Application of artificial substrate samplers to assess enrichment of metals of concern by river floodwaters to lakes across the Peace-Athabasca Delta

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Potential for downstream delivery of contaminants via Athabasca River floodwaters to lakes of the Peace-Athabasca Delta (PAD), northeastern Alberta (58.6°N, 111.8°W), has raised local to international concern. Prior investigations have shown metals concentrations in sediment of lakes supplied by river floodwaters are not enriched above pre-industrial baselines. Additional real-time aquatic ecosystem monitoring approaches are needed to complement sediment-based techniques where time intervals captured are uncertain. Here, we quantify enrichment of eight metals (Be, Cd, Cr, Cu, Ni, Pb, V, Zn) at the base of aquatic food webs, relative to sediment-based pre-industrial baselines, via analysis of biofilm-sediment mixtures accrued on artificial substrate samplers deployed during summers of 2017 and 2018 in >40 lakes spanning hydrological gradients of the PAD. Widespread flooding in spring 2018 allows for assessment of metals enrichment by Athabasca River floodwaters. A main finding is that river floodwaters are not implicated as a pathway of metals enrichment to biofilm-sediment mixtures in PAD lakes from upstream sources. MANOVA tests revealed no significant difference in residual concentrations of all eight metals in lakes that did not flood versus lakes that flooded during one or both study years. Also, no enrichment was detected for concentrations of biologically inert metals (Be, Cr, Pb), and those related to oil-sands development (Ni, V). Enrichment of Cd, Cu, and Zn at non-flooded lakes, however, suggests uptake of biologically active metals complicates comparisons of organic-rich biofilm-sediment mixtures to sediment-derived baselines for these metals. Results lend confidence that this novel approach could be adopted for lake monitoring within the Wood Buffalo National Park Action Plan.

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Chapter 1: Introduction

1.1. Need for effective environmental monitoring in the Mackenzie River Basin

Freshwater ecosystems, including rivers, streams, lakes, and wetlands, are abundant within the Mackenzie River Basin in northern Canada (Foerstel, 1980; Rosenberg and Barton, 1986). The Mackenzie River Basin forms North America's second longest continuous river system (Mackenzie-Slave-Peace-Finlay, 4241 km), and includes some of Canada's largest deltas (e.g., Peace-Athabasca, Slave and Mackenzie deltas). The deltas occur where substantial rivers enter large water bodies (Lake Athabasca, Great Slave Lake, Beaufort Sea), and they support high concentrations of small lakes and wetlands (Emmerton et al., 2007; Lewis, 1991; Marsh, 1990; Peters et al., 2006; Rouse et al., 1997). These diverse water bodies offer a spectrum of aquatic habitats for unique species and communities that are deeply integrated in human culture. While the larger water bodies boast fish, an important food source for the human population (Cohen, 1994), the myriad of small lakes serve as feeding, drinking, and nesting grounds for migratory birds and other culturally-significant wildlife (Rautio et al., 2011). Beyond the provision of these natural resources, the crucial roles of freshwater ecosystems extend to transportation, energy, and recreation (Naiman and Turner, 2000). Unfortunately, important services provided by freshwater ecosystems may be impaired by stressors induced by rapid environmental and socio-economic change (Dudgeon et al., 2006; Naiman and Turner, 2000). In northwestern Canada, major stressors of concern include anthropogenic climate change (Heino et al., 2009; Rautio et al., 2011; Rood et al., 2005; Wrona et al., 2006a; Prowse et al., 2006), river flow regulation (Dynesius and Nilsson, 1994; Peters and Prowse, 2001), and point and non-point source pollution (Macdonald et al., 2005; Schindler and Smol, 2006; Wrona et al., 2006b). Rising demand on freshwater resources and encroachment of development have generated increasing concerns about degradation of northern freshwater ecosystems.

In light of the need for effective stewardship of northern freshwater ecosystems, there is urgency to establish monitoring programs capable of supporting decisions about water resource protection (Burt, 2003; Parr et al., 2003; Vander Naald, 2019). Aquatic environmental monitoring programs, characterized by systematic, repetitive measurements over long periods, produce objective data that assess effects of human activities on aquatic ecosystems (Dowdeswell et al., 2010; Lindenmeyer and Likens, 2009, 2010; Roach and Walker, 2017). To be effective, monitoring programs must generate

information that links measured environmental effects with specific causes, and therefore must quantify the extent of degradation since exposure to known stressors (Roach and Walker, 2017).

A major challenge for aquatic ecosystem monitoring programs is to decipher cause-effect relationships due to insufficient characterization of baseline conditions that existed before the human disturbance began (Blais et al., 2015). Because monitoring programs tend to begin only after the onset of disturbance, baseline conditions of an exposed site are frequently defined by conditions measured at a comparable, yet unaffected, reference site (Blais et al., 2015; Kilgour et al., 2007; Munkittrick et al., 2002). However, in systems lacking an appropriate reference site, monitoring programs that do not extend to pre-disturbance periods are poorly equipped to tease apart the influence of anthropogenic disturbance versus natural processes on the environment. This is especially true when confounding causal variables are active in the environment, such as supply of contaminants from natural sources (Roach and Walker, 2017; Wiklund et al., 2014). Therefore, it is extremely beneficial for aquatic monitoring programs to incorporate long-term perspectives on pre-disturbance environmental conditions. The need for an aquatic monitoring program with these attributes is acute in the Peace-Athabasca Delta (PAD), one such northern freshwater ecosystem within the Mackenzie River Basin where concern about degradation of freshwater ecosystems is widespread.

1.2. Peace-Athabasca Delta

The PAD is the largest inland freshwater boreal delta on Earth, spanning a ~6000 km^2 landscape in northern Alberta, Canada (~58.6°N, 111.8°W; Peters et al., 2006). Situated at the confluence of the Peace and Athabasca rivers, the PAD is the southernmost of the three deltas within the Mackenzie River Basin. The PAD contains hundreds of shallow and productive lakes which provide invaluable habitat for migratory birds, including the endangered whooping crane (Prowse and Conly, 2000), fish (Bradford and Hanson, 1990), and other diverse wildlife (muskrat, beaver, moose, bison, black bear, wolf). The delta has long sustained hunting and fishing activities of Indigenous peoples and holds cultural importance to local First Nations (Mikisew Cree, Athabasca Chipewyan) and Metis communities (MCFN, 2014). This suite of ecosystem services merited the PAD's designation as a Ramsar Wetland of International Importance and contributed to Wood Buffalo National Park's (WBNP) (contains ~80% of the PAD) recognition as a UNESCO World Heritage Site.

Concern has been rising about ecological degradation of the PAD by multiple potential stressors. One threat comes from oil sands mining and processing activities in the Athabasca Oil Sands Region

(AOSR), located 200 km upstream of the PAD along the Athabasca River. These activities incur potential for metals and other contaminants of concern to enter the Athabasca River from tailings ponds seepage, pipeline leakage, or major spills of bitumen, oil, wastewater, and aerial deposition to the river and adjacent lands (Timoney and Lee, 2009). Subsequent delivery of the contaminants to downstream lakes of the PAD could present long-term health risks for humans and aquatic ecosystems. Metals are of concern because they are toxic at low concentrations, resist decomposition and may bioaccumulate in organisms and biomagnify along the food chain (Tchounwou et al., 2012). These concerns have heightened as oil sands production has continued to increase and because output is projected to reach up to 4.25 million barrels per day by 2035 (CAPP, 2019).

Increasing concern over supply of metals from the oil sands industry was among factors that motivated a petition by the Mikisew Cree First Nations in 2014 to enlist WBNP as "World Heritage in Danger" (MCFN, 2014). In response, the World Heritage Committee (WHC) recommended 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). More recently, the 2019 WBNP World Heritage Site Action Plan reiterated a similar goal to "establish a monitoring regime that tracks the trend of indicators across the extent of WBNP and the PAD" (WBNP 2019, p. 44) and outlined recommendations to provide better information about water quality concerns, such as rising concentrations of metals in lake and river water. Evidently, extensive attention has been given to the importance of improving monitoring efforts to safeguard the PAD.

Like many other northern Canadian landscapes, the PAD is a challenging and costly landscape to monitor because of its enormity and remote location (Mallory et al., 2018). An additional monitoring challenge is presented because the Athabasca River receives natural loadings of metals, such as Ni and V, which are present in the naturally occurring Alberta oil sands (Hodgson, 1954; Jack et al., 1979; Jacobs and Filby, 1983). When this natural supply is not quantified, it hampers interpretation of contemporary measurements such that natural versus anthropogenic sources of metals cannot be disentangled (Dowdeswell et al., 2010). For this reason, a rigorous understanding of the pre-industrial concentrations of metals and range of natural variation in the environment is required for effective monitoring of the extent of oil sands pollution in the PAD (Dowdeswell et al., 2010).

Direct measurements of pre-industrial metals concentrations in the PAD are missing because monitoring only began 30 years after the onset of oil sands development. To fill this information gap, there have

been numerous calls for paleolimnological investigations to establish temporal records of metals accumulation using radiometrically-dated sediment cores from flood-prone lakes (Dowdeswell et al., 2010; Smol, 1992; Wrona and di Cenzo, 2011). In response to these calls, paleolimnological studies have been implemented at multiple locations and the resulting information on pre-industrial concentrations of metals has served to develop knowledge of baseline metals concentrations in sediment of lakes in the Peace and Athabasca sectors of the PAD (Kay et al., 2020; Owca et al., 2020; Wiklund et al., 2012, 2014).

