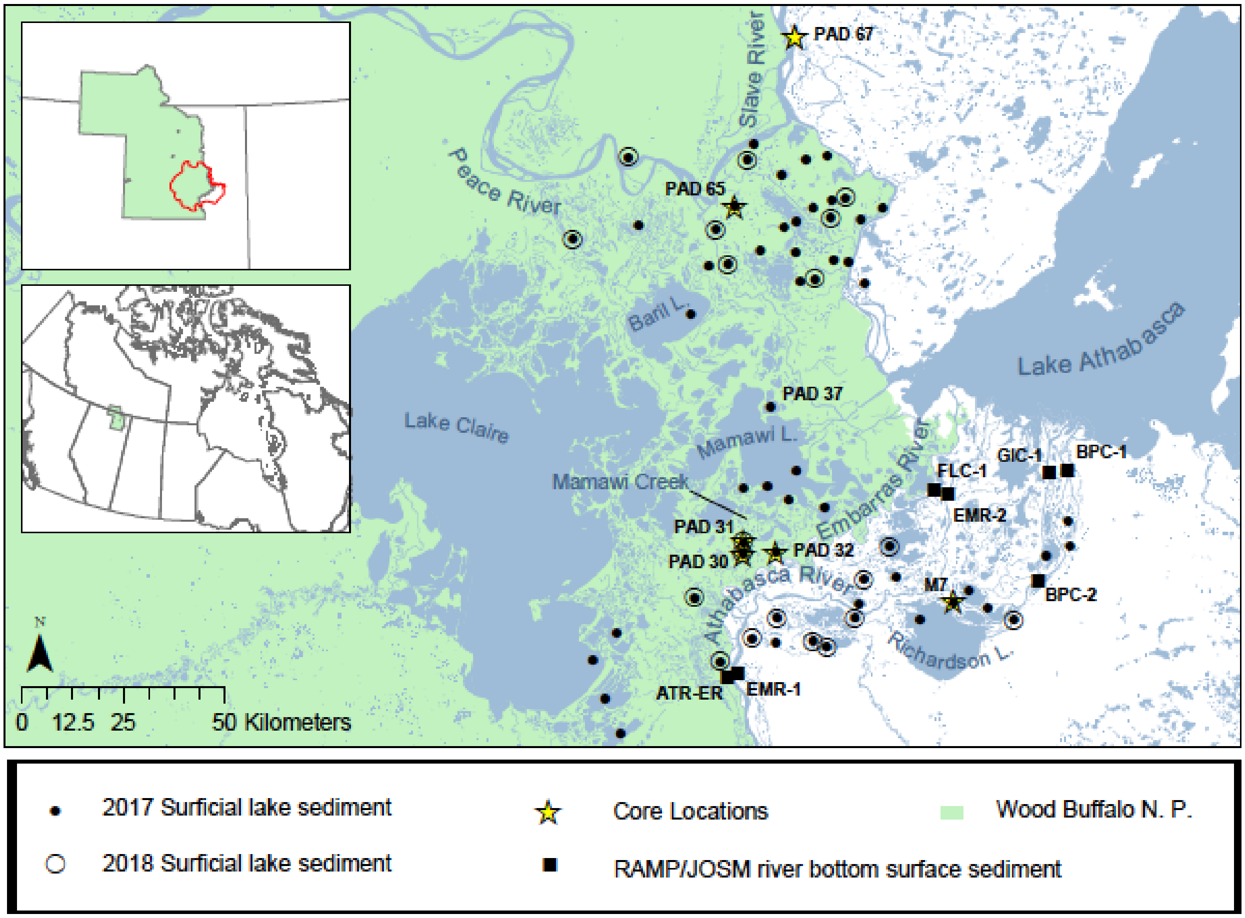

Figure 1. Map of the Peace-Athabasca Delta (PAD) and sampling locations. Lake labels are referred to in the text.

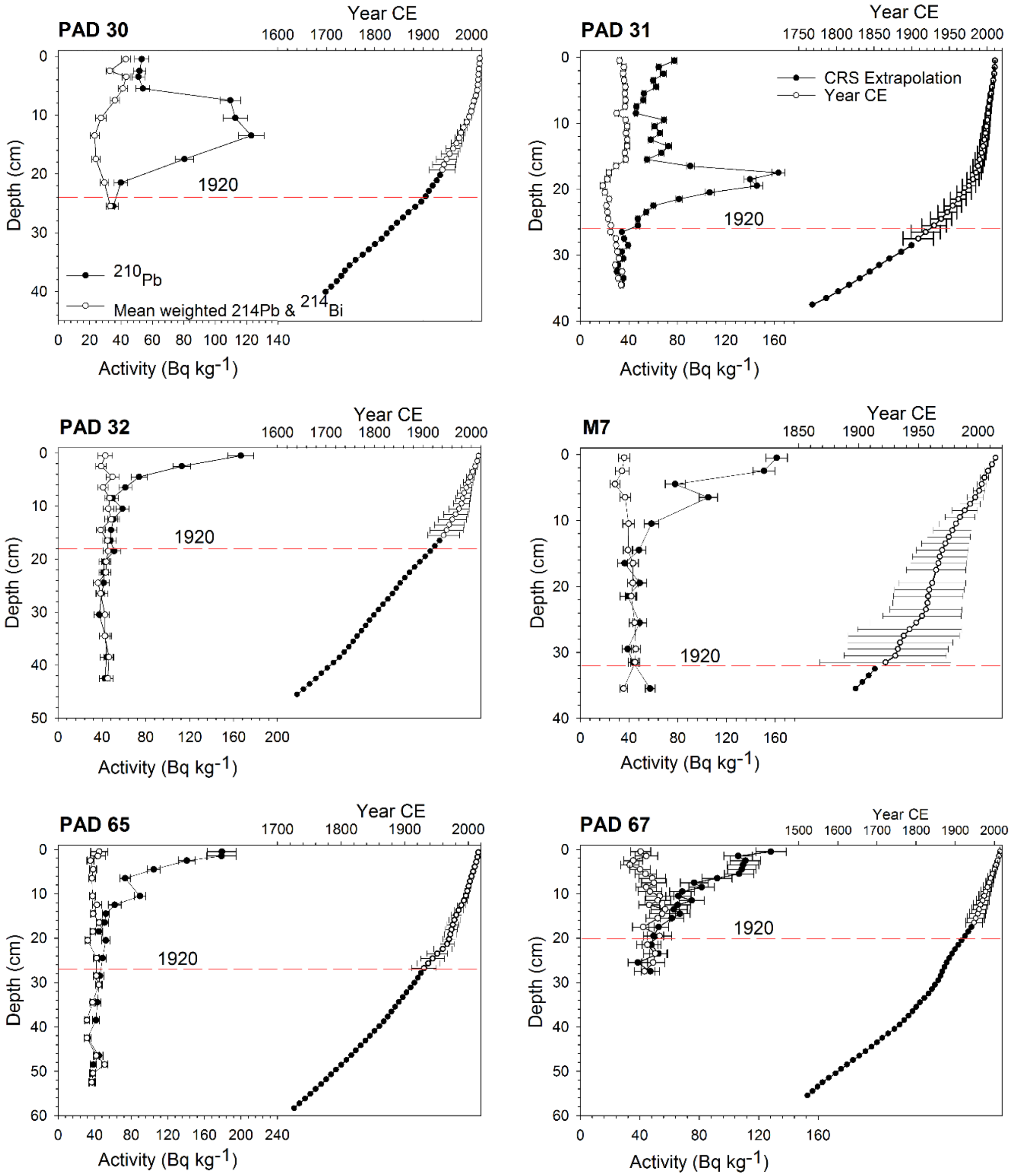

Figure 2. Activity profiles versus depth for ^{210}Pb (closed circles) and mean weighted ^{214}Pb and ^{214}Bi (open circles) for sediment cores included in the pre-1920 baselines. Age-depth profiles for measured ^{210}Pb (open circles) with error bars and extrapolated CRS model dates (closed circles).

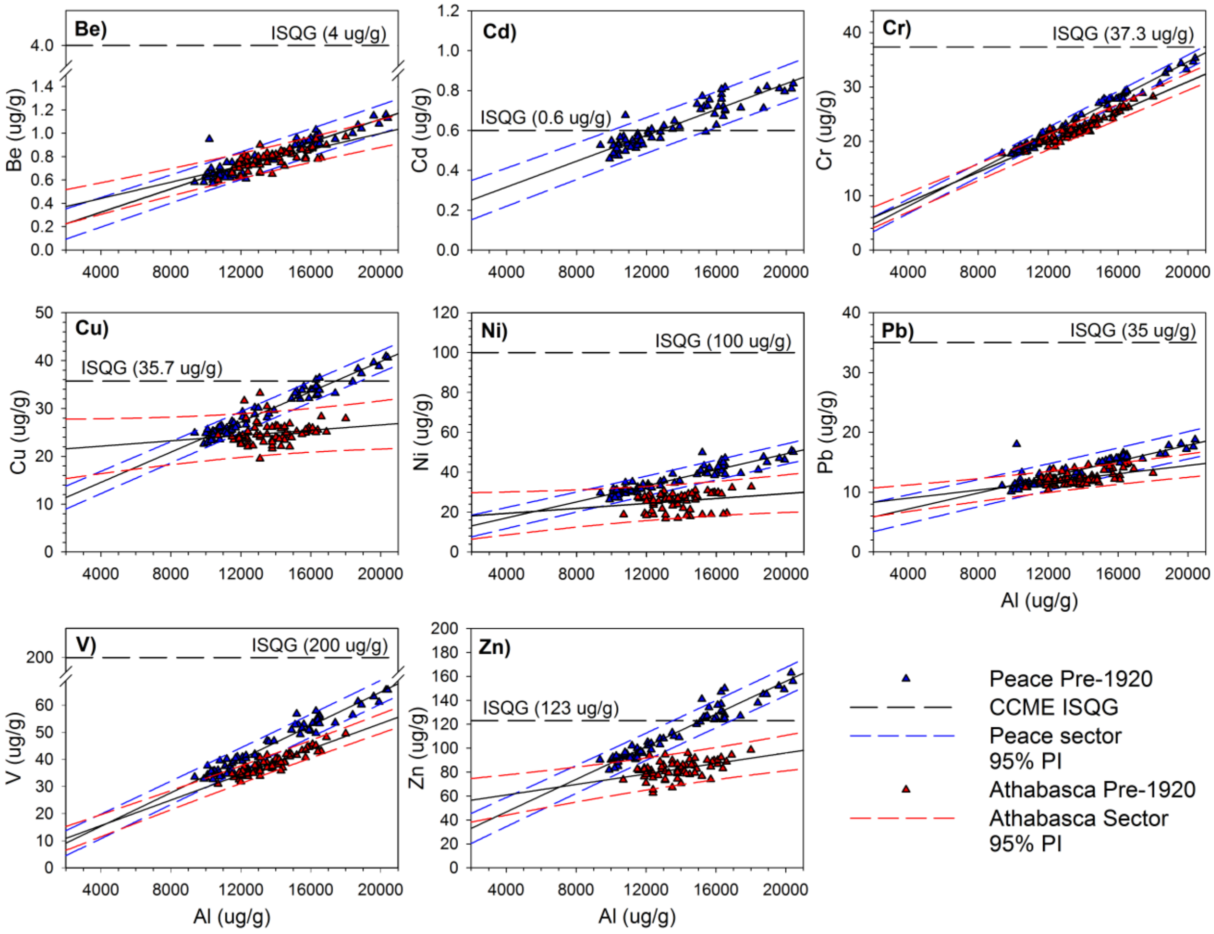

Figure 3. Cross-plots demonstrating the relationship between pre-1920 metal concentrations and the normalizing agent (Al). The Peace River 95% PI (blue dashed lines) and the regression line are based on the pre-1920 measurements of metals from PAD 65 and PAD 67 (blue triangles). The Athabasca River 95% PI (red dashed line) and regression line is based on the pre-1920 measurements of metal concentrations from PAD 30, PAD 31, PAD 32, and M7 (red triangles). Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQG) plotted on y-axis denote the guideline concentrations for the metal of concern.

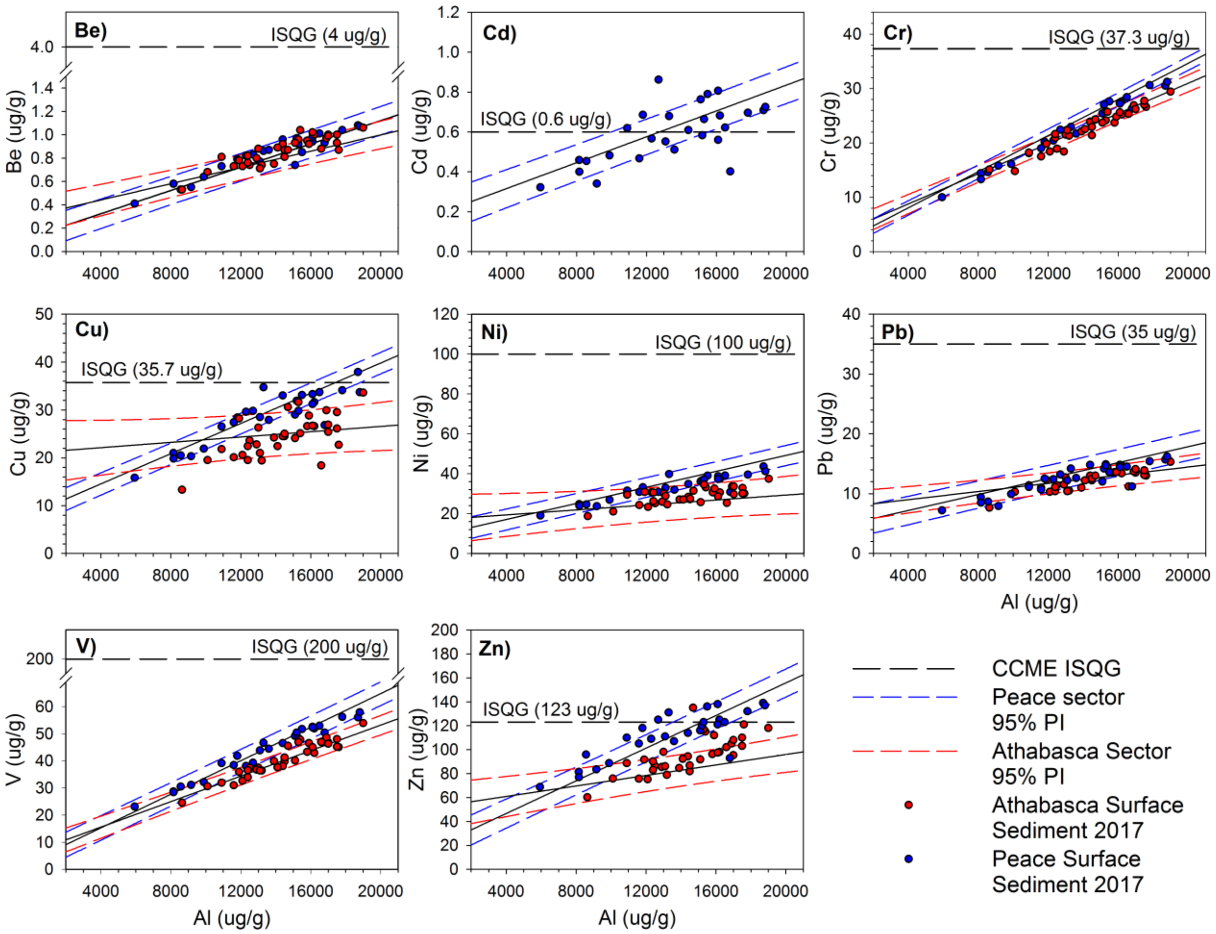

Figure 4. Surface sediment metal concentrations collected in September 2017 from Peace sector lakes (blue circles) and Athabasca sector lakes (red circles) plotted on the pre-1920 linear regressions and 95% PIs. Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQG) plotted on y-axis denote the guideline concentrations for the metal of concern.