An initial approach to quantify the degree of contemporary enrichment of metals in lakes across the PAD involved superimposing metals concentrations in surface sediment onto pre-industrial baselines, and results demonstrated that no substantial enrichment above baseline was detectable (Owca et al., 2020). The study included a delta-wide survey of 1-cm thick surface sediments collected in 2017, which captured variable time intervals of sediment deposition and may include flood and non-flood conditions. But, the study also included a subset of lakes that flooded two months prior to surface-sediment collection in 2018, which provided snapshots of metals concentrations in river sediment conveyed by floodwaters. Although the 2018 surficial-sediment flood layers were conducive to detecting enrichment of metal concentrations by upstream oil sands activities, flood events are episodic and variable by nature, and opportunistic sampling following a flood event may not always be feasible. Therefore, development and application of additional monitoring approaches of metal enrichment are helpful to provide another unique perspective to address concerns of oil sands development and delivery of metal pollutants to the PAD.

1.3. Artificial substrate samplers

There are numerous approaches for monitoring metal pollution in aquatic environments, such as collection of environmental media (water, soil, biota), deployment and retrieval of artificial substrate samplers, or use of continuous automated water sampling technologies. These approaches differ immensely in cost, timescales (frequency and duration of sample collection) and information content. All approaches incur a cost to travel to sample sites, but additional purchase cost associated with collection of environmental media is very low compared to the cost of automated sampling devices (which are generally feasible only in commercial settings or non-remote locations; Syu et al., 2020). In remote landscapes, ‘grab sampling’ of water or other media is often performed at seasonal to monthly time intervals (Elzwayie et al., 2017) and provides instantaneous measurement or snapshot of conditions

influenced by processes acting over previous days to weeks, whereas passive sampling, using artificial substrate samplers, biota, or sediment, has potential to provide information over a longer, continuous period of integration. Water and sediment metal concentration data can be compared with established quality benchmarks for ecological risk assessment (Chapman, 2018; van Dam et al., 2019), whereas metal concentrations in biota (macroinvertebrates, periphyton, fish, Resh et al. 2008; Namba et al., 2020), synthetic membrane devices (Björklund et al., 2001; Davison and Zhang, 2012), and artificial substrate samplers (Bere et al. 2012; Lavoie et al., 2012; Leguay et al., 2016) inform on bioavailability of environmental metals. Selection of an ideal monitoring approach among the plethora of options depends on characteristics of the study area and the nature of scientific questions being addressed.

In the vast remote landscape of the PAD, where episodic input of river floodwater is widely perceived to deliver metals of concern from upstream development (WBNP, 2019), monitoring metal pollution using artificial substrate samplers may be advantageous. Artificial substrate samplers accrue a mixture of biofilm, consisting of periphytic algae that are known to be representative of natural communities in the PAD (Wiklund et al., 2010), along with fungi and microbes, and entrapped sediments. They are cost-effective and offer a more consistent substrate than most natural materials, and natural materials may be difficult and time-consuming to locate and collect (MacDonald et al., 2012; Resh et al., 2008). Artificial substrate samplers also offer control of accrual time, thus allowing investigators to capture an integrated record of metals accumulation within biofilm-sediment mixtures over a known timeframe (Leguay et al., 2016). This provides the ability to link the timing of events of potential metals delivery, such as river flooding, with the timing of metals accumulation. Finally, biofilm-sediment mixtures offer a novel perspective on the concentrations of metals at the base of aquatic food webs that may bioaccumulate in culturally important organisms at higher trophic positions (i.e., fish, muskrat; Wu et al., 2017).

The benefits of monitoring using artificial substrate samplers have long compelled scientists to ascertain that metals concentrations accumulated in biofilm-sediment mixtures are representative of metals concentrations in the abiotic environment. This notion was initially validated by the finding that concentrations of metals in biofilm-sediment mixtures were generally reflective of concentrations in surface sediment and/or water at the same locations (Pederson and Vaultonburg, 1996; Ramelow et al., 1987, 1992). These studies did not measure relative proportions of organic and mineral matter, but it was suspected that the amount of trapped sediments in biofilm-sediment mixtures differed among sites and affected correspondence between metals concentrations in the various media. Subsequent testing

circumvented potential complications related to differing amounts of trapped sediments in biofilm-sediment mixtures by isolating those metals associated with the biotic component of the mixture. The demonstrated correlation between intracellular concentrations of metals in biota from the biofilms and total and/or free-ion metals in water supported use of biofilm-sediment mixtures as proxies for bioavailable metals in the environment (Behra et al., 2002; Bere et al. 2012; Holding et al., 2003; Lavoie et al., 2012; Leguay et al., 2016; Meylan et al., 2003). Differences in algal community composition were suspected to distort the relationship between metals concentrations in biofilm-sediment mixtures and water on one occasion (Anishchenko et al., 2010). However, because the body of evidence consistently shows strong relations between metals in water and intracellular metals in taxonomically diverse biofilm-sediment mixtures (Behra et al., 2002; Bere et al. 2012; Holding et al., 2003; Lavoie et al., 2012; Leguay et al., 2016; Meylan et al., 2003), it is possible that entrapped sediments were instead the cause of the distortion noted by Anishchenko et al. (2010), as has been previously observed (Pederson and Vaultonburg, 1996; Ramelow et al., 1987, 1992).

Observations that sediment-bound metals contribute substantially to metals concentrations in biofilm-sediment mixtures suggest there is potential to relate metals concentrations in biofilm-sediment mixtures to those in sediment. It is presumed this is especially applicable in turbid aquatic environments, such as floodplains or streams, where minerogenic suspended sediment may contribute substantially to the biofilm-sediment mixtures (Lehmann et al., 1999). Overlaying contemporary metals concentrations in biofilm-sediment mixtures on pre-disturbance concentrations in lake sediment cores may enable evaluation of enrichment relative to natural, pre-disturbance conditions. Although this combination of contemporary and pre-disturbance datasets has been successfully employed for surface sediment (Owca et al., 2020), application of this approach using biofilm-sediment mixtures is, to our knowledge, novel.

1.4. Objective

The overarching objective of this study is to assess roles of river floodwaters on enrichment of metals of concern at the base of food webs in lakes of the PAD. This objective will be approached in two steps. First, quantification of metals enrichment is accomplished using comparisons of metals concentrations in pre-industrial lake and river sediment with those in biofilm-sediment mixtures accrued on artificial substrate samplers during the open-water seasons of 2017 and 2018. Then, the role of river floodwaters as a pathway of metals enrichment is evaluated by linking the timeframe of metals accumulation in biofilm-sediment mixtures to the timing of known flood events. The two-year study period captures a

rare, widespread flood event in the southern Athabasca sector that inundated numerous lakes in spring 2018 (Remmer et al., 2020a). This provides opportunity to evaluate potential delivery of industry-supplied metals of concern via the Athabasca River to the Athabasca Delta. Information gathered will refine understanding of perceived threats from upstream development in the AOSR. Further, this research aims to establish a foundation for ongoing monitoring of metals concentrations in the PAD, in fulfillment of recommendations highlighted by the WHC/IUCN and Parks Canada (WHC/IUCN, 2017; WBNP, 2019*).*

The stated objectives are addressed in Chapter 2, which is intended as a peer-reviewed journal article submitted to the Journal of Hydrology: Regional Studies in a Special Issue on Water and Environmental Management in Oil Sands Regions. The eventual journal article is multi-authored by Cory A. M. Savage[a] (conceptualization, formal analysis, investigation, data collection, writing), Tanner Owca[b] (data collection), Mitchell L. Kay[a] (data collection, input on data analysis), Jelle Faber[b] (data collection), Brent B. Wolfe[b] (conceptualization, writing, review and editing, supervision, funding acquisition), and Roland I. Hall[a] (conceptualization, writing, review and editing, supervision, funding acquisition).

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Chapter 2: Application of artificial substrate samplers to assess enrichment of metals of concern by river floodwaters to lakes across the Peace-Athabasca Delta (Alberta, Canada)

2.1. Introduction

Northern freshwater ecosystems provide invaluable natural resources and hold cultural and social significance, but are increasingly threatened by anthropogenic activities (Dudgeon et al., 2006; Schindler, 2010; Schindler and Smol, 2006). To effectively safeguard these ecosystems, evidence-based management decisions need to be guided by monitoring data capable of quantifying the extent of degradation (Roach and Walker, 2017). Ability to conduct informed monitoring for contaminants of concern, however, is often hindered by a lack of understanding of pre-disturbance concentrations and natural variation, because data collection tends to be initiated after onset of anthropogenic disturbance (Blais et al., 2015). Long-term datasets that extend to pre-disturbance periods are critical to identify the influence of anthropogenic activities versus natural processes on the environment (Lindenmayer and Likens, 2009, 2010), especially when located downstream of natural sources of contaminants (Wiklund et al., 2014). It is therefore advantageous, but infrequent, to design monitoring programs that incorporate information about pre-disturbance concentrations to allow for rapid real-time determination of the degree of degradation.

One such at-risk system is the Peace-Athabasca Delta (PAD), located in northeastern Alberta, Canada. As the world's largest inland freshwater boreal delta, the hundreds of productive, shallow lakes in the PAD provide critical habitat to biota and support traditional lifestyles of local Indigenous communities (Timoney, 2013). These ecosystem services merited the PAD's designation as a Ramsar Wetland of International Importance and contributed to Wood Buffalo National Park's (WBNP) recognition as a UNESCO World Heritage Site, which contains ~80% of the PAD. However, ongoing expansion of mining in the Alberta Oil Sands Region (AOSR) has long generated concerns that contaminants are being released into the Athabasca River and delivered downstream to the PAD where they have potential to degrade water quality of rivers and lakes (Dowdeswell et al., 2010; Schindler, 2010; Timoney and Lee, 2009). The urgent need for better monitoring practices in the PAD has been emphasized in a petition by the Mikisew Cree First Nation in 2014 to enlist WBNP as "World Heritage in Danger" (MCFN, 2014), recommendations by the UNESCO World Heritage Committee (WHC/IUCN, 2017), and priorities within the Wood Buffalo National Park Action Plan (WBNP, 2019).

An approach that has been proposed for effective monitoring of oil sands pollution is paleolimnological investigation of sediment cores from lakes to establish the range of natural variability of contaminants prior to industrialization (Dowdeswell et al., 2010; Wrona and di Cenzo, 2011). This approach has been implemented in the PAD (Kay et al., 2020; Wiklund et al., 2012, 2014), and the results have served to develop knowledge of the natural variability of metals concentrations in lake sediment deposited before 1920. Sediment deposited before 1920 pre-date the earliest paleolimnological evidence of atmospheric deposition of pollutants from industrial emissions, which was followed by a decline in atmospheric deposition after ~1970 as industrial practices improved (Wiklund et al., 2012). These baselines enabled evaluation of contamination of lakes by atmospheric and fluvial pathways using contemporary concentrations of metals of concern in surface sediment of lakes across the PAD, which demonstrated no substantial enrichment above the pre-1920 baselines (Owca et al., 2020). Their study analyzed 1-cm thick surface sediment samples collected in 2017, which captured recent time periods of sediment deposition that are variable among lakes (~2 to 5 years). Also included was analysis of exclusively flood-supplied surface sediment samples collected in 2018 from lakes that had received river floodwaters two months prior. However, because such flood events are episodic and of varying magnitude, development and testing of additional 'real-time' monitoring approaches of metal concentrations are warranted.

Among the plethora of complementary approaches for monitoring contaminants, artificial substrate samplers, which accrue a mixture of biofilm, consisting of communities of periphytic algae, fungi, and microbes, and entrapped suspended sediments (Jowett and Biggs, 1997; Szlauer-Łukaszewska, 2007; Wu et al., 2017), may provide some advantages. They offer careful control of biofilm-sediment accrual time and circumvent potential difficulties associated with locating and collecting appropriate natural substrates (MacDonald et al., 2012; Wiklund et al., 2010). Because of these advantages, artificial substrate samplers have been tested and used for monitoring water quality (Biggs, 1989), including metals content (Holding et al., 2003; Namba et al., 2020; Pederson and Vaultonburg, 1996; Ramelow et al., 1987, 1992; Tang et al., 2014). For several metals of concern, concentrations in biofilm-sediment mixtures accrued on artificial substrate samplers have been shown to correspond well with concentrations in sediment from the same locations (Holding et al., 2003; Ramelow et al., 1987, 1992). This suggests there is potential to combine use of artificial substrate samplers with measurements of pre-industrial metal concentrations in sediment cores to evaluate for evidence of enrichment relative to natural conditions, which, to our knowledge, is a novel approach.

Here, we use concentrations of metals in pre-industrial (pre-1920) lake sediment and in biofilm-sediment mixtures accrued on artificial substrate samplers during the open-water season to quantify enrichment of metals of concern at the base of food webs in lakes of the PAD. To assess the role of river floodwaters, our study spans two years (2017, 2018), which includes numerous lakes inundated by the large ice-jam flood event in spring 2018 (Remmer et al., 2020a). Most of the flooding in spring 2018 occurred in the southern Athabasca sector of the delta, which provides opportunity to evaluate extent of contamination in Athabasca River water by upstream oil sands development. The suite of metals selected for this study follow those analyzed in prior studies of sediment and water in this region (Kay et al., 2020; Kelly et al., 2010; Owca et al., 2020; Wiklund et al., 2014) and 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), and zinc (Zn)), as well as vanadium (V) which is a known indicator for oil sands pollution (Gosselin et al., 2010; Jacobs and Filby, 1982; Reynolds et al., 1989). The study aims to refine current understanding of perceived threats from upstream oil sands development and evaluate an approach that could be adopted for integrated hydrological and contaminants monitoring for lakes of the PAD within the federal WBNP Action Plan (WBNP, 2019).

2.1.1. Site description

Centered at 58.6°N, 111.8°W in northeastern Alberta, Canada, the 6000 km^2 PAD contains hundreds of shallow lakes (Fig. 1, 2). The PAD is composed of two hydrologically distinct sectors: the northern Peace sector and the southern Athabasca sector. Lakes in the relic delta of the northern Peace sector experience limited river connectivity. Episodic ice-jam events on the Peace River during the spring freshet are required to generate widespread flooding (Peters et al., 2006). In contrast, lakes in the relic and active delta portions of the southern Athabasca sector experience a spectrum of limited, intermittent, or continuous surface connection with the northward-flowing Athabasca River and its distributaries (Remmer et al., 2020b; Wolfe et al., 2007).

Previous research has documented extent of ice-jam and open-water flooding with respect to the study lakes in the PAD during 2017 and 2018 (Remmer et al., 2020a, 2020b; Fig. 1). Ice-jam flooding was more widespread in the Athabasca sector in spring 2018 than in spring 2017. Compared to spring ice-jam flooding, a smaller number of lakes in the Athabasca sector also received open-water flooding in summer 2017 and summer and fall 2018. In the Peace sector, no lakes were flooded in 2017, limited ice-

jam flooding occurred in spring 2018, and one lake (PAD 54) also received open-water flooding in summer and fall 2018.

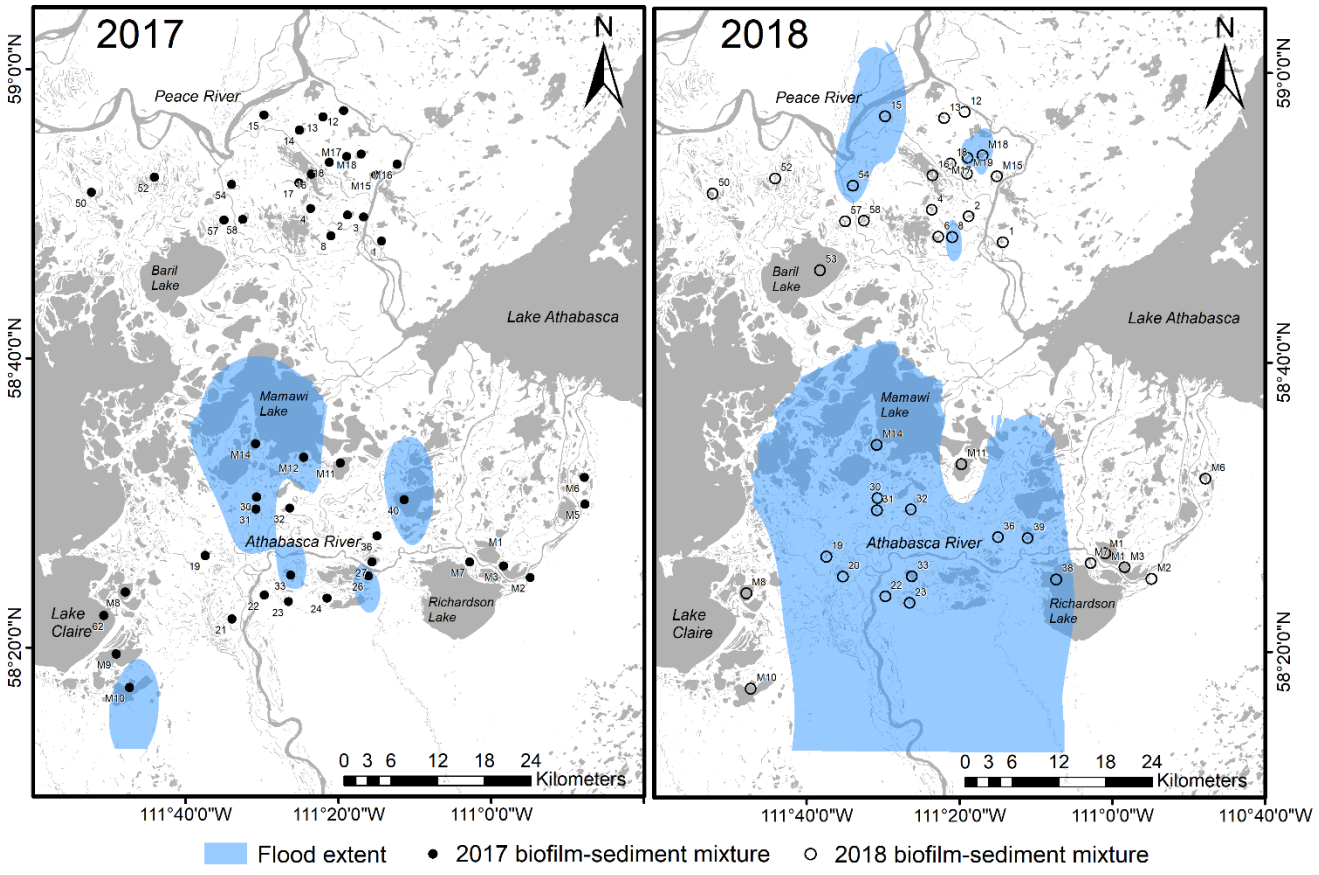

Fig. 1. Map of the Peace-Athabasca Delta (PAD), Alberta, showing the location of lakes from which biofilm-sediment mixtures were collected (n = 49 in 2017; n = 42 in 2018) and the extent of spring ice-jam and open-water flooding in 2017 (left) and 2018 (right). Extent of flooding adapted from Remmer et al. (2020a,b).

2.2. Methods

2.2.1. Field work

Artificial substrate samplers were deployed from the pontoon of a helicopter into 25 lakes in the Athabasca sector and 24 lakes in the Peace sector on May 22-24, 2017 and retrieved on September 12-14, 2017 (Fig. 2). Samplers were deployed again the following year on May 21-23, 2018 and retrieved from 20 lakes in the Athabasca sector and 22 lakes in the Peace sector on September 15-17, 2018 (Fig. 2). Samplers were retrieved from the same lake in both years for 15 lakes in the Athabasca sector and 16 lakes in the Peace sector.