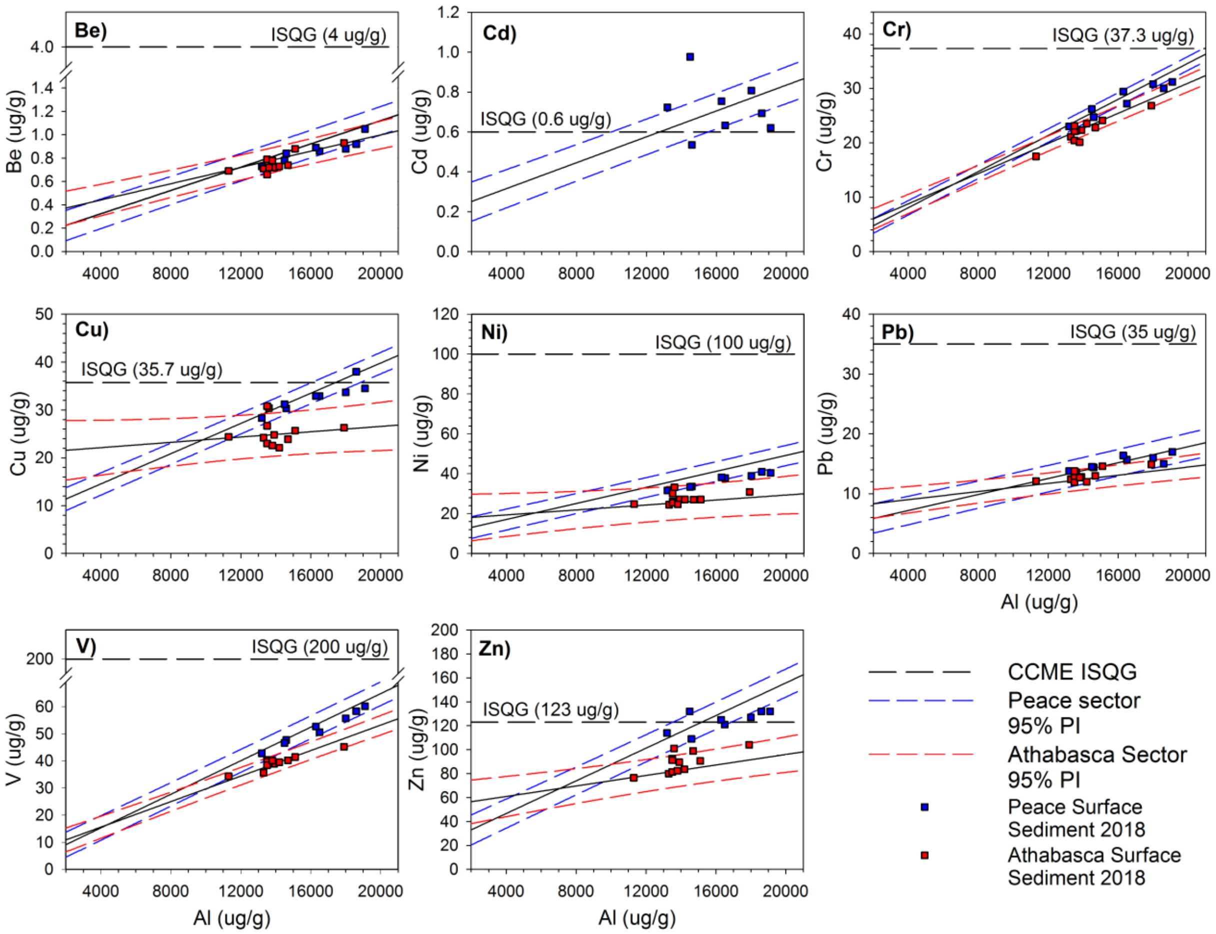

Figure 5. Surface sediment metal concentrations collected in July 2018 after spring flooding from Peace sector lakes (blue squares) and Athabasca sector lakes (red squares) plotted on the pre-1920 linear regressions and 95% PIs. Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQG) plotted on y-axis denote the guideline concentrations for the metal of concern.

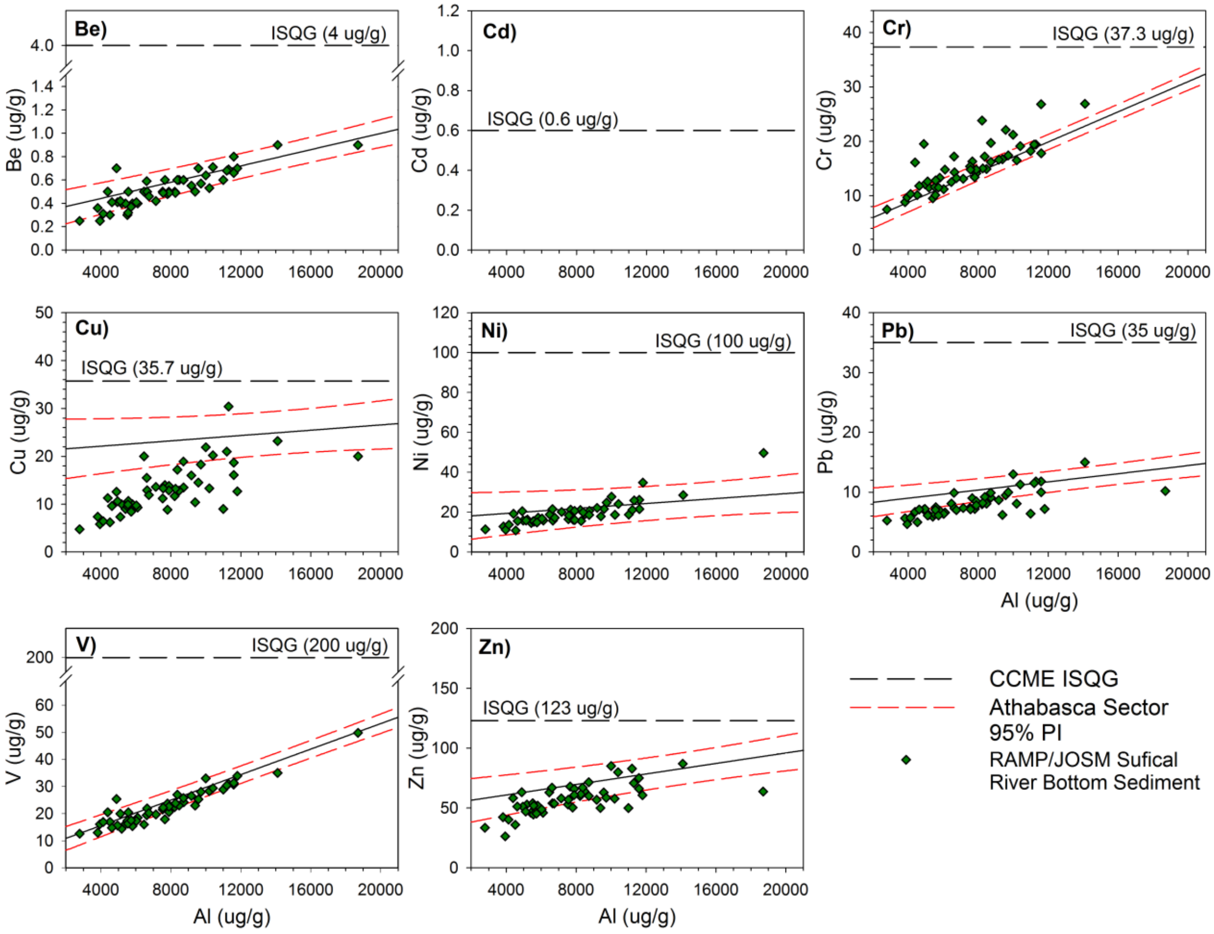

Figure 6. River-bottom sediment metals concentrations collected by RAMP and JOSM from 2000-2015 (RAMP, 2019). Athabasca sector locations (ATR-ER, BPC-1, BPC-2, EMR-1, EMR-2, FLC-1, GIC-1) denoted by green diamonds plotted on the pre-1920 linear regressions and 95% PIs. Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guidelines (ISQG) plotted on y-axis denoting the guideline concentrations for the metal of concern.

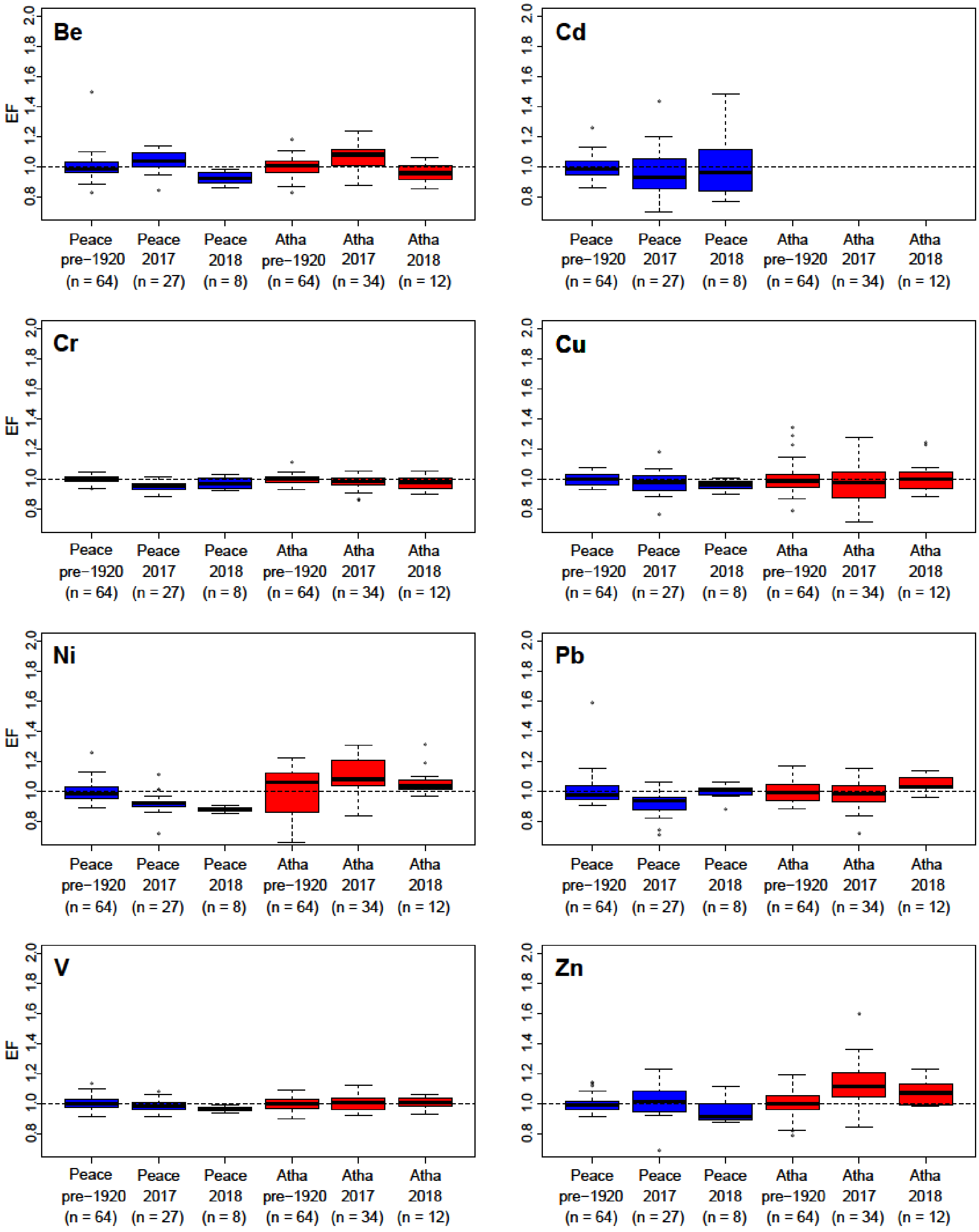

Figure 7. Enrichment factors for metals (Be, Cd, Cr, Cu, Ni, Pb, V and Zn) relative to sector specific pre-1920 baseline concentrations. Enrichment factors were created for Peace sector (PS; blue) surface sediment and Athabasca sector (AS; red) surface sediment from 2017 and 2018 sampling campaigns. Black dashed line at an EF value of 1 (indicating no enrichment).

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Chapter 3: Conclusions

Key findings and relevance of research

This study has linked aspects of scientific research and environmental monitoring and in doing so, has developed and applied a framework to assess for metals contamination in sediment of lakes of the Peace-Athabasca Delta (PAD). The establishment of baseline (pre-1920) conditions from lake sediment cores has provided the ability to assess lake and river sediment for metal pollution from upstream industrial developments. These methods provide the foundation to evaluate metal contamination in sediment for the past, present and future. The development of this monitoring framework has addressed the WHC/IUCN's Recommendation #9 that states the need to "expand the scope of monitoring and project assessments to encompass possible individual and cumulative impacts on the Outstanding Universal Value of the property and in particular the PAD" (WHC/IUCN, 2017, p. 4)

Key differences in normalized-metals relations between the Peace and Athabasca sectors has led to the development of sector specific baselines enabling more accurate assessment of metals concentrations conveyed by the Peace and Athabasca rivers. Statistical analyses indicate that normalized-metals relations between the Peace and Athabasca sectors are significantly different. These differences are likely caused by the differing geological terranes associated with the drainage basin of each river. The Peace River flows over several sedimentary exhalative deposits, whereas, the Athabasca River flows through the bitumen-rich McMurray Formation. Identifying these key differences in normalized-metals relations between sectors is an important contribution for future assessment of metals concentrations because if sediment metals concentrations from lakes from the Peace sector were plotted on Athabasca baselines, for either Cu, Ni, V or Zn, results could easily be misinterpreted as enriched. This is an important consideration for future monitoring, because Ni and V are metals associated with oil sands contamination (Wiklund et al., 2014; Klemt, 2018). Therefore, the misinterpretation of either Ni or V could lead to erroneous conclusions that oil sands operations are contaminating the PAD.

The development of sector-specific baselines has provided long-needed methods to accurately assess for evidence of contamination in sediment of lakes and rivers within the PAD. Assessment of surficial lake sediment collected in 2017 and 2018, and RAMP/JOSM river bottom sediment for metals concentrations, has demonstrated that few measured samples are enriched relative to pre-1920 baseline metal conditions. The enrichment of Cd and Zn in the Peace sector, Zn in the Athabasca sector, and Cr in river bottom sediment have all been linked to possible mineral deposits located along the rivers (processes which may not have been fully captured by the pre-1920 sediment concentrations) and therefore are likely eroded into river sediment loads (Godfrey, 1985; Rice, 2003; Pana, 2003; Mudaliar et al., 2007). For most surficial lake sediment metals, median EF values were close to 1.0, and interquartile (25-75th percentile) ranges were typically narrow and centered near 1.0. This provides confidence that metals contamination from oil sands operations are currently not yet detectable in the PAD, consistent with results reported by Wiklund et al. (2012, 2014).

It is envisioned that the methods used and framework developed in this study can be adopted by current and future monitoring agencies to continue assessing metal concentrations for ongoing monitoring, as proposed by Wood Buffalo National Park (Parks Canada, 2019). Collaboration has been cited as one of the fundamental underlying factors of a successful monitoring program (Lindenmayer & Likens, 2010). Therefore, the doors of Wilfrid Laurier University and University of Waterloo remain open for continued collaboration in monitoring the Peace-Athabasca Delta to ensure its outstanding universal value is maintained.