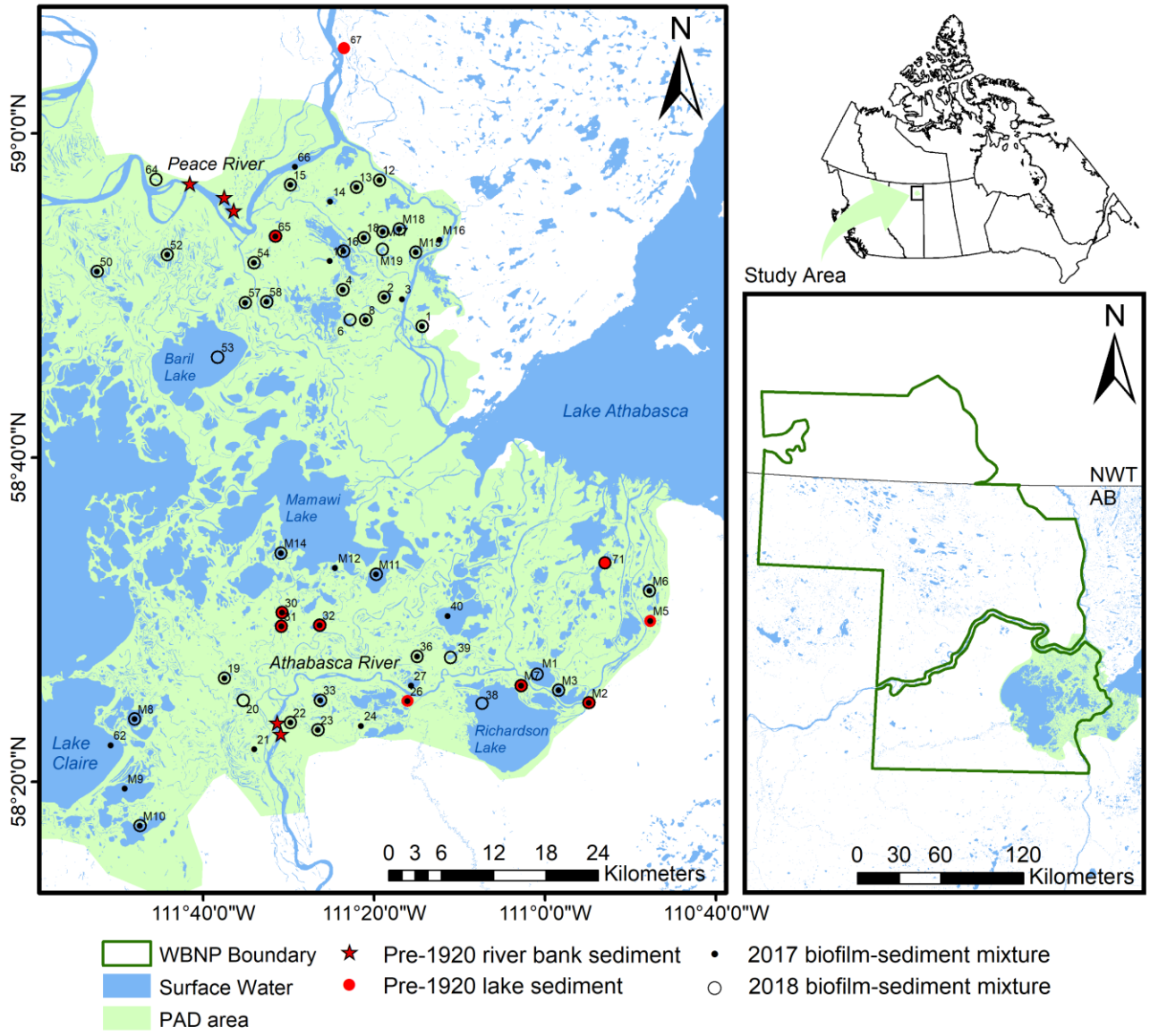

Fig. 2. Map of the Peace-Athabasca Delta (PAD), Alberta, and the location of lakes from which biofilm-sediment mixtures were collected (n = 49 in 2017; n = 42 in 2018) and the location of lakes and riverbank sites from which pre-1920 sediment was collected.

Samplers consisted of 52.5 cm by 18 cm high-density polypropylene shields attached by rope on one end to a wooden float covered in Styrofoam to maintain buoyancy, and to a rock on the other end to remain anchored to the lake bottom (Fig. 3). Rope lengths were sufficient to ensure that samplers were suspended approximately 10-15 cm deep in the water column (Fig. 3). Upon retrieval of the samplers, shields were placed individually into plastic *Ziploc* bags, frozen, and transported to University of Waterloo where they remained frozen until processed for analysis.

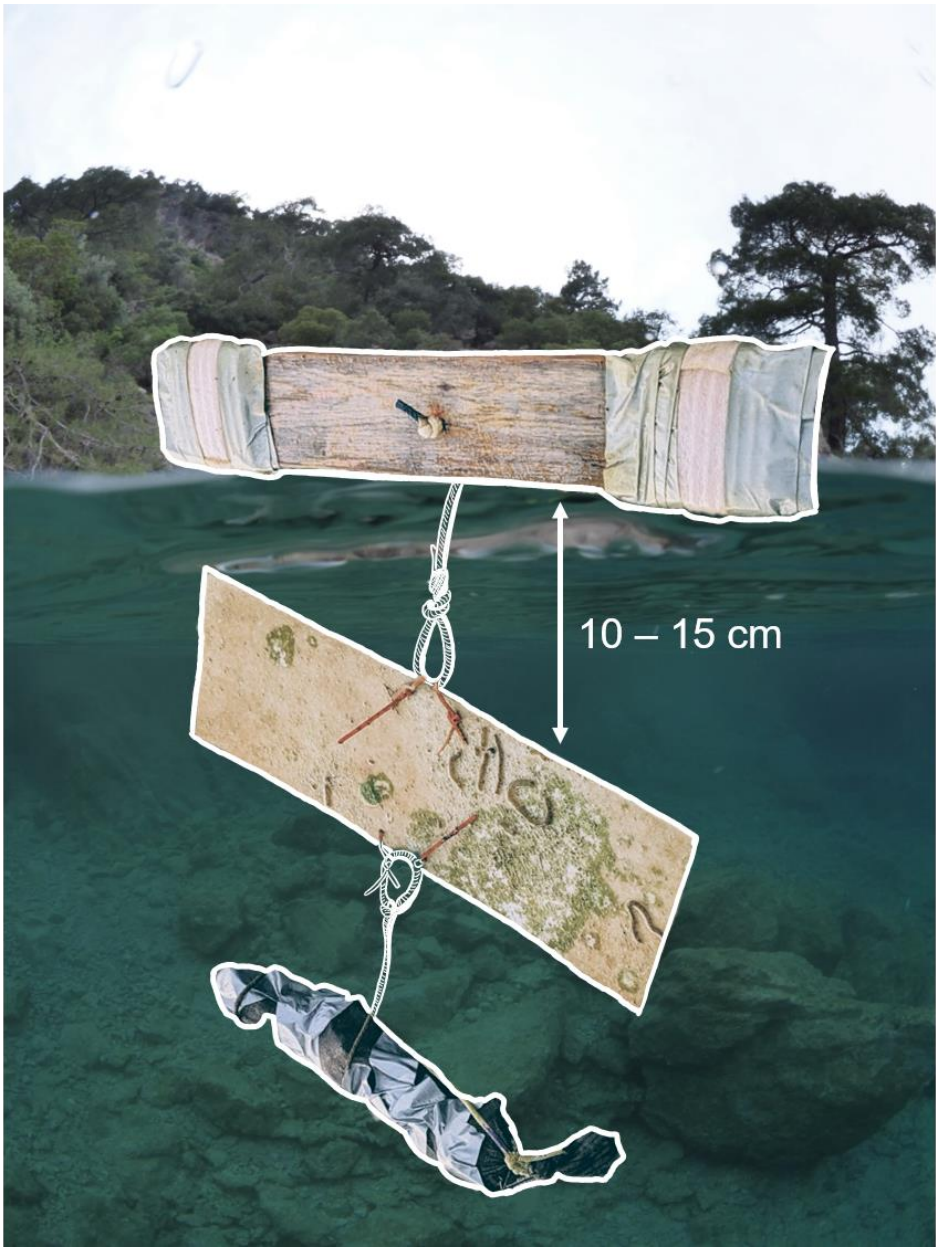

Fig. 3. Schematic of artificial substrate sampler installed in lake, with shield suspended 10-15 cm deep in the water column.

2.2.2. Laboratory analyses

All processing was performed on the shields after they were removed from the freezer and thawed. The biofilm-sediment mixtures were removed from the shields by scraping and rinsing with a recorded volume of high-performance liquid chromatography (HPLC) grade water. The final volume of contents (biofilm-sediment mixture plus rinse water) was also recorded before further subsampling. For loss-on-ignition (LOI) analysis, 20 ml were pipetted into a glass scintillation vial. For metals analysis, the remaining contents were added to a plastic cup and frozen until further processing.

LOI was performed to measure the dry mass and organic matter content (%OM) of biofilm-sediment samples following standard methods (Heiri et al., 2001). For each lake, the 20 ml LOI subsample was added to a pre-weighed porcelain crucible. The crucibles were then dried in an oven at 90^{o}C for 18 hours to determine the dry sample mass. The crucibles were combusted in a muffle furnace at 550°C for 2 hours, cooled and reweighed to determine %OM (relative to dry mass).

For determination of metals concentrations, periphyton subsamples were freeze-dried, weighed, and submitted to ALS Environmental Laboratories (Waterloo, ON) for analyses following EPA Method 200.3/6020A. This is a hotblock digestion with HNO_3 and HCl, in combination with H_2O_2, which provides a conservative estimate of bioavailable metals in organic tissue. These methods are modified from EPA Method 6020A (US EPA, 1998), which was followed for analysis of metals concentrations used to establish pre-industrial baselines from lake sediment cores (Kay et al., 2020; Owca et al., 2020). Uncertainties are ±231.8 mg/kg for Al, ±0.022 mg/kg for Be, ±0.01332 mg/kg for Cd, ±0.3564 mg/kg for Cr, ±1.352 mg/kg for Cu, ±0.678 mg/kg for Ni, ±0. 0.7146 mg/kg for Pb, ±0.738 mg/kg for V, and ±2.398 mg/kg for Zn based on mean difference of 4 sample repeats in 2017 and 1 sample repeat in 2018.

2.2.3. Data handling and analysis

Pre-industrial baselines were established in previous studies from concentrations of metals in sediment deposited before 1920 at two lakes in the Peace sector (n = 65 sediment samples; Owca et al., 2020) and at eight lakes in the Athabasca sector (n = 122 sediment samples; Kay et al., 2020; Fig. 2). For our study, we added concentrations of metals in sediment from riverbank exposures at sites situated along the lower Peace (3 sites, n = 33 samples) and Athabasca (2 sites, n = 37 samples for all metals except n = 26 for Be, n = 29 for Cd, n = 34 for Cr) rivers to these pre-1920 baselines (Fig. 2). The riverbank samples were collected at locations sampled by Hugenholtz et al. (2009) and from strata older than 1920 based on their chronological data. Pre-1920 baselines are represented as linear relations with 95%

prediction intervals (PI) between concentrations of the metals of interest (Be, Cd, Cr, Cu, Ni, Pb, V, Zn) and Al. Normalization to Al accounts for variations in sediment-metal concentrations associated with energy conditions and grain size (Covelli and Fontolan, 1997; Forstner and Müller, 1981; Kersten and Smedes, 2002; Loring, 1991), and has been widely used in the region (AOSR and PAD; Cooke et al., 2017; Kay et al., 2020; Klemt et al., 2020; Owca et al., 2020). Owca et al. (2020) determined that Al is the best normalizing agent for the metals of interest in both sectors of the PAD and that the slopes of all metal-Al relations differed between sectors. Therefore, separate linear relations for each metal were used for each sector.

As a first step of data exploration, we compared concentrations of metals measured in sediment-biofilm mixtures obtained in 2017 and 2018 to the pre-1920 baselines using a series of cross-plots with Al as the independent variable and each metal of interest as the dependent variable. This step was performed on samples from all biofilm-sediment mixtures that were retrieved during both study years, and cross-plots are presented separately for 2017 (n = 49) and 2018 (n = 42) and by sector.

Lakes where artificial substrate samplers were retrieved in both study years (n = 31) provided opportunity for paired-samples comparisons to elucidate the influence of river flooding on concentrations of metals in the biofilm-sediment mixtures. These lakes were assigned to a 'flood-category' based on the number of years, out of the two study years, that the lakes received river floodwaters. Lakes were placed in the '0' category if they did not receive river floodwaters in either year (Athabasca sector, n = 6; Peace sector, n = 11), in the '1' category if they received river floodwaters in 2018 but not in 2017 (Athabasca sector, n = 5; Peace sector, n = 5), or in the '2' category if they received river floodwaters in both years (Athabasca sector, n = 4, Peace sector, n = 0). No lakes received river floodwaters in 2017 but not 2018. Designation of the flood-category for each lake followed Remmer et al. (2020b).

We assessed enrichment of metals in biofilm-sediment mixtures for the paired-samples analysis of flood influence using residual concentrations. The residual concentrations were calculated as the difference between the measured concentration of the metal in the biofilm-sediment mixtures and the mean pre-1920 concentration of the metal determined from the baseline linear metal-Al relation at the measured concentration of Al in the biofilm-sediment mixtures. For a given metal, X, this calculation is expressed as: $[residual]_X = [measured]_X - [mean\ pre-1920]_X\ at\ [measured]_{Al}$.

To evaluate if residual concentrations exceeded the range of variability before 1920, we calculated an enrichment threshold for each metal in each sector as the upper 95% prediction interval (PI) for residual concentrations at an Al concentration of 1000 mg/kg, which closely approximates the median Al concentration of all biofilm samples obtained in this study. Use of residual concentrations to quantify enrichment is consistent with the study by Wiklund et al. (2014), and expresses enrichment in units of concentration of the metal of interest. Enrichment factors have also been used to quantify enrichment of metals in lake and river sediment in the PAD and Lower Athabasca River (Cooke et al., 2017; Kay et al., 2020; Klemt et al., 2020; Owca et al., 2020; Wiklund et al., 2014), but were inapplicable across the full range of concentration in our study because baseline concentrations were not sufficiently characterized at the low range of Al concentrations in biofilm-sediment mixtures for some metals and resulted in some illogical EFs (i.e., values below zero).

Using two series of boxplots and statistical tests, distributions of residual metals concentrations in biofilm-sediment mixtures were grouped to compare among the lake flood-categories and study years in the Athabasca sector and in the Peace sector. When the upper whisker of the boxplots for the residual metal concentrations in a flood-category exceeded the enrichment threshold, this was considered enriched above the expected range of pre-1920 variability.

We used Multivariate Analysis of Variance (MANOVA) tests to determine if the residual concentrations of the suite of all 8 metals differ significantly for the above two comparisons. The use of a single test to assess for differences in residual concentrations of the suite of all 8 metals achieves the pre-determined type-1 error rate, which is not readily achieved by multiple tests on each metal individually. We ran two different repeated-measures two-way MANOVA tests, one on samples from lakes in the Athabasca sector and one on samples from lakes in the Peace sector. These tests allowed us to determine differences in residual metals concentrations between the study years (within-subject factor), among the flood-categories (between-subject factor), and the interaction of these two factors. MANOVA tests were performed using R version 3.5.3 (R Core Team, 2020) and function multRM() in the MANOVA.RM package (Friedrich et al., 2020). We report the MANOVA-type statistic (MATS) because it does not assume multivariate normality, covariance homogeneity, and singularity of covariance matrices (Friedrich and Pauly, 2018; Friedrich et al., 2017, 2019). We also report p-values based on re-sampling approaches (parametric bootstrap with 9,999 iterations), which are robust for small sample sizes (Friedrich and Pauly, 2018; Friedrich et al., 2017, 2019). For all tests, alpha was set to 0.05.

2.3. Results

2.3.1. Assessment of metals concentrations in biofilm-sediment mixtures relative to pre-1920 baselines

The dataset used to establish pre-1920 baseline linear relations between the 8 metals of interest (Be, Cd, Cr, Cu, Ni, Pb, V, Zn) and Al was derived from previous studies (Kay et al., 2020; Owca et al., 2020), plus coarser-grained riverbank sediment deposited before 1920 that captured Al concentrations comparable to the low values in the biofilm-sediment mixtures (Fig. 4). Statistically significant (at alpha = 0.05) positive linear relationships between all metals in both sectors and Al enabled development of Al-normalized baselines (Table 1). Slopes between concentrations of all metals, except Cr, and concentrations of Al are higher in lakes in the Peace sector than in the Athabasca sector. We note that Al-normalized baselines for Cd and Cu in the Athabasca sector were not possible with former datasets that did not include the riverbank sediment samples (Kay et al., 2020; Owca et al., 2020).

Table 1. Regression equations and adjusted R-squared values for pre-1920 baselines metal-Al linear regression for the Peace and Athabasca sectors. All p-values are $<2.2x10^{-16}$.

Sector	Metal	Regression equation	Adjusted R-squared
Peace	Be	$y=6.167x10^{-5}-0.05342$	0.9445
	Cd	$y=4.056x10^{-5}+0.06952$	0.8539
	Cr	$y=1.332x10^{-3}+6.320$	0.9422
	Cu	$y=2.113x10^{-3}+0.4144$	0.9094
	Ni	$y=2.126x10^{-3}+7.301$	0.9155
	Pb	$y=8.973x10^{-4}+1.148$	0.9106
	V	$y=2.593x10^{-3}+10.21$	0.9328
	Zn	$y=7.666x10^{-3}+6.874$	0.9620
Athabasca	Be	$y=4.730x10^{-5}+0.1092$	0.9145
	Cd	$y=1.787x10^{-5}+0.08797$	0.4304
	Cr	$y=1.478x10^{-3}+1.934$	0.9882
	Cu	$y=1.756x10^{-3}+0.5241$	0.8706
	Ni	$y=1.577x10^{-4}+4.323$	0.7895
	Pb	$y=7.935x10^{-4}+1.086$	0.9302
	V	$y=2.458x10^{-3}+4.328$	0.9438
	Zn	$y=5.257x10^{-3}+8.4858$	0.8918