Future recommendations

The foundation of a successful sediment monitoring program requires knowledge of baseline metal concentrations and natural variation to accurately detect environmental changes due to anthropogenic activities (Smol, 1992; Lindenmayer & Likens, 2009; Dowdeswell et al., 2010; Wrona & di Cenzo, 2011). The development of this framework using lake sediment cores to construct pre-1920 metal conditions was intended to build the foundation for continued aquatic sediment monitoring in the PAD, as a contribution to implementing Wood Buffalo National Park's Action Plan (Parks Canada, 2019). An important discovery is the need for Peace and Athabasca sector-specific baselines due to different metal-normalizer relations. The full 61-lake dataset is spatially comprehensive, spans the range of hydrological conditions and might be considered to be re-sampled every 6 years to track ongoing changes as the oil sands industry expands closer to the PAD. Metals concentrations exceeded CCME ISQG for protection of aquatic life only in the Peace sector lakes, including in sediments deposited before 1920, a finding that implies future potential contamination of anthropogenic sources could have greatest effects in those lakes. Given that the main concern is contamination from the oil sands via the Athabasca River, the Athabasca sector lakes may be preferential to sample those lakes more frequently (e.g., every 3 years). If coupled with routine water isotope monitoring of hydrological conditions (see Remmer et al., in review), then opportunistic lake surface-sediment sampling should be conducted soon after flood events to capture freshly deposited river-derived sediment, as was done in July 2018, to provide a snapshot of spring river metals concentrations.

As mining operations continue to expand northward, the potential for atmospheric pollution is increasing in the Peace-Athabasca Delta. Additional baseline conditions for atmospherically-sensitive lakes need to be developed to obtain a spatially comprehensive framework for atmospheric pollution. Previously, a single baseline has been constructed for a closed-drainage lake elevated above the floodplain in the Peace sector (see Wiklund et al., 2012). Lake 'PAD 18', utilized by Wiklund et al. (2012), only receives hydrological inputs from precipitation and catchment runoff unlike most other lakes in the PAD (Figure 10; Yi et al., 2008). This lake serves as a recorder of airborne metals pollution because metals accumulating in the sediment will be solely derived from atmospheric deposition and catchment erosion (Wiklund et al., 2012).

PAD 18 was originally integrated into the 2018 surface sediment sampling campaign. Analysis of metal concentrations relative to pre-1920 floodplain lake-derived baselines demonstrated that normalized-metal relations for Cd, Cu, Ni, Pb and Zn plot considerably lower than lakes receiving periodic river floodwaters (Figure 11). This confirms that different sources are supplying metals to floodplain lakes versus those elevated above the floodplain. Thus, unique baselines are required to monitor atmospheric contamination. The addition of separate baselines capable of detecting aerial deposition will provide a more comprehensive and complete monitoring framework that encompasses the two major pathways that may lead to the accumulation of metals contaminants in lakes of the PAD.

The Athabasca oil sands region is influenced by occasional south-north winds along the Athabasca River corridor meaning that the expansion of mining operations northward along the Athabasca River is increasing the potential for atmospheric pollution to reach the PAD (Cho et al., 2014). As potential for aerial pollution increases, it is recommended that a transect of lakes, in the prevailing wind direction, should be cored to develop pre-1920 baselines and to assess for recent atmospheric-derived metals contamination. Currently, ‘climate-sensitive’ lakes are being collected for paleohydrological reconstructions (Katie Brown, MSc in progress, University of Waterloo). These lakes will likely be uninfluenced by river floodwaters and could theoretically be used to establish additional atmospherically-sensitive baselines to expand the transect from PAD 18.

Although no considerable enrichment of metals is detected in floodplain lakes within the PAD, studies have demonstrated that oil sands operations are indeed releasing metal contaminants to the surrounding environment (Kelly et al., 2010; Kirk et al., 2014; Klemt, 2018). Metals deposited on the landscape surrounding oil developments may be moving overland slowly or be retained for considerable periods (Dillon & Evans, 1982; Blais & Kalff, 1993; Huang et al., 2015), resulting in metal contaminants not entering the aquatic environment for an extensive amount of time (Blais & Kalff, 1993). Further investigation is required to understand the catchment erosion that supplies metals to the river system. More specifically, studies could quantify the concentrations of contaminants conveyed to rivers during spring freshet, to better understand the role of the Athabasca River in the transportation of metals to the PAD.

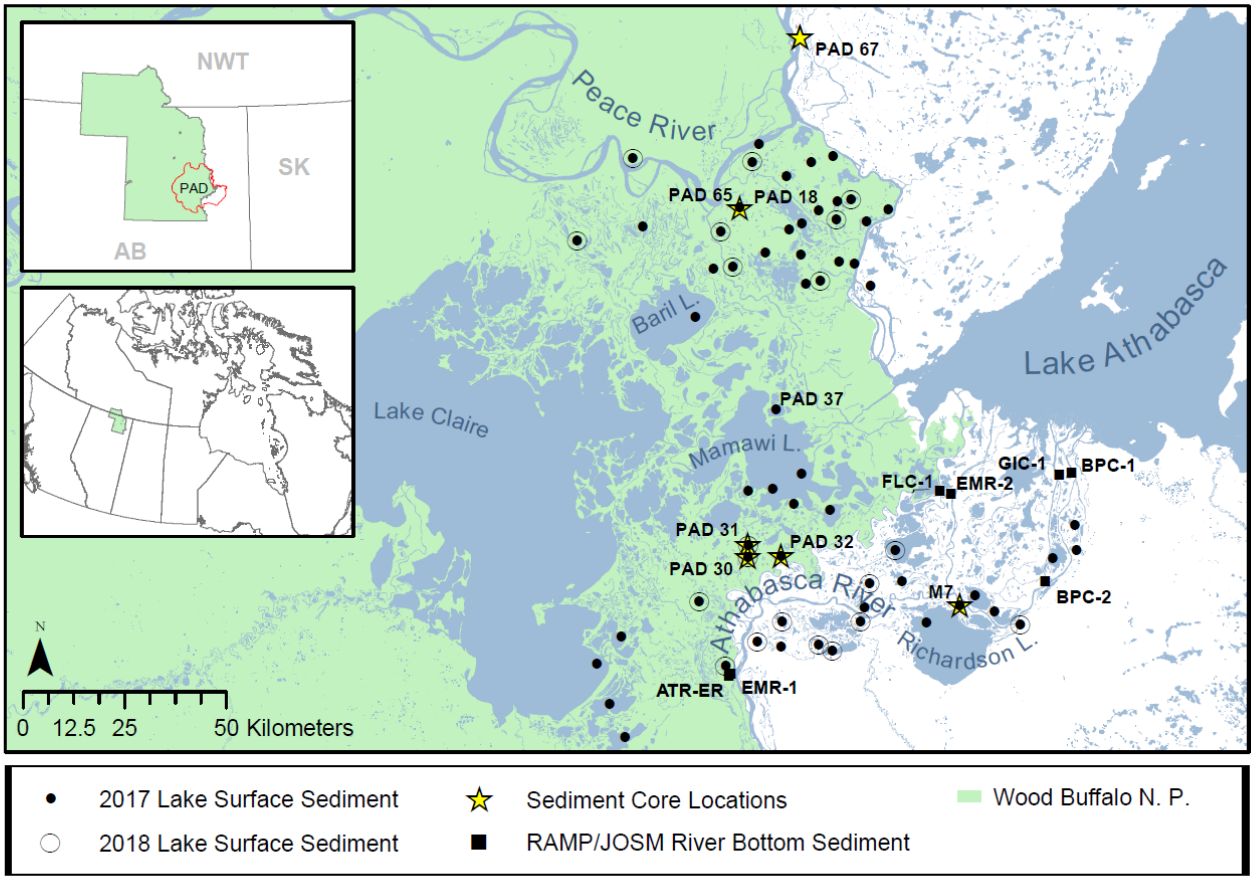

Figure 8. Map of the Peace-Athabasca Delta (PAD) and sampling locations with the addition of PAD 18. Labels are referred to in Chapter 2.

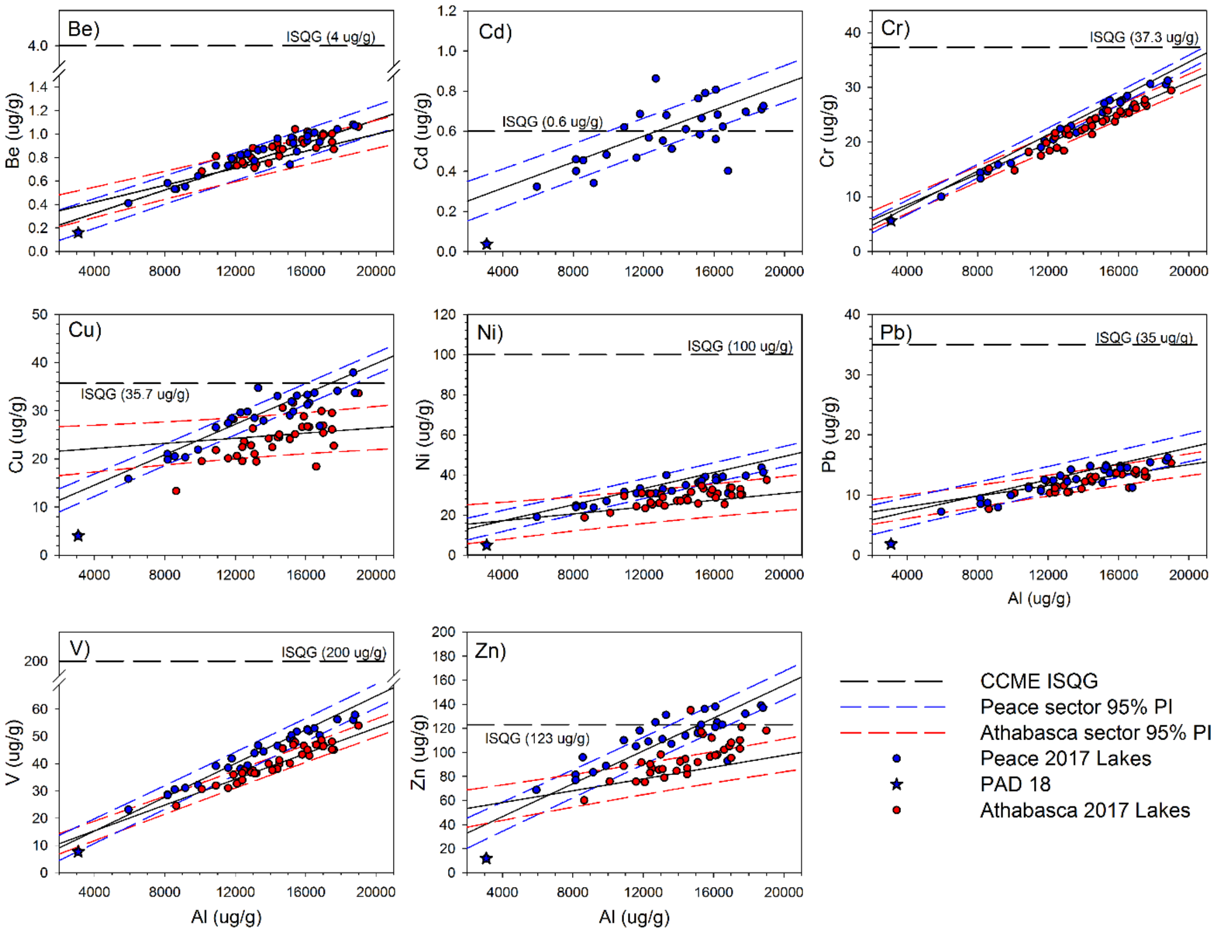

Figure 9. Surface sediment metal concentrations (μg/g), collected in September 2017, from Peace sector lakes (blue circles) and PAD 18 (blue star). In addition to Athabasca sector lakes (red circles) plotted on the pre-1920 linear regressions and 95% PIs. CCME Interim Sediment Quality Guidelines plotted on y-axis denoting the guideline concentrations for the metal of concern.

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Appendices

Appendix A. Study site locations.

Table A1. Lake sediment core locations

Site ID	Latitude	Longitude
PAD 30	N58 30.605	W111 31.025
PAD 31	N58 29.763	W111 31.101
PAD 32	N58 29.838	W111 26.592
M7	N58 26.172	W111 02.801
PAD 65	N58.897	W111.5
PAD 67	N59.09129	W111.402

Table A2. Surface sediment locations

Site ID	Latitude	Longitude
M 1	N58 26.857	W111 00.908
M 2	N58 25.099	W110 54.823
M 3	N58 25.882	W110 58.359
M 4	N58 29.513	W110 50.628
M 5	N58 30.149	W110 47.585
M 6	N58 32.006	W110 47.633
M 7	N58 26.172	W111 02.801
M 8	N58 23.950	W111 48.244
M 9	N58 19.651	W111 49.335
M 10	N58 17.359	W111 47.507
M 11	N58 33.004	W111 19.950
M 12	N58 33.379	W111 24.808
M 14	N58 34.282	W111 31.193
M 15	N58 52.889	W111 15.412
M 16	N58 53.656	W111 12.547
M 17	N58 54.154	W111 19.329
M 18	N58 54.332	W111 17.365
M 19	N58 53.071	W111 19.392
PAD 1	N58 48.334	W111 14.609
PAD 2	N58 50.110	W111 19.147
PAD 3	N58 49.994	W111 17.022
PAD 4	N58 50.553	W111 24.072
PAD 5	N58 50.698	W111 28.722

PAD 6	N58 48.698	W111 23.193
PAD 8	N58 48.697	W111 21.341
PAD 12	N58 57.337	W111 19.741
PAD 13	N58 56.891	W111 22.511
PAD 14	N58 55.989	W111 25.650
PAD 15	N58 57.005	W111 30.415
PAD 16	N58 52.938	W111 24.030
PAD 17	N58 52.326	W111 25.665
PAD 18	N58 53.772	W111 21.620
PAD 19	N58 26.535	W111 37.731
PAD 21	N58 25.169	W111 35.541
PAD 22	N58 22.156	W111 34.134
PAD 23	N58 23.823	W111 29.915
PAD 24	N58 23.377	W111 26.682
PAD 25	N58 23.645	W111 21.603
PAD 26	N58 23.093	W111 19.781
PAD 27	N58 25.192	W111 16.171
PAD 30	N58 26.147	W111 15.727
PAD 31	N58 30.605	W111 31.025
PAD 32	N58 29.763	W111 31.101
PAD 33	N58 29.838	W111 26.592
PAD 36	N58 25.218	W111 26.413
PAD 37	N58 27.960	W111 15.062
PAD 38	N58 40.262	W111 26.718
PAD 39	N58 25.052	W111 07.365
PAD 40	N58 27.893	W111 11.137
PAD 45A	N58 30.459	W111 11.479
PAD 45B	N58 35.051	W111 22.659
PAD 46 (M 13)	N58 33.021	W111 32.856
PAD 50	N58 51.535	W111 53.358
PAD 52	N58 52.625	W111 45.027
PAD 53	N58 46.337	W111 38.927
PAD 54	N58 52.181	W111 34.664
PAD 57	N58 49.718	W111 35.667
PAD 58	N58 49.779	W111 33.139
PAD 62	N58 22.312	W111 51.033
PAD 64	N58.95443	W111.774761
PAD 65	N58.897	W111.5
PAD 66	N58.96979	W111.492

Table A3. RAMP and JOSMP river bottom sediment sampling locations

Site ID	**Latitude**	**Longitude**
ATR-ER	58.353315518	W111.541848318
BPC-1	58.5907912847	W110.795243421
BPC-2	58.4627140544	W110.859829974
EMR-1	58.3582683953	W111.550145375
EMR-2	58.5674999992	W111.092222222
FLC-1	58.5645392417	W111.062197762
GIC-1	58.5881005107	W110.835251004

Appendix B. Chronology Information.