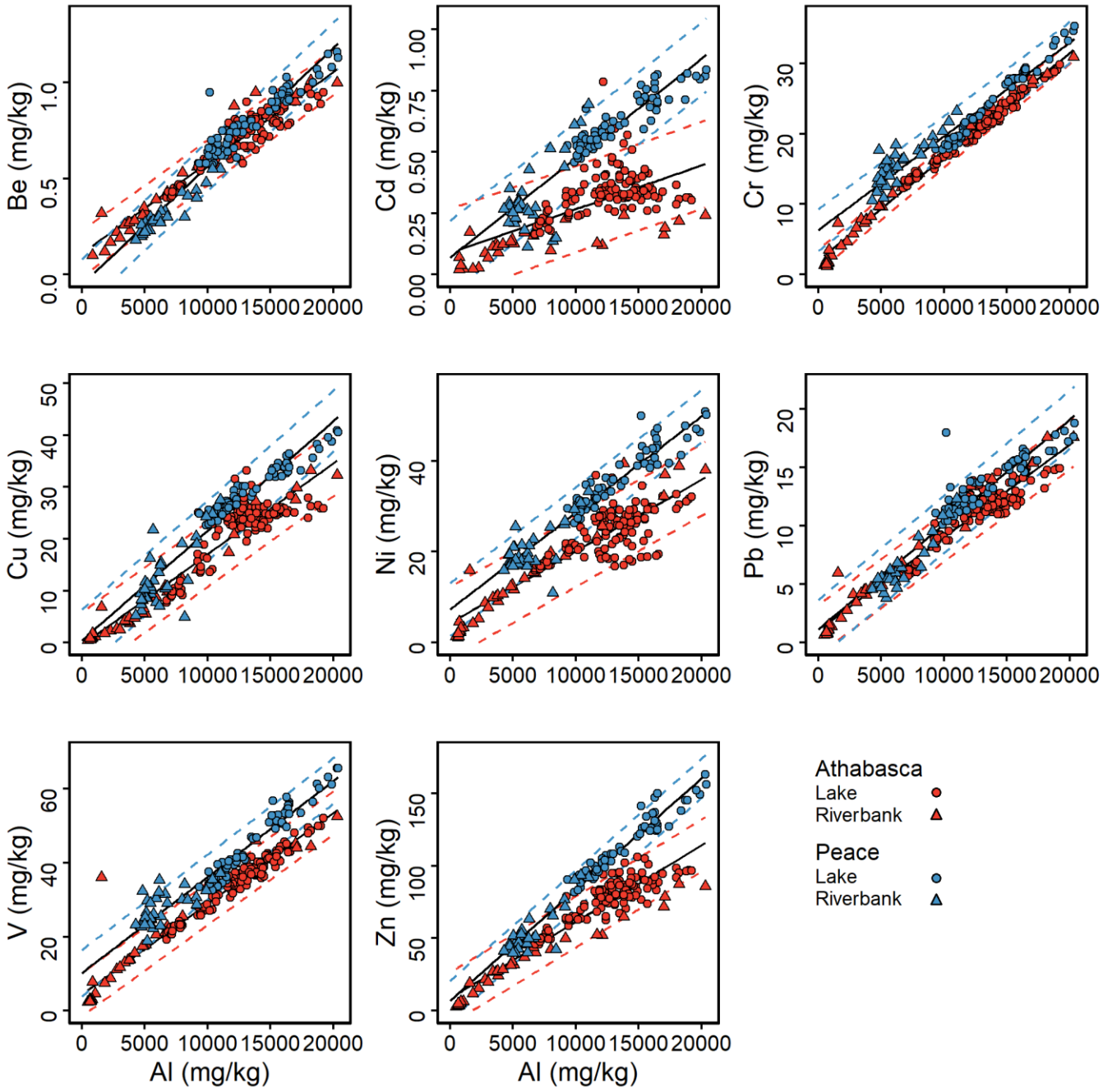

Fig. 4. Cross-plots demonstrating the linear relations between pre-1920 metal concentrations and the geochemical normalizer (Al) in lake and riverbank sediment samples. The Peace River 95% PI (blue dashed line) and regression lines are based on the pre-1920 measurements of metals from lake sediment (PAD 65, PAD 67; blue circles; n = 65) and riverbank sediment (blue triangles; n = 33). The Athabasca River 95% PI (red dashed lines) and regression lines are based on the pre-1920 measurements of metals concentrations from lake sediment (PAD 26, PAD 30, PAD 31, PAD 32, M2, M5, M7, and PAD 71; red circles; n = 122) and riverbank sediment (red triangles; n = 37 for all metals except n = 26 for Be, n = 29 for Cd, n = 34 for Cr).

The organic content of biofilm-sediment mixtures varied among lakes, consistent with observation of different textures of material accrued on the shields (Figs. 5, 6). Nonetheless, the majority of metals concentrations in biofilm-sediment mixtures that accrued on artificial substrate samplers in 2017 and 2018 are captured within the pre-1920 baseline metals concentrations for the Peace and Athabasca sectors (Figs. 5, 6). In 2017, concentrations of Be, Cr, Ni, Pb, and V are primarily along the baseline linear relations with Al concentration in both sectors, although concentrations of Cr, Ni, and V in the Peace sector and Be in the Athabasca sector more closely follow the lower 95% PI (Fig. 5). In contrast, concentrations of Cd, Cu, and Zn are well above the upper 95% PI for several OM-rich (>60% OM) biofilm-sediment mixtures at the low end of the Al concentration range, and this is more apparent in the Peace sector than the Athabasca sector. The relations between metals concentrations in biofilm-sediment mixtures and pre-1920 baselines are similar for samples obtained in 2018 (Fig. 6). Concentrations of metals are within pre-1920 baselines for both sectors, apart from some OM-rich exceptions for Cd, Cu, and Zn. In contrast to 2017, a small number of biofilm-sediment mixtures in 2018 also have concentrations of Cr, Ni, and Pb that exceed the upper 95% PIs.

Overall, metals concentrations in biofilm-sediment mixtures from both sectors in 2017 and 2018 follow similar Al-normalized concentrations as the pre-1920 baselines. The exceptional cases include primarily concentrations of Cd, Cu, and Zn in biofilms with high OM content and low Al concentration, which are above the upper 95% PI. These results indicate that the sediment-derived baselines permit calculation of residual metals concentrations (as the difference between the metal concentration in the biofilm and the baseline linear relation) and comparison to enrichment thresholds (i.e., the upper 95% PI) to quantify and interpret the extent of enrichment above the range of natural variability.

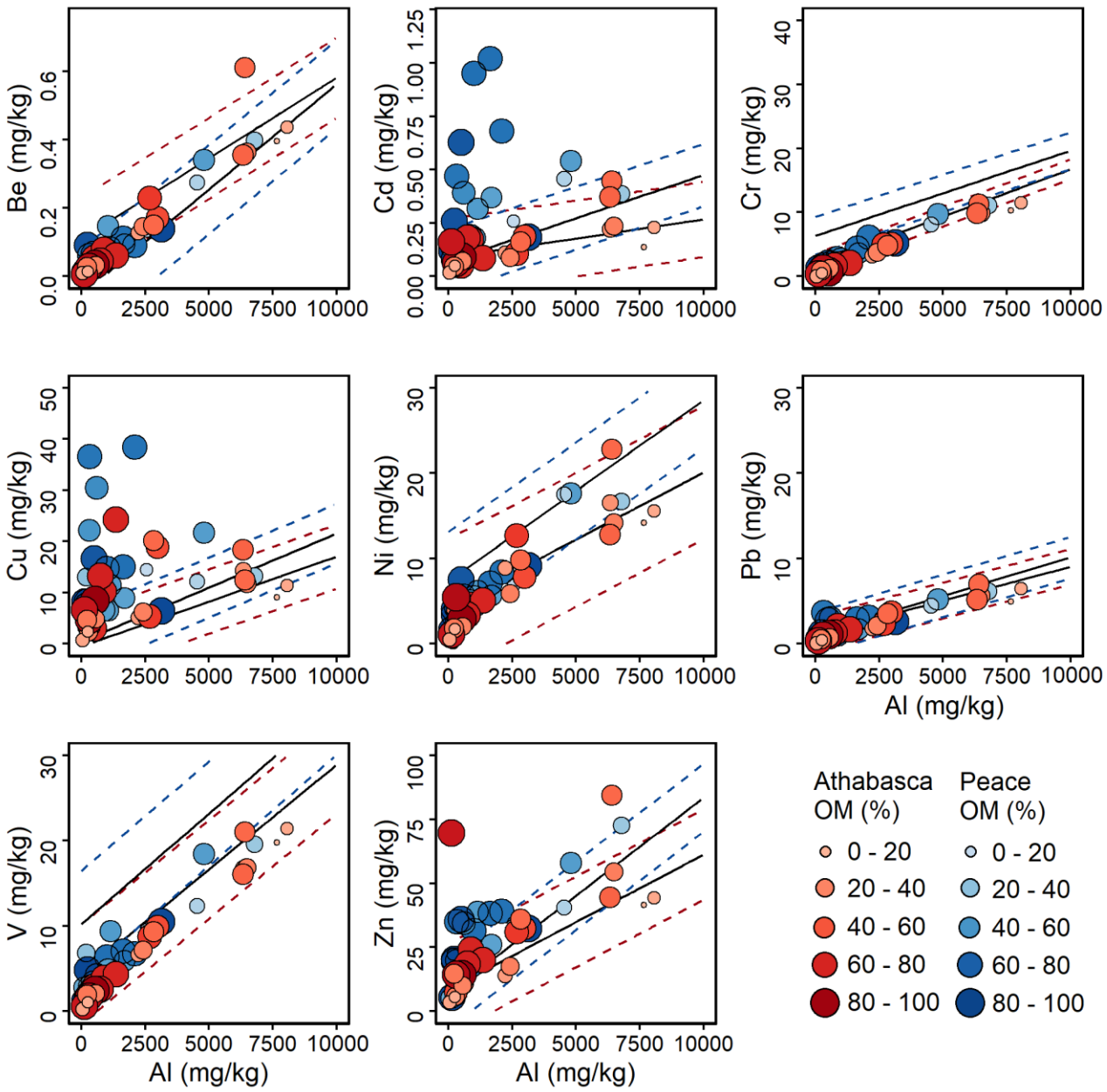

Fig. 5. Metals concentrations in biofilm-sediment mixtures accrued from May to September 2017 from Peace sector lakes (blue circles) and Athabasca sector lakes (red circles) plotted on the pre-1920 linear regressions and 95% PIs. Circles are sized according to organic matter (OM) content.