Table B1. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based chronology for lake PAD 30. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.5	2016.37	0.42	3.1872	0.2715	0.1467	0.0383	2.5808	0.1725
1.5	2015.92	1.09	3.1476	0.3641				
2.5	2014.94	1.37	3.1083	0.2427	0.1081	0.0322	1.9655	0.1379
3.5	2014.01	1.63	3.0627	0.2367	0.0481	0.0279	2.5922	0.1539
4.5	2013.39	2.00	3.1468	0.3549				
5.5	2012.66	2.17	3.2325	0.2645	0.1042	0.0364	2.4669	0.1664
6.5	2011.19	2.53	4.7106	0.4776				
7.5	2008.44	2.74	6.5823	0.3977	0.4173	0.0499	2.1633	0.1750
8.5	2004.70	3.08	5.6789	0.3977				
9.5	2001.45	3.29	6.2092	0.4569				
10.5	1998.93	3.57	6.7716	0.4569	3.4272	0.1043	1.6267	0.1976
11.5	1995.11	4.20	6.7786	0.4569				
12.5	1989.71	5.14	7.0759	0.4861				
13.5	1983.06	6.71	7.3818	0.4861	2.6872	0.0970	1.3891	0.1802
14.5	1977.85	7.47	6.6733	0.7684				
15.5	1973.99	8.84	6.0116	0.5951				
16.5	1968.53	10.90	5.3952	0.6870				
17.5	1961.64	14.21	4.8225	0.3433	4.1589	0.0944	1.4356	0.1613
18.5	1954.42	17.69	4.1060	0.5480				
19.5	1948.17	21.16	3.4642	0.4272				
20.5	1943.13	24.01	2.8932	0.4972				
21.5	1939.43	26.33	2.3887	0.2543	0.0697	0.0394	1.7589	0.1646
22.5	1934.86		2.3141	0.4103				
23.5	1927.96		2.2412	0.3219				
24.5	1919.72		2.1698	0.3776				
25.5	1911.91		2.1000	0.1974				
26.5	1904.91							
27.5	1896.22							
28.5	1883.61							
29.5	1869.79							
30.5	1858.09							
31.5	1845.80							
32.5	1834.32							
33.5	1824.65							
34.5	1814.00							

35.5	1800.52							
36.5	1787.63							
37.5	1774.89							
38.5	1760.35							
39.5	1748.05							
40.5	1738.76							
41.5	1730.90							
42.5	1721.64							
43.5	1710.38							
44.5	1698.62							

Table B2. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based chronology for lake PAD 31. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.5	2010.2943	0.00	4.6572	0.1338	0.0907	0.0100	1.9426	0.0984
1.5	2010.0719	0.33	3.8827	0.1190	0.1943	0.0141	2.1611	0.1010
2.5	2009.2613	0.68	4.1206	0.1491	0.1921	0.0170	2.1236	0.1208
3.5	2007.9828	1.10	3.6108	0.1155	0.0514	0.0073	2.1735	0.0999
4.5	2006.5805	1.49	3.7585	0.1297	0.0678	0.0093	2.2315	0.1137
5.5	2005.1561	1.92	3.1507	0.1050	0.1065	0.0101	2.2059	0.0974
6.5	2003.8084	2.31	3.1160	0.1246	0.0805	0.0106	2.2417	0.1203
7.5	2002.5329	2.73	2.7833	0.0959	0.1327	0.0110	2.2200	0.0983
8.5	2001.4596	3.03	2.7590	0.0923	0.0309	0.0052	1.8069	0.0843
9.5	2000.5040	3.37	4.1421	0.1255	0.1215	0.0115	2.2500	0.1070
10.5	1999.2410	3.81	3.6742	0.1334	0.1578	0.0147	2.3246	0.1232
11.5	1997.7840	4.24	3.9475	0.1141	0.1378	0.0113	2.2676	0.0999
12.5	1996.2781	4.66	3.4880	0.1147	0.1827	0.0138	2.3353	0.1069
13.5	1994.6919	5.06	4.3658	0.1595	0.2001	0.0180	2.3279	0.1336
14.5	1992.5982	5.67	4.0184	0.1255	0.2654	0.0172	2.2083	0.1080
15.5	1990.0902	6.21	3.3052	0.1093	0.1992	0.0141	2.2553	0.1036
16.5	1987.7871	6.68	5.4414	0.1910	0.9758	0.0432	1.7804	0.1259
17.5	1985.1161	7.30	9.7967	0.3242	2.5945	0.0904	1.4233	0.1411
18.5	1981.1053	8.05	8.3946	0.2864	2.4672	0.0836	1.3404	0.1294
19.5	1975.7786	8.82	8.7347	0.2918	2.4825	0.0836	1.1209	0.1185
20.5	1969.1903	9.66	6.4033	0.2160	2.6602	0.0746	1.2234	0.1064
21.5	1961.7874	10.50	4.8789	0.1570	2.5689	0.0605	1.4381	0.0959
22.5	1954.4097	11.41	3.6201	0.1232	2.2579	0.0513	1.2984	0.0822

23.5	1947.0229	12.44	3.2600	0.0959	2.0628	0.0402	1.3560	0.0685
24.5	1939.0015	14.07	2.8471	0.0853	1.5644	0.0333	1.3830	0.0665
25.5	1929.5469	16.54	2.8541	0.0941	1.1262	0.0312	1.5187	0.0782
26.5	1918.3756	19.45	2.0603	0.0679	0.4745	0.0171	1.4979	0.0652
27.5	1908.6969	20.18	2.1665	0.0658	0.1810	0.0100	1.7644	0.0669
28.5	1899.5797	22.17	2.3710	0.0745	0.2218	0.0115	1.7813	0.0728
29.5	1885.9867	29.21	2.0620	0.0698	0.1213	0.0090	1.8445	0.0753
30.5	1870.4987	27.95	2.1391	0.0709	0.0251	0.0042	1.9171	0.0773
31.5	1856.8224		1.8805	0.0625			1.7298	0.0674
32.5	1844.2526		1.8167	0.0587			2.0750	0.0701
33.5	1830.9647		2.1518	0.0568			1.8857	0.0595
34.5	1816.8856		2.0711	0.0652			2.0207	0.0736
35.5	1802.4206							
36.5	1786.3467							
37.5	1768.1525							

Table B3. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based chronology for lake PAD 32. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.50	2014.73	0.57	9.9960	0.7006	1.1003	0.0961	2.5802	0.3988
1.50	2012.20	1.77	6.7928	0.4682	1.3807	0.0703		
2.50	2007.92	3.57	6.7637	0.4875	1.6740	0.0790	2.3526	0.2873
3.50	2002.82	5.77	5.5133	0.6523				
4.50	1998.03	7.74	4.4274	0.4334	1.8028	0.0715	2.9718	0.3404
5.50	1993.74	9.67	4.0381	0.5588				
6.50	1989.53	11.86	3.6724	0.3528	0.5292	0.0481	2.4622	0.2704
7.50	1985.46	13.71	3.3073	0.4743				
8.50	1982.50	14.78	2.9673	0.3171	0.5197	0.0431	2.8244	0.2594
9.50	1979.91	16.39	3.2349	0.4727				
10.50	1974.78	20.94	3.5182	0.3506	0.2954	0.0467	2.7451	0.2913
11.50	1967.58	24.99	3.2684	0.4758				
12.50	1960.74	28.69	3.0306	0.3216	0.0608	0.0428	2.9043	0.3568
13.50	1954.66	30.94	2.9641	0.4609				
14.50	1948.88	34.03	2.8986	0.3301	0.0964	0.0421	2.3287	0.2579
15.50	1942.76	32.89	2.8804	0.4620				
16.50	1934.40		2.8623	0.3231	0.0565	0.0423	2.6980	0.2628
17.50	1924.91		2.9641	0.4624				

18.50	1915.48		3.0684	0.3307			2.7397	0.2719
19.50	1904.70		2.7842	0.4302				
20.50	1893.76		2.5181	0.2752			2.6241	0.2533
21.50	1882.81		2.5060	0.3729				
22.50	1872.32		2.4938	0.2516			2.6146	0.2675
23.50	1862.59		2.5001	0.3888				
24.50	1853.25		2.5064	0.2965	0.0379	0.0402	2.1788	0.2428
25.50	1845.21		2.4419	0.4336				
26.50	1837.22		2.3786	0.3164	0.0001	0.0014	2.3197	0.2383
27.50	1827.77		2.3448	0.5268				
28.50	1817.90		2.3113	0.4213				
29.50	1808.46		2.2782	0.5048				
30.50	1798.94		2.2454	0.2782			2.5708	0.2383
31.50	1790.12		2.3268	0.5113				
32.50	1781.96		2.4101	0.4290				
33.50	1773.34		2.4955	0.5391				
34.50	1764.50		2.5828	0.3266			2.5565	0.2775
35.50	1756.23		2.5994	0.5783				
36.50	1747.39		2.6160	0.4772				
37.50	1737.87		2.6328	0.5907				
38.50	1727.62		2.6496	0.3480	0.0169	0.0564	2.7827	0.2703
39.50	1715.68		2.6261	0.5763				
40.50	1702.60		2.6028	0.4594				
41.50	1690.45		2.5797	0.5486				
42.50	1678.93		2.5566	0.2998			2.7169	0.2727
43.50	1666.41							
44.50	1653.70							
45.50	1640.36							

Table B4. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based chronology for lake M7. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.5	2014.49	0.67	9.6750	0.5203	0.7402	0.0671	2.1630	0.2709
1.5	2011.60	1.65	9.3586	0.7497				
2.5	2008.21	2.59	9.0491	0.5397	0.7037	0.0706	2.0566	0.3333
3.5	2005.17	3.46	6.6228	0.7329				
4.5	2003.00	4.00	4.6746	0.4959	0.5481	0.0616	1.7152	0.2437

5.5	2000.82	4.96	5.4500	0.6698				
6.5	1997.47	6.49	6.3068	0.4503	0.9744	0.0648	2.2086	0.2611
7.5	1993.23	8.41	5.5021	0.7273				
8.5	1988.82	10.52	4.7690	0.5711			0.0000	0.2817
9.5	1984.83	12.43	4.1041	0.6705				
10.5	1981.44	14.28	3.5041	0.3513	1.0081	0.0529	2.3774	0.2869
11.5	1978.46	15.99	3.3430	0.6011				
12.5	1975.55	17.96	3.1869	0.4877			0.0000	0.2695
13.5	1972.69	19.77	3.0358	0.5935				
14.5	1970.01	21.82	2.8895	0.3383	0.6508	0.0479	2.3512	0.2306
15.5	1967.91	22.82	2.5171	0.4823				
16.5	1966.80	23.23	2.1781	0.3438	0.4538	0.0465	2.5960	0.2698
17.5	1964.90	24.86	2.5369	0.4732				
19.5	1961.59	28.05	2.9330	0.3251	0.7793	0.0473	2.5856	0.2705
20.5	1959.15	29.03	2.6265	0.4960				
21.5	1958.29	29.03	2.3422	0.3747	0.6116	0.0522	2.5063	0.2801
22.5	1957.75	29.07	2.4793	0.6299				
23.5	1956.41	30.13	2.6217	0.5064			0.0000	0.2962
24.5	1953.15	32.64	2.7694	0.6103				
25.5	1948.30	38.44	2.9226	0.3406	0.0194	0.0556	2.6776	0.2594
26.5	1942.73	43.46	2.7659	0.5560				
27.5	1937.90	46.51	2.6149	0.4395			0.0000	0.2670
28.5	1934.79	43.94	2.4694	0.5198				
29.5	1932.90	42.04	2.3295	0.2777			2.7337	0.2260
30.5	1930.79	42.63	2.4643	0.3724				
31.5	1922.64	54.71	2.6041	0.2481			2.7008	0.2244
32.5	1913.80		2.7998	0.4243				
33.5	1908.63		3.0050	0.3442			0.0000	0.2191
34.5	1903.24		3.2200	0.4188				
35.5	1897.64		3.4450	0.2386			2.1361	0.1875

Table B5. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based for lake PAD 65. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.50	2016.00	0.31	10.7435	0.9436	0.3556	0.1554	2.6924	0.5690
1.50	2014.51	0.72	10.7280	0.9617	0.3127	0.1510	2.6083	0.4861
2.50	2012.45	1.01	8.4477	0.5517	0.3839	0.0680	2.1139	0.2264
3.50	2010.20	1.45	7.3066	0.7002				
4.50	2007.81	1.85	6.2732	0.4312	0.3477	0.0587	2.3009	0.2238
5.50	2005.23	2.42	5.2791	0.5507				
6.50	2002.73	2.85	4.3961	0.3426	0.4182	0.0525	2.2161	0.2193
7.50	2000.61	3.26	4.6270	0.6132				
8.50	1998.49	3.73	4.8659	0.5086				
9.50	1996.22	4.24	5.1128	0.6324				
10.50	1993.17	5.14	5.3680	0.3759	0.6387	0.0571	2.2624	0.2003
11.50	1989.12	6.19	4.4894	0.5657				
12.50	1984.80	7.16	3.7123	0.4227	0.5317	0.0861	2.5505	0.2918
13.50	1981.14	7.81	3.4137	0.4816				
14.50	1978.20	8.65	3.1314	0.2307	1.2147	0.0464	2.3018	0.1684
15.50	1975.63	9.10	3.0938	0.3498				
16.50	1973.55	9.45	3.0565	0.2630	1.4220	0.0582	2.6977	0.1951
17.50	1971.72	9.57	2.8629	0.3593				
18.50	1969.74	9.97	2.6776	0.2449	0.5743	0.0474	2.2729	0.1861
19.50	1966.71	10.72	2.8978	0.3628				
20.50	1959.93	14.10	3.1297	0.2677	0.6302	0.0484	1.9428	0.1674
21.50	1950.95	16.19	3.0747	0.4516				
22.50	1943.85	18.32	3.0204	0.3637				
23.50	1937.02	17.98	2.9667	0.4392				
24.50	1930.39	19.48	2.9136	0.2462	0.2446	0.0419	2.5172	0.1879
25.50	1925.51		2.8704	0.4314				
26.50	1920.75		2.8276	0.3542				
27.50	1915.42		2.7853	0.4363				
28.50	1909.28		2.7434	0.2547	0.0662	0.0358	2.5109	0.1886
29.50	1903.01		2.7120	0.3334				
30.50	1897.06		2.6809	0.2152			2.6667	0.1983
31.50	1890.80		2.6536	0.3779				
32.50	1884.82		2.6264	0.3106				
33.50	1879.27		2.5995	0.3828				
34.50	1873.32		2.5727	0.2239			2.2593	0.1739
35.50	1867.04		2.5475	0.3875				
36.50	1860.16		2.5226	0.3163				

37.50	1852.51		2.4977	0.3872				
38.50	1845.27		2.4731	0.2234			1.8942	0.1619
39.50	1838.28		2.3284	0.3809				
40.50	1830.77		2.1894	0.3084				
41.50	1823.22		2.0561	0.3746				
42.50	1816.00		1.9283	0.2126			1.8867	0.1677
43.50	1808.43		2.0993	0.3956				
44.50	1800.25		2.2802	0.3337				
45.50	1791.98		2.4712	0.4212				
46.50	1784.12		2.6726	0.2571			2.5049	0.1851
47.50	1776.58		2.4858	0.3300				
48.50	1768.60		2.3079	0.2069			3.0583	0.1977
49.50	1759.98		2.2755	0.2905				
50.50	1751.74		2.2434	0.2040			2.2862	0.1789
51.50	1743.32		2.2366	0.2891				
52.50	1734.55		2.2298	0.2048			2.2064	0.1707
53.50	1726.16							

Table B6. Radiometric values (^{210}Pb, ^{137}Cs, ^{226}Ra) in dpm/g and CRS-based for lake PAD 67. Beige coloured boxes indicate extrapolated dates.