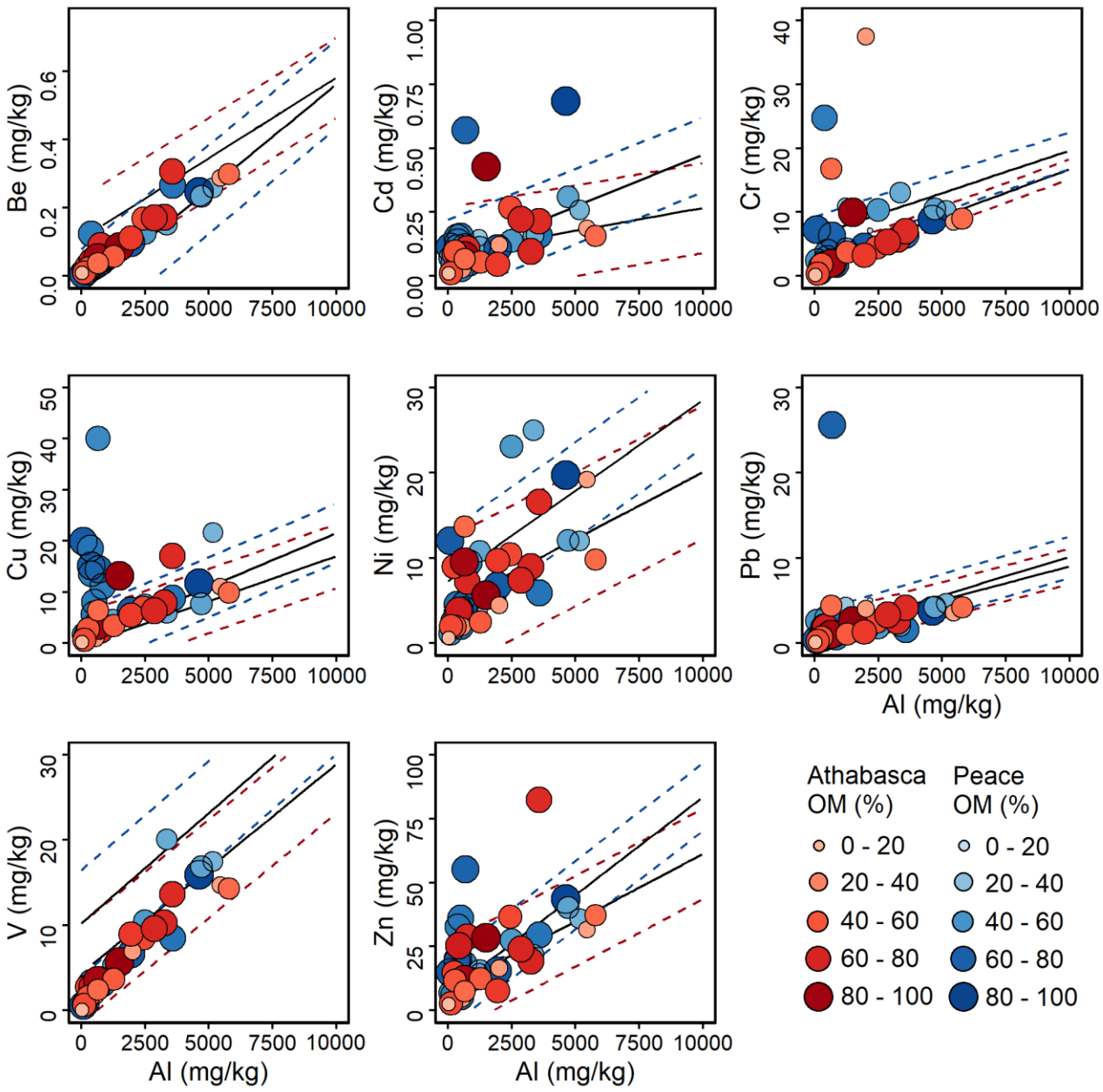

Fig. 6. Metals concentrations from biofilm-sediment mixtures accrued from May to September 2018 from Peace sector lakes (blue circles) and Athabasca sector lakes (red circles) plotted on the pre-1920 linear regressions and 95% PIs. Circles are sized according to organic matter (OM) content.

2.3.2. Assessment of residual concentrations of metals for enrichment

For lakes from which biofilm-sediment mixtures were collected in both study years, concentrations of metals in the mixtures were converted to residual concentrations relative to baseline concentrations, and are displayed as a series of boxplots in Figures 7 and 8 for lakes in the Athabasca and Peace sectors, respectively. Lakes are categorized by flood-category ('0' = not flooded in 2017 nor in 2018, '1' = flooded in 2018 only, '2' = flooded in both 2017 and 2018) and measurements are colour-coded by study year (dark = 2017, light = 2018), generating 6 groups for each of 8 metals, and a total of 48 groups in the Athabasca Sector, and 4 groups for each of 8 metals, for a total of 32 groups in the Peace Sector. There were fewer groups for the Peace sector because none of the lakes received floodwaters in both years.

Table 2. Summary of enrichment thresholds for metals (Be, Cd, Cr, Cu, Ni, Pb, V, and Zn) for each sector. Enrichment thresholds represents the residual concentration of metal corresponding to the upper 95% prediction interval at an Al value of 1000 mg/kg based on pre-1920 baselines.

Metal	Peace sector enrichment threshold (mg/kg)	Athabasca sector enrichment threshold (mg/kg)
Be	0.1323	0.1204
Cd	0.1498	0.1794
Cr	2.9465	1.5697
Cu	5.9568	6.3578
Ni	5.7715	7.9111
Pb	2.5114	2.1127
V	6.2172	5.8320
Zn	13.6122	17.8708

We assess for enrichment of each metal above the range of natural variability by comparison of the upper whisker for each group against the enrichment thresholds for each metal. The upper whiskers of residual metals concentrations are below the enrichment thresholds for most groups, indicating concentrations in the biofilm-sediment mixtures are within the range of natural variation that existed before 1920 (Figs. 7, 8; Table 2). In the Athabasca sector, there are six exceptions to this general pattern among the 48 groups: 1) enrichment of Cr above the threshold is observed for flood-category '2' lakes in 2018; 2-4) enrichment of Cu above the threshold is observed for all three flood-categories in 2017; 5) enrichment of Ni above the threshold is observed for flood-category '2' lakes in 2018, and, 6)

enrichment of Zn above the threshold is observed for flood-category ‘0’ lakes in 2017 (Fig. 7). In the Peace sector, there are nine exceptions to this general pattern among the 32 groups: 1-2) enrichment of Cd above the threshold is observed for flood-category ‘0’ and flood-category ‘1’ lakes in 2017; 3-6) enrichment of Cu above the threshold is observed for lakes in flood-categories ‘0’ and ‘1’ in 2017 and in 2018; 7) enrichment of Ni above the threshold is observed for flood-category ‘0’ lakes in 2018; and, 8-9) enrichment of Zn above the threshold is observed for lakes in flood-categories ‘0’ and ‘1’ in 2017 (Fig. 8). The combined total of these 15 exceptions in both sectors identifies that most occurrences of enrichment (11 of 15) are associated with measurements of Cd, Cu, Ni, and Zn at lakes that did not flood. Two of the remaining occurrences of enrichment (2 of 15) are for Cu at lakes that received floodwaters: in 2017 at flood-category ‘2’ lakes in the Athabasca sector, and in 2018 at flood-category ‘1’ lakes in the Peace sector. But, enrichment of Cu occurred at all flood-categories in 2017 in the Athabasca sector and at all flood-categories in 2018 in the Peace sector. The last two occurrences (2 of 15) are for Cr and Ni in 2018 at flood-category ‘2’ lakes in the Athabasca sector that received floodwaters that year. However, these flood-category ‘2’ lakes do not exhibit enrichment of Cr and Ni in 2017 when they also flooded, nor do flood-category ‘1’ lakes that flooded in 2018. Thus, there is no consistent association between enrichment of any metal and lakes that received floodwaters from the Athabasca or Peace rivers.