Sediment mid depth (cm)	CRS Chronology	CRS Error ± 2 sigma	^{210}Pb dpm/g	^{210}Pb error (1 std. dev.) dpm/g	^{137}Cs dpm/g	^{137}Cs error (1 std. dev.) dpm/g	^{226}Ra dpm/g	^{226}Ra error (1 std. dev.) dpm/g
0.5	2014.43	0.71	7.6952	0.6137	0.7493	0.0680	2.4345	0.4119
1.5	2012.02	1.50	6.3722	0.5786	0.8139	0.0709	2.6669	0.4560
2.5	2008.78	2.36	6.6670	0.6243	0.7994	0.0742	2.1305	0.3814
3.5	2004.84	3.34	6.5732	0.6353	0.6549	0.0733	2.0037	0.3605
4.5	2000.59	4.51	6.5161	0.5680	0.6961	0.0672	2.4160	0.4205
5.5	1995.80	6.08	6.4107	0.5883	0.7717	0.0705	2.6345	0.4336
6.5	1990.91	7.61	5.5256	0.6058	0.7168	0.0762	2.9067	0.5394
7.5	1987.13	8.64	4.5988	0.5569	0.7085	0.0724	2.9753	0.5041
8.5	1982.76	10.95	4.8992	0.5148	0.7671	0.0672	2.6611	0.4167
9.5	1977.77	12.64	4.1169	0.5044	0.7940	0.0683	2.8103	0.4797
10.5	1974.36	13.47	3.9618	0.5065	0.8204	0.0695	3.2039	0.5670
11.5	1970.42	15.85	4.5027	0.5077	0.7107	0.0672	3.1308	0.5183
12.5	1964.92	18.71	3.9353	0.5135	0.7132	0.0684	2.7810	0.4276
13.5	1961.05	18.67	3.7771	0.5454	0.7163	0.0741	3.4204	0.5706
14.5	1957.67	20.56	4.0228	0.4153	0.6343	0.0558	3.3105	0.5250
15.5	1953.09	21.82	3.6944	0.4787	0.7112	0.0646	3.1293	0.4747

16.5	1948.07	21.34	3.4207	0.6261				
17.5	1941.76		3.1609	0.4036	0.4946	0.0536	2.5399	0.4348
18.5	1933.97		3.0589	0.5704				
19.5	1925.35		2.9590	0.4031	0.3906	0.0521	3.2002	0.4893
20.5	1916.60		2.9178	0.5469				
21.5	1908.11		2.8769	0.3697	0.0869	0.0466	2.7091	0.4343
22.5	1899.89		3.0155	0.5216				
23.5	1892.12		3.1584	0.3680			3.0275	0.4669
24.5	1884.61		2.7179	0.5413				
25.5	1878.07		2.3204	0.3970			2.9445	0.4664
26.5	1872.60		2.5669	0.5414				
27.5	1867.36		2.8303	0.3681			2.5913	0.4135
28.5	1862.94							
29.5	1856.68							
30.5	1848.42							
31.5	1840.62							
32.5	1832.18							
33.5	1821.18							
34.5	1809.86							
35.5	1800.38							
36.5	1791.08							
37.5	1780.96							
38.5	1769.77							
39.5	1758.28							
40.5	1744.92							
41.5	1728.88							
42.5	1713.89							
43.5	1700.50							
44.5	1686.34							
46.5	1671.27							
47.5	1655.18							
48.5	1638.98							
49.5	1623.60							
50.5	1608.83							
51.5	1594.70							
52.5	1577.39							
53.5	1561.34							
54.5	1548.52							
55.5	1535.64							

Appendix C. Raw Metals Concentrations.

Table C1. 2017 surface sediment raw metal concentrations

Lake	Al (mg/kg)	Be (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
M 1	17000	1.00	0.459	26.2	25.4	29.7	13.5	46.8	95.4
M 2	17600	0.87	0.400	26.6	22.7	30.1	13.0	45.0	121
M 3	16200	1.00	0.389	25.2	26.6	30.6	13.4	42.9	97.9
M 4	8640	0.53	0.219	15.1	13.3	18.7	7.64	24.5	60.2
M 5	16600	0.88	0.345	25.3	18.4	25.3	11.2	46.9	102
M 6	11600	0.73	0.309	17.5	20.1	24.3	11.0	31.0	75.6
M 7	14500	0.81	0.351	21.4	24.5	27.2	12.2	39.8	81.9
M 8	16900	0.97	0.554	26.9	29.9	33.6	13.7	48.6	105
M 9	10900	0.81	0.422	18.2	21.8	29.4	11.4	31.9	88.6
M 10	15400	1.04	0.600	25.7	25.1	33.1	14.3	47.8	115
M 11	17000	0.99	0.396	26.2	26.9	33.6	14.1	46.3	108
M 12	11900	0.78	0.480	19.8	28.2	30.8	12.3	35.9	91.6
M 14	15800	0.95	0.446	23.7	26.6	30.6	13.6	43.3	96.2
M 15	15300	0.96	0.686	24.1	31.6	34.5	14.9	46.9	117
M 16	5930	0.41	0.322	10.0	15.8	19.0	7.20	23.1	68.7
M 17	13100	0.77	0.552	21.6	28.5	32.9	12.2	43.8	111
M 18	11600	0.73	0.467	19.0	27.4	30.8	10.7	38.4	105
M 19	16100	0.98	0.560	27.2	31.2	37.3	14.4	52.3	121
PAD 1	8570	0.53	0.454	14.6	20.5	24.6	8.66	30.5	95.9
PAD 2	9890	0.64	0.482	16.1	21.9	26.9	9.92	32.1	88.6
PAD 3	10900	0.73	0.619	18.1	26.5	31.5	11.1	39.1	110
PAD 4	8150	0.58	0.459	14.4	21.0	24.7	9.41	28.7	81.4
PAD 5	13300	0.86	0.679	22.9	34.7	39.8	14.2	46.6	131
PAD 6	16800	0.93	0.402	26.3	26.8	30.8	11.2	50.4	92.9
PAD 8	14400	0.96	0.609	23.9	33.0	34.8	14.8	46.5	114
PAD 12	18700	1.08	0.709	30.5	37.9	43.6	15.7	56.0	139
PAD 13	11800	0.79	0.686	20.2	28.4	33.2	12.5	41.8	118

PAD 14	9160	0.55	0.341	15.8	20.3	23.7	7.92	31.1	83.4
PAD 15	13600	0.87	0.511	21.7	27.9	31.9	12.6	44.4	107
PAD 16	16200	1.01	0.682	27.6	31.6	37.4	14.7	51.9	125
PAD 17	12300	0.82	0.567	20.4	29.6	30.7	12.4	38.1	109
PAD 18	16500	1.01	0.622	28.4	33.7	39.1	14.5	52.9	123
PAD 19	3080	0.16	0.037	5.59	4.01	4.96	1.85	7.70	11.7
PAD 21	13000	0.88	0.398	21.5	26.3	30.1	12.7	37.5	98.1
PAD 22	17500	0.93	0.451	27.0	29.5	32.8	13.1	48.0	110
PAD 23	15900	0.92	0.531	24.8	28.8	32.5	13.6	46.5	112
PAD 24	10100	0.68	0.320	14.8	19.5	21.0	10.3	30.6	75.8
PAD 25	12500	0.74	0.329	18.9	23.6	25.2	11.4	37.4	86.6
PAD 26	12900	0.80	0.325	18.4	22.8	25.9	11.5	36.7	85.5
PAD 27	16100	1.02	0.369	25.6	26.7	28.6	14.8	45.0	97.5
PAD 30	15100	0.93	0.349	23.7	24.1	25.7	12.1	40.1	91.7
PAD 31	17500	1.00	0.394	27.7	26.1	30.1	13.9	45.2	103
PAD 32	14400	0.92	0.360	23.8	24.5	28.4	13.0	38.0	94.4
PAD 33	19000	1.06	0.493	29.4	33.6	37.4	15.3	53.9	118
PAD 36	14500	0.87	0.369	22.9	25.0	27.5	12.5	41.2	86.8
PAD 37	13900	0.75	0.366	22.1	24.2	27.0	11.0	39.9	84.6
PAD 38	14700	0.87	0.848	24.3	30.6	31.4	13.0	45.5	135
PAD 39	13200	0.74	0.312	21.3	19.4	24.6	10.5	36.4	78.9
PAD 40	12100	0.73	0.311	18.4	20.6	23.3	10.3	32.6	75.1
PAD 45A	14100	0.89	0.405	22.5	22.4	27.0	12.2	37.6	92.2
PAD 45B	12400	0.76	0.367	20.9	19.5	26.2	10.4	33.9	83.0
PAD 46 (M 13)	13100	0.71	0.378	22.3	21.0	28.8	10.4	36.4	86.0
PAD 50	16100	0.94	0.806	27.4	33.3	38.7	14.7	52.5	138
PAD 52	15100	0.74	0.763	25.4	29.0	36.1	12.0	49.1	116
PAD 53	18800	1.07	0.725	31.2	33.7	41.2	16.2	57.9	137
PAD 54	17800	1.04	0.696	30.6	34.1	39.5	15.4	56.2	132
PAD 57	15500	0.85	0.790	27.6	33.1	39.0	13.6	51.7	136
PAD 58	12700	0.83	0.862	22.4	29.8	30.8	13.2	39.3	125
PAD 62	12400	0.82	0.406	21.6	22.4	30.5	11.1	36.5	90.2

PAD 64	15200	0.97	0.583	27.0	31.9	36.7	14.2	50.4	120
PAD 65	8160	0.58	0.400	13.3	19.8	23.9	8.50	28.4	76.9
PAD 66	15300	0.92	0.664	25.8	29.8	37.1	14.7	48.3	123

Table C2. 2018 surface sediment raw metal concentrations

Lake	Al (mg/kg)	Be (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
M12	13600	0.72	0.591	22.2	30.4	33.3	13.6	39.5	101
M17	14600	0.84	0.536	24.7	30.3	33.6	14.4	47.7	109
M18	19100	1.05	0.621	31.2	34.5	40.5	17.0	60.1	132
PAD 8	18600	0.92	0.694	30.0	38.0	41.0	15.0	58.3	132
PAD 15	16300	0.89	0.754	29.4	32.9	38.2	16.4	52.7	125
PAD 19	13500	0.79	0.438	22.1	26.7	30.1	13.8	39.7	91.3
PAD 21	13900	0.72	0.416	22.3	24.8	27.1	12.8	38.9	89.7

PAD 22	14700	0.74	0.515	22.8	23.9	27.0	13.0	40.2	98.9
PAD 24	13500	0.66	0.423	20.4	30.8	26.0	12.7	40.3	92.5
PAD 25	13800	0.78	0.294	20.1	22.6	24.7	12.7	40.1	82.3
PAD 26	15100	0.88	0.395	24.1	25.7	27.1	14.6	41.4	90.6
PAD 30	13500	0.79	0.325	23.1	23.0	25.5	11.9	38.4	81.4
PAD 31	14200	0.73	0.378	23.5	22.1	27.1	12.0	39.5	83.6
PAD 33	13300	0.71	0.335	21.1	24.2	24.5	12.4	35.6	80.0
PAD 36	11300	0.69	0.331	17.5	24.4	24.8	12.1	34.3	76.5
PAD 40	17900	0.93	0.464	26.8	26.3	30.9	14.9	45.2	104
PAD 50	13200	0.73	0.724	23.0	28.3	31.6	13.8	42.8	114
PAD 54	18000	0.88	0.808	30.8	33.7	39.0	16.0	55.7	127
PAD 58	14500	0.78	0.977	26.2	31.2	33.4	14.5	46.6	132
PAD 64	16500	0.86	0.633	27.2	32.9	37.9	15.7	50.6	121

Table C3. RAMP and JOSMP river bottom sediment raw metals concentrations

Site ID	Sampling Date	Al (mg/kg)	Be (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	V (mg/kg)	Zn (mg/kg)
ATR-ER	15 Sep 2000	11800	0.7	0.2	61.3	12.7	34.8	7.2	33.9	60.8
ATR-ER	18 Oct 2001	9390	0.5	0.2	16.7	10.4	17.9	6.2	23	50.0
ATR-ER	17 Sep 2002	5190	0.4	0.2	11.5	10	16.3	6.2	14.4	53.0
ATR-ER	12 Sep 2005	6100	0.4	0.2	14.8	9.3	15.8	6.6	18.5	46
ATR-ER	08 Sep 2007	5410	0.4	0.2	9.5	9.0	14.5	5.9	16.2	46
ATR-ER	06 Sep 2008	5570	0.5	0.2	12.8	10.7	15.2	7.5	20.5	52
ATR-ER	19 Sep 2009	3820	0.36	0.19	8.81	7.38	12.8	5.65	13.0	42.3
ATR-ER	04 Sep 2010	3940	0.25	0.11	9.68	5.8	11.2	4.66	16.1	26.3
ATR-ER	03 Sep 2011	1300	< 0.2	< 0.1	3.11	1.43	5.41	2.34	5.36	20.3
ATR-ER	01 Sep 2012	566	< 0.2	< 0.1	1.97	0.78	2.35	1.17	3.73	8.4
ATR-ER	10 Sep 2013	3170	< 0.2	< 0.1	7.13	2.06	8.23	3.32	12.2	26.1
BPC-1	16 Sep 2000	18700	0.9	0.3	92.0	20	49.7	10.2	49.8	63.7
BPC-1	17 Oct 2001	4390	0.5	0.3	16.1	11.3	19.2	6.7	20.5	58.3
BPC-1	17 Sep 2002	7660	0.6	0.2	16.3	14	21.2	9	17.9	68.0

BPC-1	13 Sep 2005	7530	0.5	0.2	15.4	11.2	16.5	7.4	21.5	53
BPC-1	09 Sep 2007	8470	0.6	0.3	14.9	12.8	19.0	8.1	23.0	64
BPC-1	07 Sep 2008	6640	0.5	0.3	14.3	12.9	15.7	7.3	21.9	54
BPC-1	19 Sep 2009	6620	0.59	0.36	17.2	15.5	21.5	9.91	19.4	67
BPC-1	04 Sep 2010	9720	0.57	0.33	17.4	18.3	24.8	9.98	28.0	58.7
BPC-1	03 Sep 2011	6030	0.41	0.19	11.2	9.74	16.8	6.38	17.3	48.9
BPC-1	01 Sep 2012	4130	0.31	0.14	10.3	6.44	13.7	5.73	16.9	40.3
BPC-1	10 Sep 2013	4050	0.25	< 0.1	7.93	3.06	9.25	3.85	13.8	30.9
BPC-1	21 Aug 2014	7890	0.49	0.25	14.8	12.9	16.1	7.81	22.6	60.9
BPC-1	31 Aug 2015	6750	0.46	0.222	13.2	11.9	17.2	7.0	20.2	53.7
BPC-2	13 Sep 2005	9570	0.7	0.3	22.1	14.5	21.6	9.5	25.3	63
EMR-1	12 Sep 2005	8730	0.6	0.3	19.7	13.5	20.6	9.1	24.2	60
EMR-1	03 Sep 2011	472	< 0.2	< 0.1	1.56	5.47	2.57	1.53	2.3	17.2
EMR-2	13 Sep 2005	14100	0.9	0.4	26.9	23.2	28.6	15.0	35.0	87
EMR-2	04 Sep 2010	11300	0.69	0.32	19.4	30.4	25.9	11.8	30.9	70.8
EMR-2	01 Sep 2012	10000	0.64	0.38	21.2	21.9	27.8	13.0	33.0	85.1

EMR-2	10 Sep 2013	11600	0.66	0.28	17.8	16.1	21.5	10.0	31.3	66.1
EMR-2	19 Aug 2014	11200	0.68	0.31	19.4	21.0	21.1	11.5	30.4	83
EMR-2	31 Aug 2015	10400	0.71	0.30	19.1	20.2	24.1	11.3	29.4	79.9
FLC-1	17 Oct 2001	11000	0.6	0.2	18.2	9	18.8	6.4	28.9	50.0
FLC-1	17 Sep 2002	5810	0.4	0.2	13.3	10	17.2	6.9	15.4	52.0
FLC-1	13 Sep 2005	8220	0.5	0.2	23.8	11.7	21.1	8.0	22.4	60
FLC-1	08 Sep 2007	7890	0.5	0.3	14.1	13.8	20.6	8.5	20.6	66
FLC-1	06 Sep 2008	4520	0.3	0.1	10.1	6.2	10.8	5.0	16.9	36
FLC-1	19 Sep 2009	4950	0.41	0.25	12.1	10.6	15.8	7.21	15.6	51.1
FLC-1	04 Sep 2010	9180	0.55	0.28	16.6	16.0	22.1	8.68	26.5	56.9
FLC-1	03 Sep 2011	5550	0.32	0.18	10.1	9.93	15.5	7.05	16.3	44.6
FLC-1	01 Sep 2012	2780	0.25	0.12	7.46	4.74	11.4	5.27	12.6	33.5
FLC-1	10 Sep 2013	10200	0.53	0.25	16.5	13.3	18.7	8.1	28.3	57.8
FLC-1	19 Aug 2014	8260	0.49	0.25	15.0	13.2	15.6	8.18	23.8	61.5
FLC-1	31 Aug 2015	5730	0.37	0.162	11.5	8.45	14.8	6.12	17.5	45.4
GIC-1	17 Oct 2001	4890	0.7	0.2	19.5	12.6	20.5	7.1	25.4	63.2

GIC-1	17 Sep 2002	6470	0.5	0.2	12.5	20	18.8	8.1	16	63.0
GIC-1	13 Sep 2005	11600	0.8	0.3	26.8	18.7	26.2	11.8	30.7	75
GIC-1	09 Sep 2007	5520	0.3	0.2	11.6	9.5	15.4	6.3	17.4	54
GIC-1	07 Sep 2008	8370	0.6	0.3	17.2	17.2	19.9	9.2	27.0	67
GIC-1	19 Sep 2009	4630	0.41	0.21	11.8	9.61	15.6	7.09	14.8	51.3
GIC-1	04 Sep 2010	3670	0.22	< 0.1	7.71	3.92	10.5	3.85	12.9	26.6
GIC-1	03 Sep 2011	7140	0.42	0.25	13.1	13.6	20.1	7.36	19.7	58
GIC-1	01 Sep 2012	5110	0.42	0.17	12.6	7.36	15.8	6.1	20.0	47
GIC-1	10 Sep 2013	7800	0.48	0.18	13.4	8.85	16.2	7.19	23.7	50.4
GIC-1	20 Aug 2014	8720	0.6	0.34	16.2	18.9	18.6	9.89	25.7	71.5
GIC-1	01 Sep 2015	7560	0.49	0.257	14.8	13.3	18.3	7.16	22.2	56.9

Appendix D. LOI and Organic Carbon and Nitrogen Elemental and Isotope Data.

Table D1. 2017 Surface sediment LOI results.

Lakes	**%H_2O**	**%OM**	**%MM**	**%$CaCO_3$**
M 1	56.19	11.18	88.82	9.96
M 2	77.48	13.22	86.78	6.39
M 3	62.88	12.45	87.55	8.94
M 4	61.42	7.90	92.10	12.17
M 5	90.33	25.10	74.90	7.96
M 6	65.29	16.07	83.93	13.84
M 7	66.32	17.20	82.80	13.98
M 8	69.66	15.60	84.40	8.86
M 9	62.70	15.89	84.11	8.19
M 10	73.22	12.91	87.09	8.26
M 11	59.59	11.87	88.13	9.55
M 12	73.95	22.25	77.75	12.56
M 13	70.74	18.60	81.40	12.59
M 14	69.75	19.89	80.11	9.70
M 15	97.21	52.35	47.65	-3.05
M 16	94.96	41.91	58.09	5.85
M 17	93.49	30.23	69.77	1.32
M 18	82.37	20.19	79.81	11.29
M 19	98.04	76.53	23.47	-4.64
PAD 1	88.70	27.51	72.49	15.23
PAD 2	98.34	49.47	50.53	14.35
PAD 3	79.30	24.83	75.17	18.74
PAD 4	69.20	22.68	77.32	11.07
PAD 5	84.40	30.05	69.95	10.30
PAD 6	75.34	16.50	83.50	17.48
PAD 8	66.91	12.86	87.14	7.34
PAD 12	87.11	32.48	67.52	6.87
PAD 13	99.69	64.71	35.29	66.84
PAD 14	91.83	30.23	69.77	10.35
PAD 15	71.66	8.92	91.08	9.10
PAD 16	74.45	21.07	78.93	15.43
PAD 17	89.11	37.66	62.34	7.17
PAD 18	78.74	3.33	96.67	0.36
PAD 19	69.72	15.65	84.35	5.47
PAD 21	74.74	19.33	80.67	6.76
PAD 22	83.05	19.64	80.36	8.24
PAD 23	94.66	49.48	50.52	6.34
PAD 24	86.48	28.36	71.64	7.09
PAD 25	93.64	28.57	71.43	5.96
PAD 26	62.20	10.56	89.44	8.52

PAD 27	77.42	13.39	86.61	11.78
PAD 30	68.80	10.65	89.35	9.42
PAD 31	64.99	6.77	93.23	11.08
PAD 32	72.41	18.80	81.20	6.27
PAD 33	66.83	13.40	86.60	14.30
PAD 36	83.83	20.06	79.94	9.31
PAD 37	86.39	30.99	69.01	3.52
PAD 38	54.90	9.14	90.86	5.44
PAD 39	93.31	26.14	73.86	16.14
PAD 40	65.59	9.05	90.95	10.79
PAD 45A	68.65	6.68	93.32	7.88
PAD 45B	44.00	6.58	93.42	5.20
PAD 50	67.60	14.75	85.25	8.99
PAD 52	74.07	14.34	85.66	14.60
PAD 53	50.78	7.97	92.03	6.25
PAD 54	68.23	7.17	92.83	7.43
PAD 57	73.32	15.22	84.78	15.02
PAD 58	69.91	14.79	85.21	5.30
PAD 62	49.04	7.42	92.58	5.68
PAD 64	83.75	12.82	87.18	12.07
PAD 65	88.25	38.40	61.60	14.72
PAD 66	50.80	6.29	93.71	7.28

Table D2. 2017 surface sediment organic carbon and nitrogen elemental and isotope composition**.**

Lakes	**%C**	**%N**	**δ^{13}C**	**δ^{15}N**
M 1	6.41	0.60	-26.47	1.60
M 2	5.56	0.47	-30.66	0.59
M 3	6.23	0.61	-26.94	1.29
M 4	4.70	0.55	-24.38	0.88
M 5	12.63	1.27	-30.38	-0.53
M 6	9.94	0.98	-27.05	0.16
M 7	11.30	1.15	-25.13	0.13
M 8	7.87	0.89	-27.09	3.65
M 9	8.69	0.88	-27.75	4.22
M 10	6.32	0.71	-26.61	1.63
M 11	13.70	1.23	-30.27	0.62
M 12	13.56	1.42	-27.63	0.98
M 13	11.14	1.07	-26.72	2.25
M 14	13.15	1.28	-28.38	2.73
M 15	40.99	3.45	-27.87	-0.29
M 16	24.33	1.92	-27.17	-0.61
M 17	18.90	1.76	-28.21	0.05
M 18	10.18	1.07	-26.02	1.00
M 19	43.31	3.55	-28.81	-0.33
PAD 1	18.00	1.94	-24.21	-0.46
PAD 2	28.70	3.19	-26.12	-0.64
PAD 3	18.59	2.00	-25.92	-0.35
PAD 4	14.58	1.55	-25.66	0.58
PAD 5	24.94	2.50	-20.08	1.14
PAD 6	10.61	1.16	-24.46	1.90
PAD 8	4.86	0.55	-27.05	1.06
PAD 12	21.10	2.37	-25.02	-25.02
PAD 13	33.80	3.33	-28.59	-28.59
PAD 14	21.21	1.87	-24.43	-24.43
PAD 15	3.63	0.43	-26.30	-26.30
PAD 16	12.35	1.19	-26.35	-26.35
PAD 17	23.79	1.96	-27.78	-27.78
PAD 18	11.20	1.10	-26.04	-26.04
PAD 19	7.55	0.63	-28.34	-28.34
PAD 21	10.67	0.97	-27.44	-0.52
PAD 22	13.01	1.27	-28.36	-0.66
PAD 23	27.33	2.34	-27.83	-0.40
PAD 24	22.70	1.95	-27.06	-1.02
PAD 25	17.24	1.67	-27.26	0.40
PAD 26	5.03	0.57	-26.34	0.59
PAD 27	5.63	0.61	-25.70	0.72

PAD 30	4.61	0.44	-28.91	1.45
PAD 31	2.42	0.21	-26.72	1.12
PAD 32	12.35	1.03	-26.67	-0.07
PAD 33	5.95	0.58	-25.71	0.46
PAD 36	9.74	0.94	-25.31	-0.40
PAD 37	17.95	1.77	-29.94	2.21
PAD 38	3.41	0.34	-26.88	1.73
PAD 39	14.78	1.79	-23.44	-0.56
PAD 40	3.94	0.38	-26.63	1.32
PAD 45A	2.42	0.22	-26.50	2.67
PAD 45B	1.93	0.17	-27.16	1.99
PAD 50	7.76	0.75	-26.76	1.50
PAD 52	8.05	0.88	-26.28	-0.44
PAD 53	2.76	0.30	-26.34	2.39
PAD 54	2.10	0.22	-28.50	1.34
PAD 57	9.63	1.09	-26.69	0.51
PAD 58	6.53	0.67	-27.00	1.09
PAD 62	2.93	0.35	-26.55	2.81
PAD 64	5.05	0.55	-26.66	0.15
PAD 65	19.92	2.08	-26.29	-1.44
PAD 66	1.96	0.19	-26.89	1.32

Appendix E. Statistical Analyses.

Table E1. AICc values for normalizers used for metals of concern in the Peace sector.

Metal of Concern	Normalizer	Order of strength	AICc coefficient	Delta AICc	AICc weight
Be	Li	1	-255.258	0	1
Be	Al	2	-177.328	77.9301	1.20x10^{-17}
Be	Ti	3	-98.7436	156.5146	1.03x10^{-34}
Be	Zr	4	-59.9762	195.2819	3.94x10^{-43}
Cd	Al	1	-213.0188	0	1
Cd	Li	2	-195.7156	17.3033	17.4x10^{-4}
Cd	Zr	3	-120.5578	92.4611	8.36x10^{-21}
Cd	Ti	4	-109.1544	103.8645	2.79x10^{-23}
Cr	Al	1	122.8169	0	1
Cr	Li	2	252.1387	129.3218	8.28x10^{-29}
Cr	Zr	3	352.8972	230.0803	1.09x10^{-50}
Cr	Ti	4	373.7033	250.8863	3.32x10^{-55}
Cu	Al	1	195.6049	0	1
Cu	Li	2	263.6881	68.0833	1.64x10^{-15}
Cu	Zr	3	350.6677	155.0628	2.13x10^{-34}
Cu	Ti	4	378.5462	182.9413	1.88x10^{-40}
Ni	Al	1	299.9726	0	1
Ni	Li	2	323.9603	23.9877	6.18x10^{-6}
Ni	Zr	3	392.5817	92.6090	7.77x10^{-21}
Ni	Ti	4	417.2645	117.2918	3.39x10^{-26}
Pb	Li	1	170.8444	0	1
Pb	Al	2	198.4352	27.5908	1.02x10^{-6}
Pb	Zr	3	232.8280	61.9836	3.47x10^{-14}
Pb	Ti	4	278.7717	107.9273	3.66x10^{-24}
V	Al	1	280.6179	0	1
V	Li	2	344.8625	64.2446	5.20x10^{-26}
V	Zr	3	436.7883	156.1704	4.90x10^{-28}
V	Ti	4	455.1171	174.4992	2.59x10^{-44}
Zn	Al	1	407.2074	0	1
Zn	Li	2	450.7297	43.5222	3.54x10^{-10}
Zn	Zr	3	547.0623	139.8548	4.27x10^{-31}
Zn	Ti	4	570.0306	162.8231	4.40x10^{-36}

Table E1. Results of Aikaike information criterion with a correction for small sample size (AICc) to determine the best pre-1920 vanadium-normalizer model for the Peace and Athabasca sectors.

Metal of Concern	Normalizer	Order of strength	AICc coefficient	Delta AICc	AICc Weight
Be	Li	1	-255.258	0	0.9267
Be	Al	2	-177.328	77.9301	0.0732
Be	Ti	3	-98.7436	156.5146	3.48x10^{-8}
Be	Zr	4	-59.9762	195.2819	1.97x10^{-15}
Cd	Al	1	-213.0188	0	0.5491
Cd	Li	2	-195.7156	17.3033	0.2673
Cd	Zr	3	-120.5578	92.4611	0.1562
Cd	Ti	4	-109.1544	103.8645	0.0274
Cr	Al	1	122.8169	0	1
Cr	Li	2	252.1387	129.3218	5.55x10^{-37}
Cr	Zr	3	352.8972	230.0803	9.65x10^{-38}
Cr	Ti	4	373.7033	250.8863	6.10x10^{-55}
Cu	Al	1	195.6049	0	0.9533
Cu	Li	2	263.6881	68.0833	0.0177
Cu	Zr	3	350.6677	155.0628	0.0145
Cu	Ti	4	378.5462	182.9413	0.0145
Ni	Al	1	299.9726	0	1
Ni	Li	2	323.9603	23.9877	2.31x10^{-6}
Ni	Zr	3	392.5817	92.6090	7.33x10^{-7}
Ni	Ti	4	417.2645	117.2918	1.04x10^{-8}
Pb	Li	1	170.8444	0	1
Pb	Al	2	198.4352	27.5908	2.75x10^{-6}
Pb	Zr	3	232.8280	61.9836	4.54x10^{-7}
Pb	Ti	4	278.7717	107.9273	6.03x10^{-11}
V	Al	1	280.6179	0	1
V	Li	2	344.8625	64.2446	1.12x10^{-14}
V	Zr	3	436.7883	156.1704	1.22 x10^{-34}
V	Ti	4	455.1171	174.4992	1.28 x10^{-38}
Zn	Al	1	407.2074	0	1
Zn	Li	2	450.7297	43.5222	4.21x10^{-5}
Zn	Zr	3	547.0623	139.8548	1.14x10^{-7}
Zn	Ti	4	570.0306	162.8231	2.25x10^{-8}

Appendix F. Maps of the Spatial Distribution of Metals in the PAD.

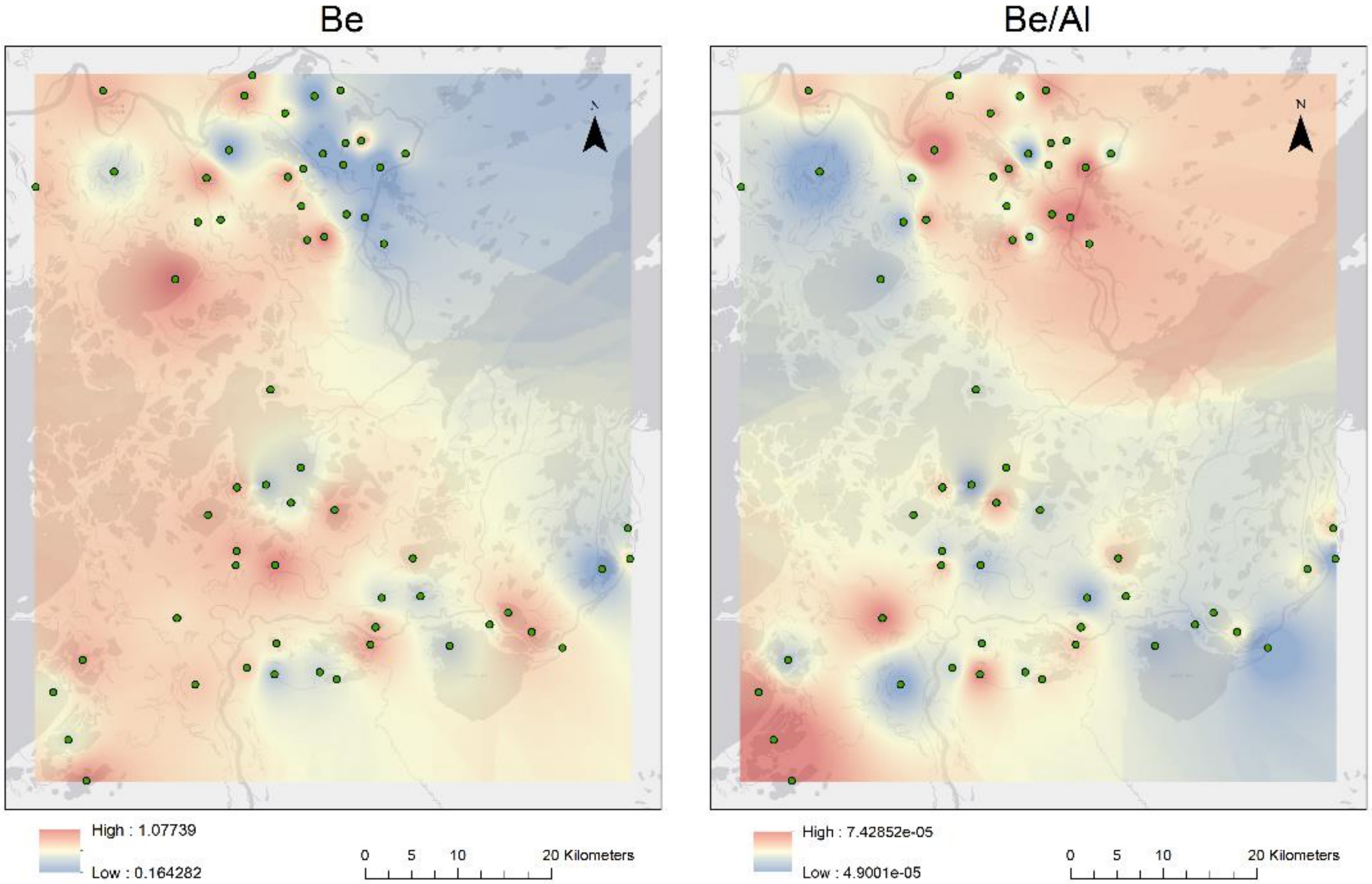

Figure F1. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Be (Moran's = 0.03) on the left and Al-normalized concentrations of Be (Moran's I = -0.72) on the right.

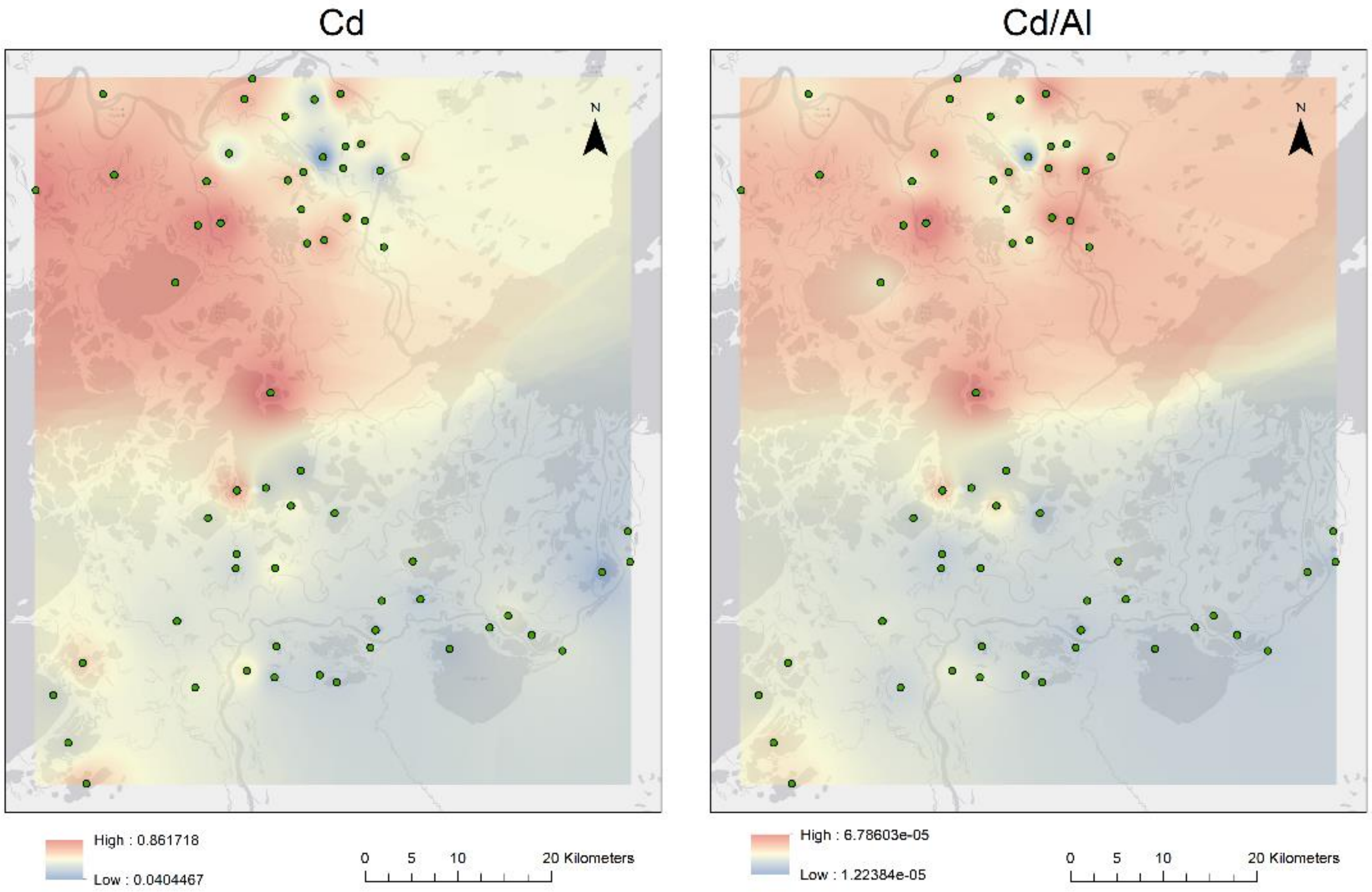

Figure F2. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Cd (Moran's I = -0.56) on the left and Al-normalized concentrations of Cd (Moran's I = -1.23) on the right.

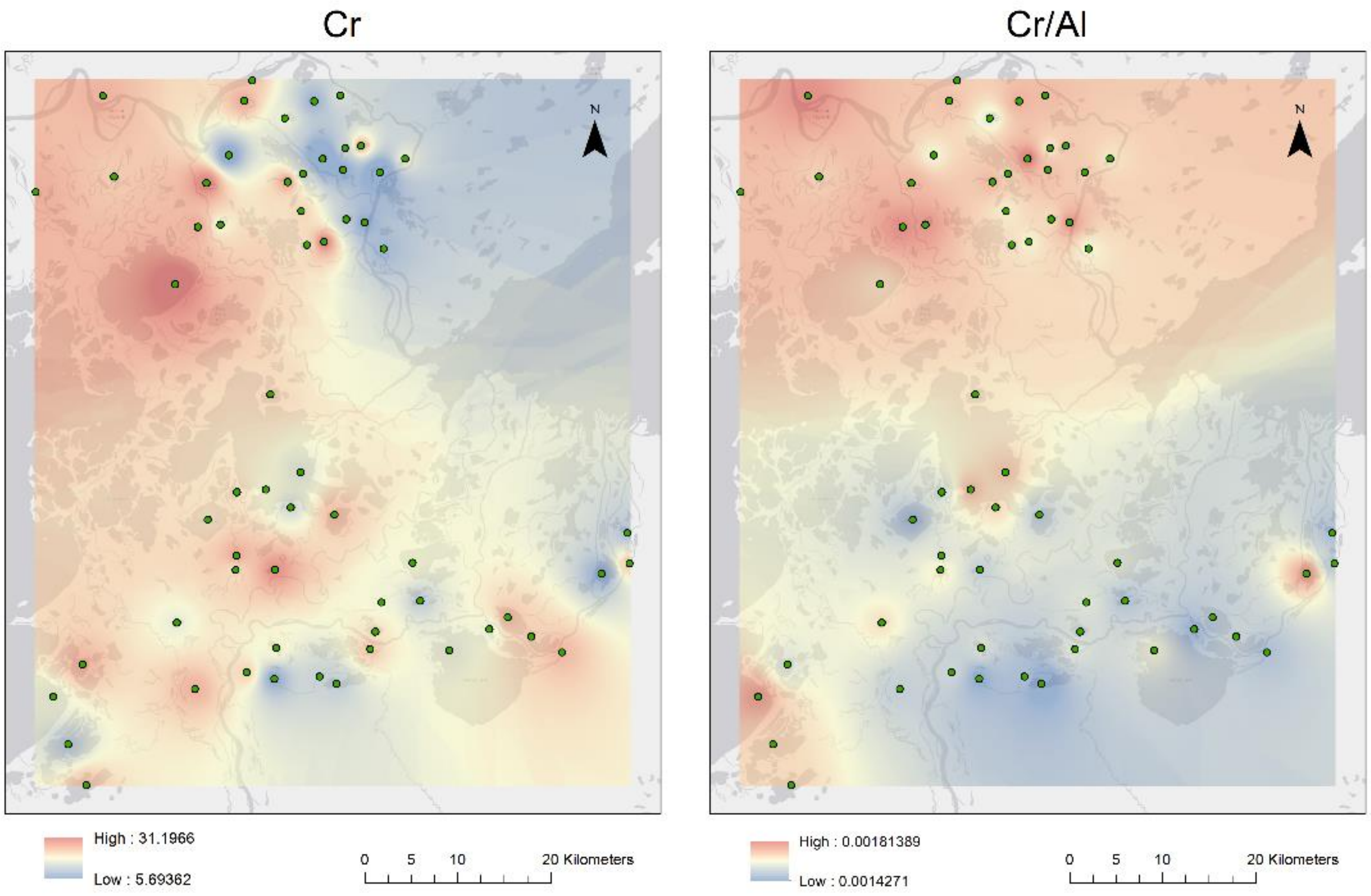

Figure F3. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Cr (Moran's I = 0.08) on the left and Al-normalized concentrations of Cr (Moran's I = -0.77) on the right.

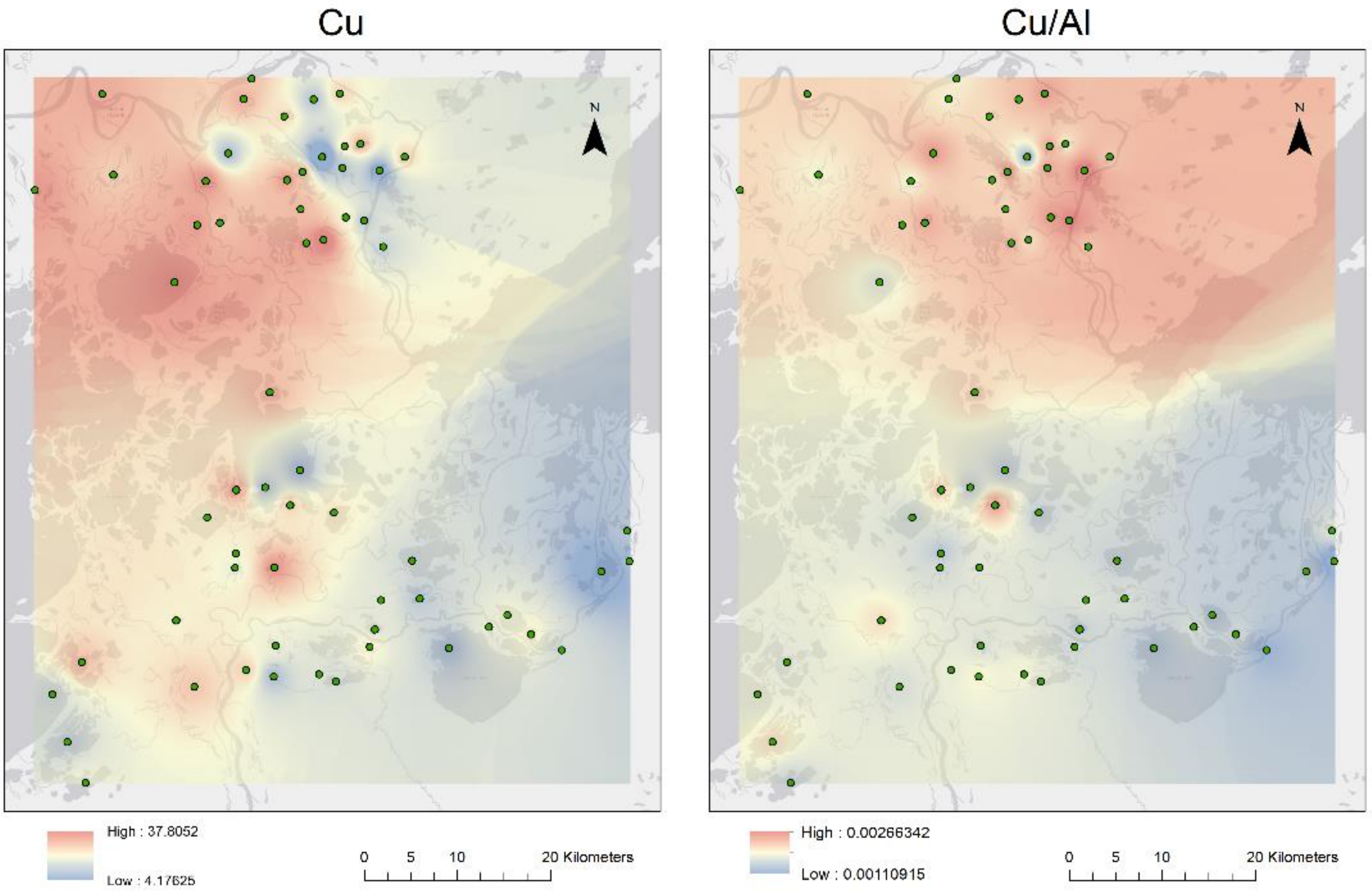

Figure F4. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Cu (Moran's I = 0.22) on the left and Al-normalized concentrations of Cu (Moran's I = -1.77) on the right.

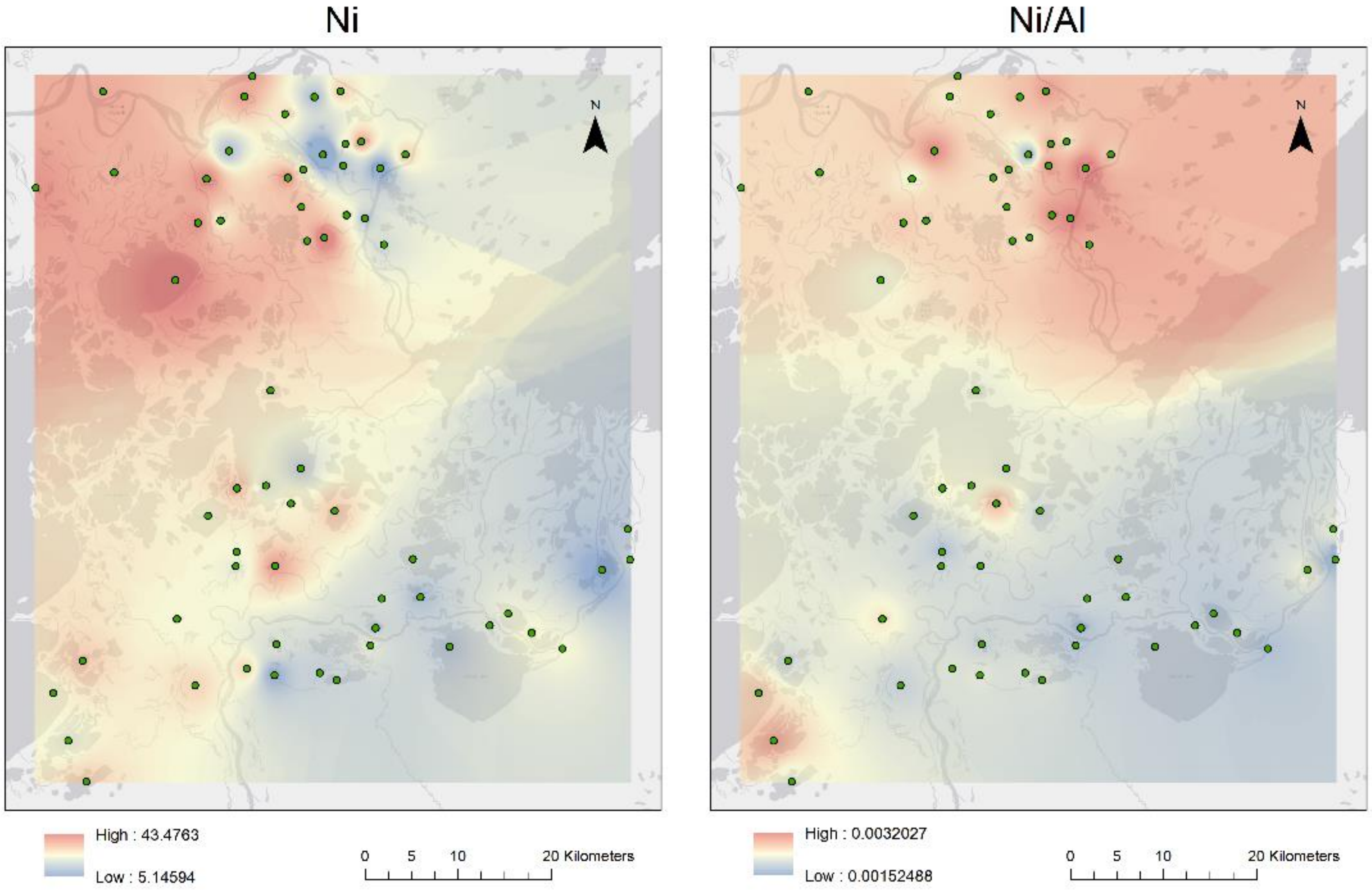

Figure F5. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Ni (Moran's I = 0.13) on the left and Al-normalized concentrations of Ni (Moran's I = -2.00) on the right.

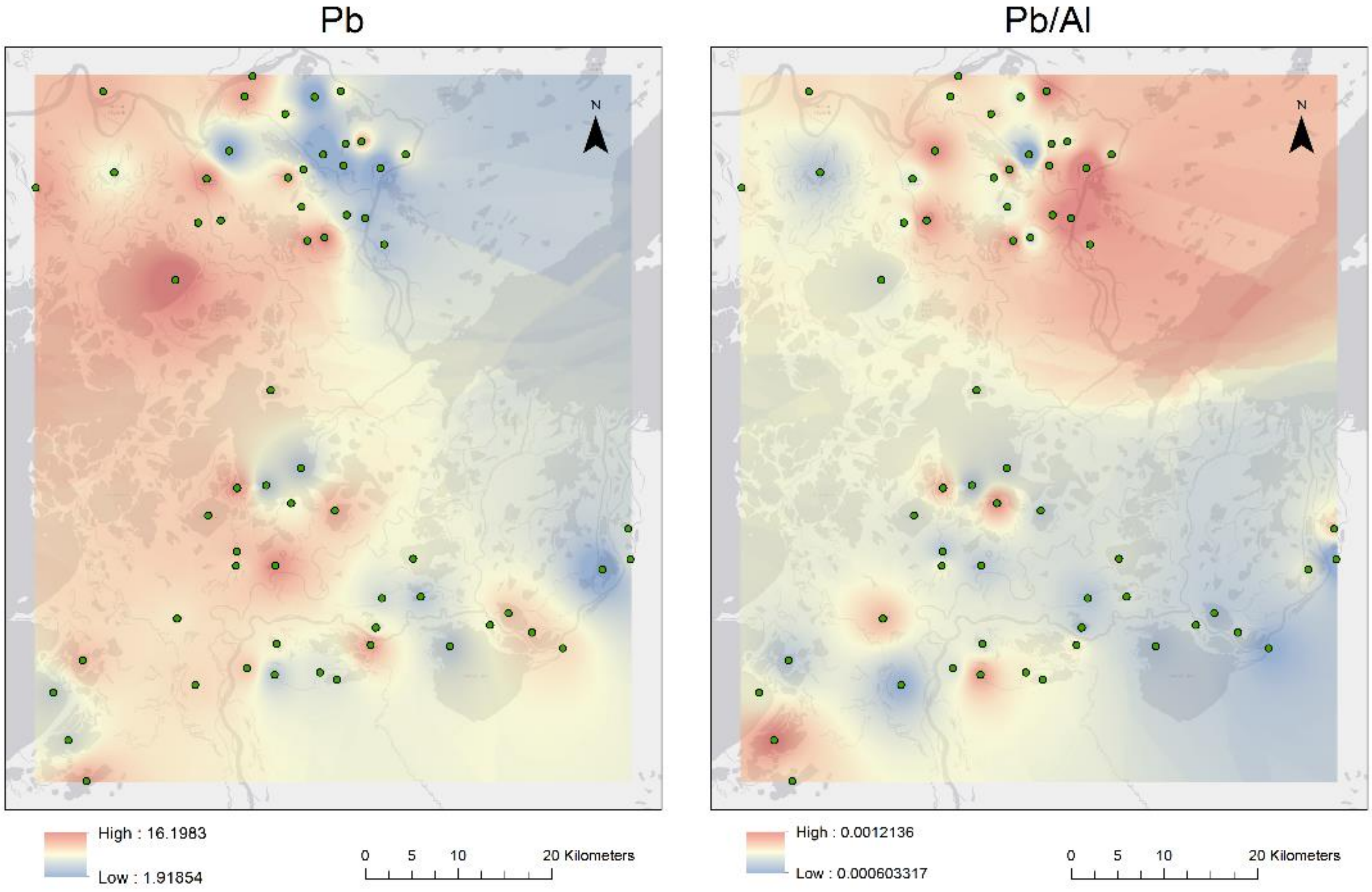

Figure F6. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Pb (Moran’s I = -0.31) on the left and Al-normalized concentrations of Pb (Moran’s I = -3) on the right.

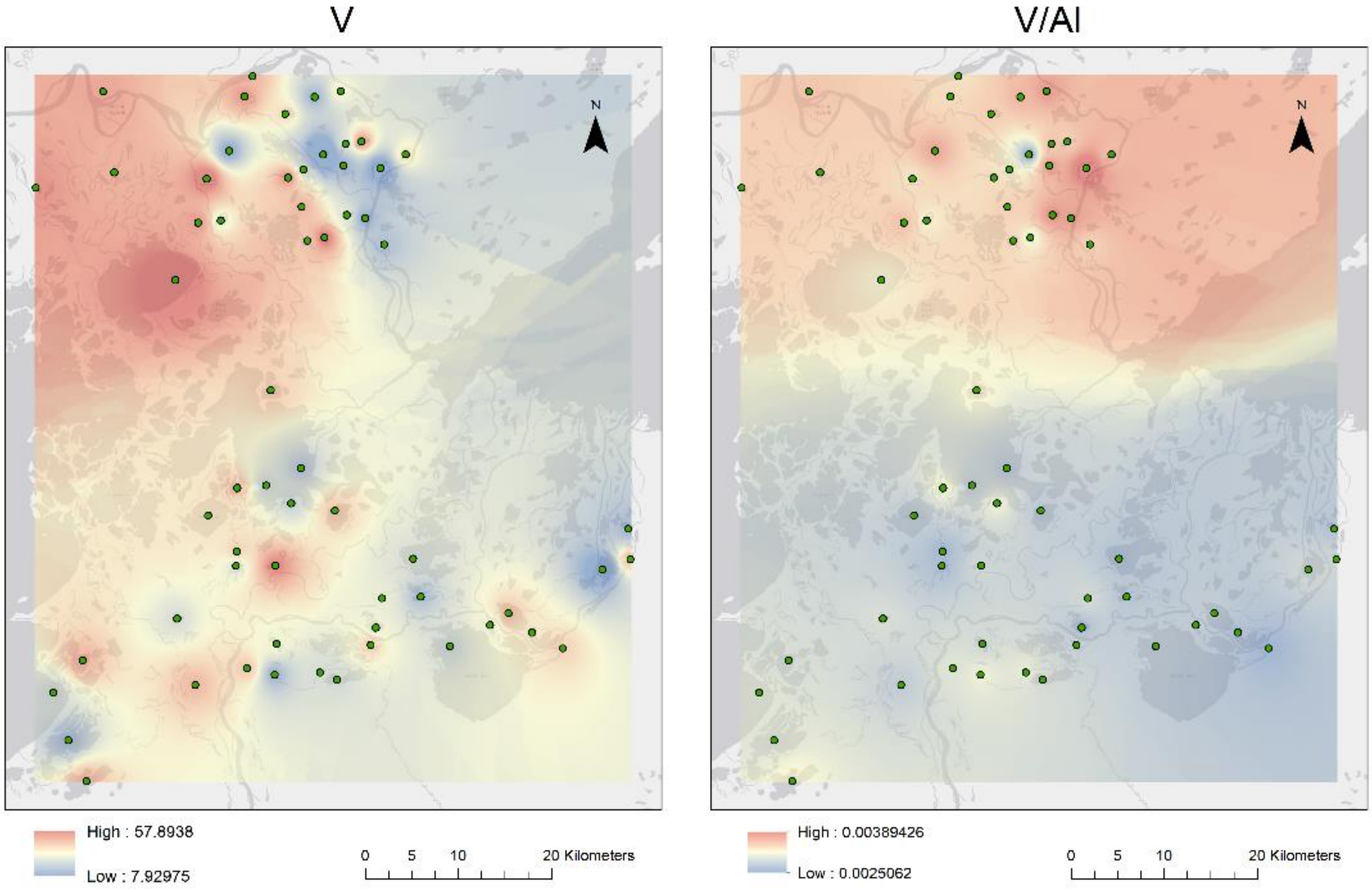

Figure F7. Inverse distance weighted (IDW) interpolated maps for raw concentrations of V (Moran's I = 0.54) on the left and Al-normalized concentrations of V (Moran's I = -0.13) on the right.

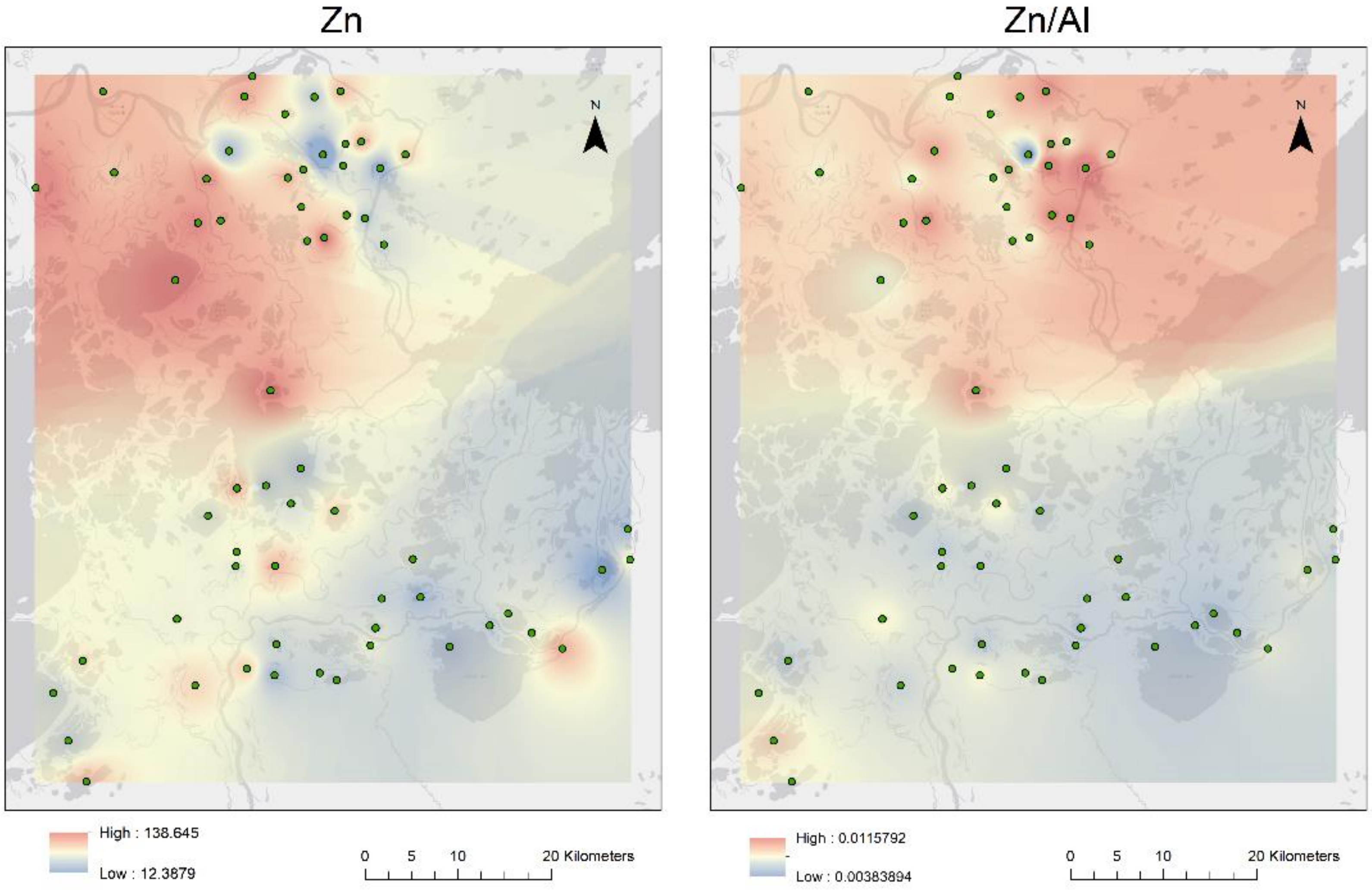

Figure F8. Inverse distance weighted (IDW) interpolated maps for raw concentrations of Zn (Moran's I = -0.48) on the left and Al-normalized concentrations of Zn (Moran's I = 0.38) on the right.