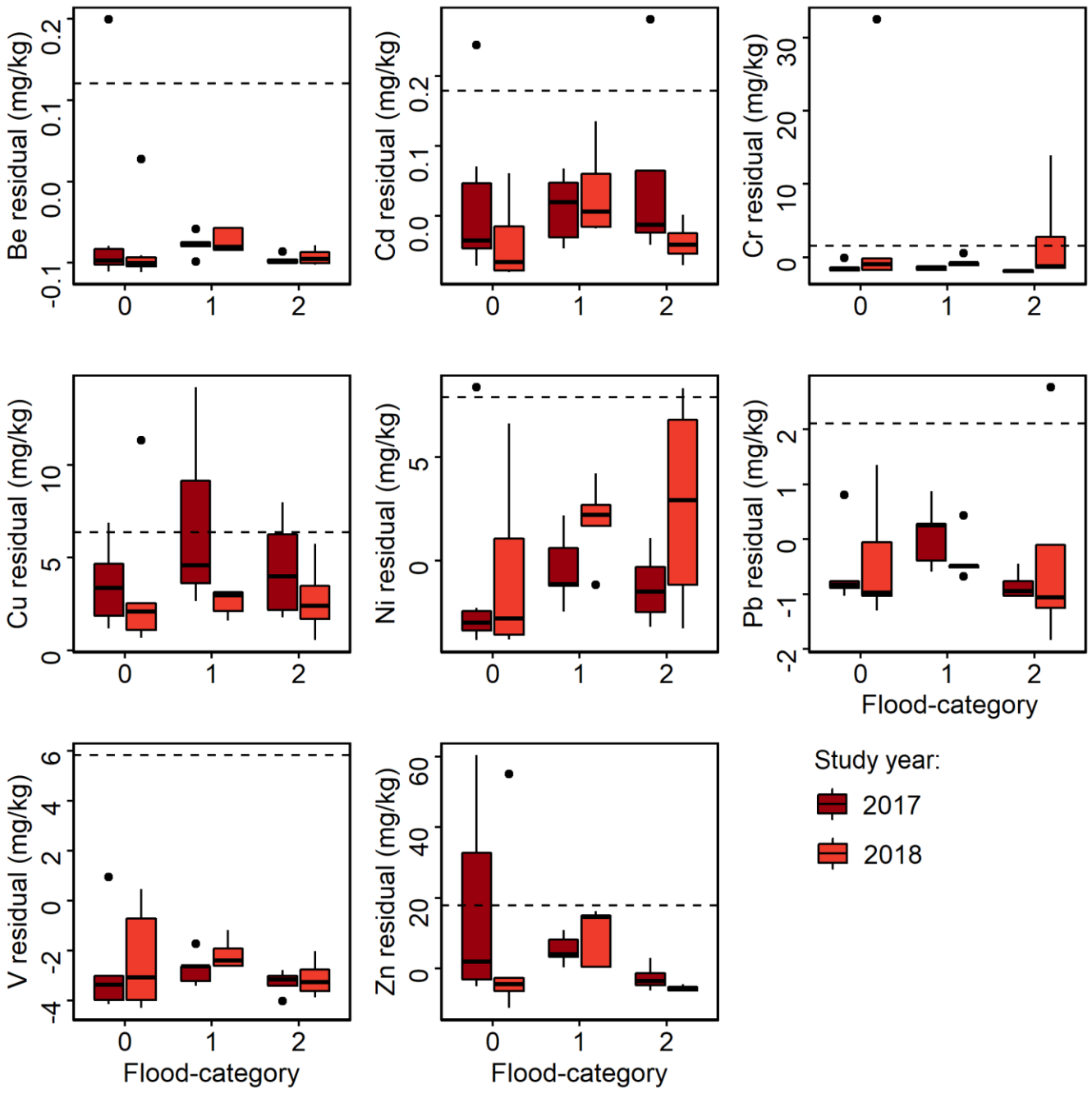

Fig. 7. Clustered boxplots showing the distribution of residual concentrations of metals from pre-1920 baselines in biofilm-sediment mixtures collected from lakes across the Athabasca sector of the Peace-Athabasca Delta. Lakes are categorized by flood year, where "0" represents lakes that did not flood in 2017 nor 2018 (n = 6) and "1" represents lakes that flooded in 2018 but not in 2017 (n = 5), and "2" represents lakes that flooded in both 2017 and 2018 (n = 4). Dark red boxes represent the 2017 study year and light red boxes represent the 2018 study year. Dashed lines indicate the enrichment threshold, which represents the residual concentration metal corresponding to the upper 95% prediction interval for a metal residual at an Al value of 1000 mg/kg based on pre-1920s baselines for the Athabasca sector.

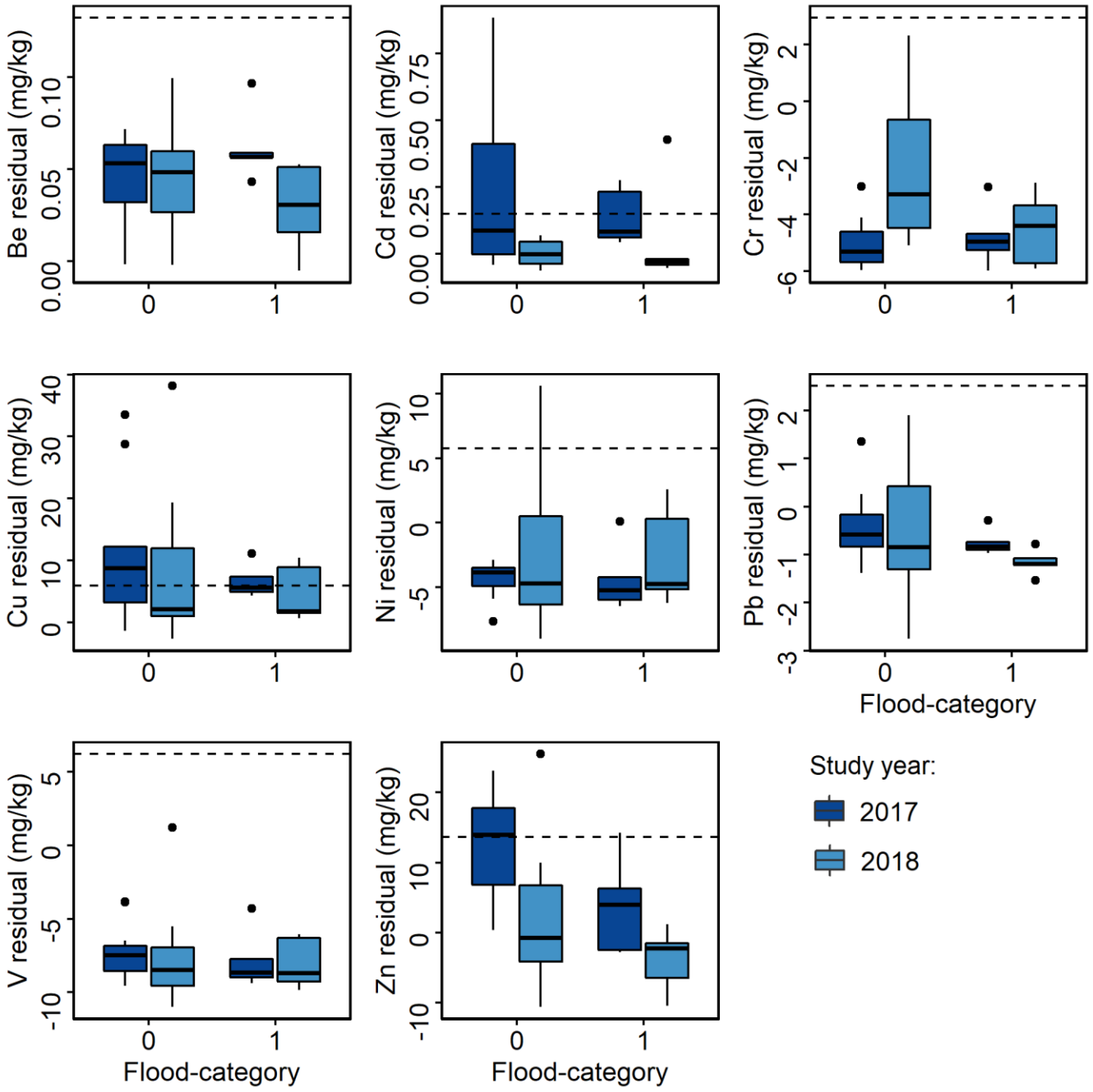

Fig. 8. Clustered boxplots showing the distribution of residual concentrations of metals from pre-1920 baselines in biofilm-sediment mixtures collected from lakes across the Peace sector of the Peace-Athabasca Delta. Lakes are categorized by flood year, where "0" represents lakes that did not flood in 2017 nor 2018 (n = 11) and "1" represents lakes that flooded in 2018 but not in 2017 (n = 5). Dark blue boxes represent the 2017 study year and light blue boxes represent the 2018 study year. Dashed lines indicate the enrichment threshold, which represents the residual concentration of metal corresponding to the upper 95% prediction interval at an Al value of 1000 mg/kg based on pre-1920s baselines for the Peace sector.

2.3.3. Statistical tests of residual concentrations of metals among flood-categories and between study years within each sector

Repeated-measures two-way MANOVA tests were conducted on the subset of 31 lakes where artificial substrate samplers were retrieved in both study years to provide a paired comparison, by lake, of residual metals concentrations among flood-categories. Two tests were run to assess if residual concentrations of the suite of 8 metals differs among 1) the 6 groups in the Athabasca sector (2 years x 3 flood-categories (0, 1, 2)), and 2) the 4 groups in the Peace sector (2 years x 2 flood-categories (0, 1)). The interaction terms (Athabasca, MATS = 12.268, P = 0.553, d.f. = 2, 12, 14; Peace, MATS = 9.246, P = 0.298, d.f. = 2, 3, 15) were not significant (Table 3), thus the interaction term was removed from the model and each factor was tested individually. Residual concentrations of the 8 metals did not differ significantly among the flood-categories in either sector (Athabasca, P = 0.124; Peace, P = 0.167), suggesting occurrence of flooding in one or both study years does not alter concentrations relative to non-flooded lakes (Table 3). Consistent with this result, the pooled boxplots for both study years illustrate broad overlap of interquartile ranges for most metals in all flood-categories for both sectors (i.e., first 8 panels of Figs. 9, 10). The MANOVA tests also determined that residual concentrations of all 8 metals do not differ significantly between 2017 and 2018 in the Athabasca sector (P = 0.171; Table 3), but differ significantly between 2017 and 2018 in the Peace sector (P = 0.007; Table 3). A non-significant inter-annual difference in the Athabasca sector is depicted by differences in residual concentrations (2018 residual – 2017 residual) which have interquartile ranges that intersect zero for all metals (last panel of Fig. 9). In contrast, a significant inter-annual difference in the Peace sector is depicted by interquartile ranges of differences in residual concentrations that are substantially below zero for Zn, and marginally below zero for V (last panel of Fig. 10). Thus, residual concentrations of metals remained relatively unchanged from 2017 to 2018, except for Zn and, to a lesser extent, V in the Peace sector, which decreased from 2017 when there was no lake flooding to 2018 when a few lakes received floodwaters that spring.

Table 3. Summary of results of two repeated-measures two-way MANOVA tests used to test for differences in residual concentrations of metals between study years (within-subject factor) and among flood-categories (between-subjects factor) in each of the Athabasca and the Peace sector.

	Factor	Modified ANOVA-type statistic	p-values paramBS (MATS)	$d.f._{Groups}$, $d.f._{Error}$, $d.f._{Total}$
Athabasca Sector	Flood-category	53.077	0.124	2, 12, 14
	Study year	11.980	0.171	1, 13, 14
Peace Sector	Flood-category	16.026	0.167	2, 13, 15
	Study year	31.259	0.007	1, 14, 15

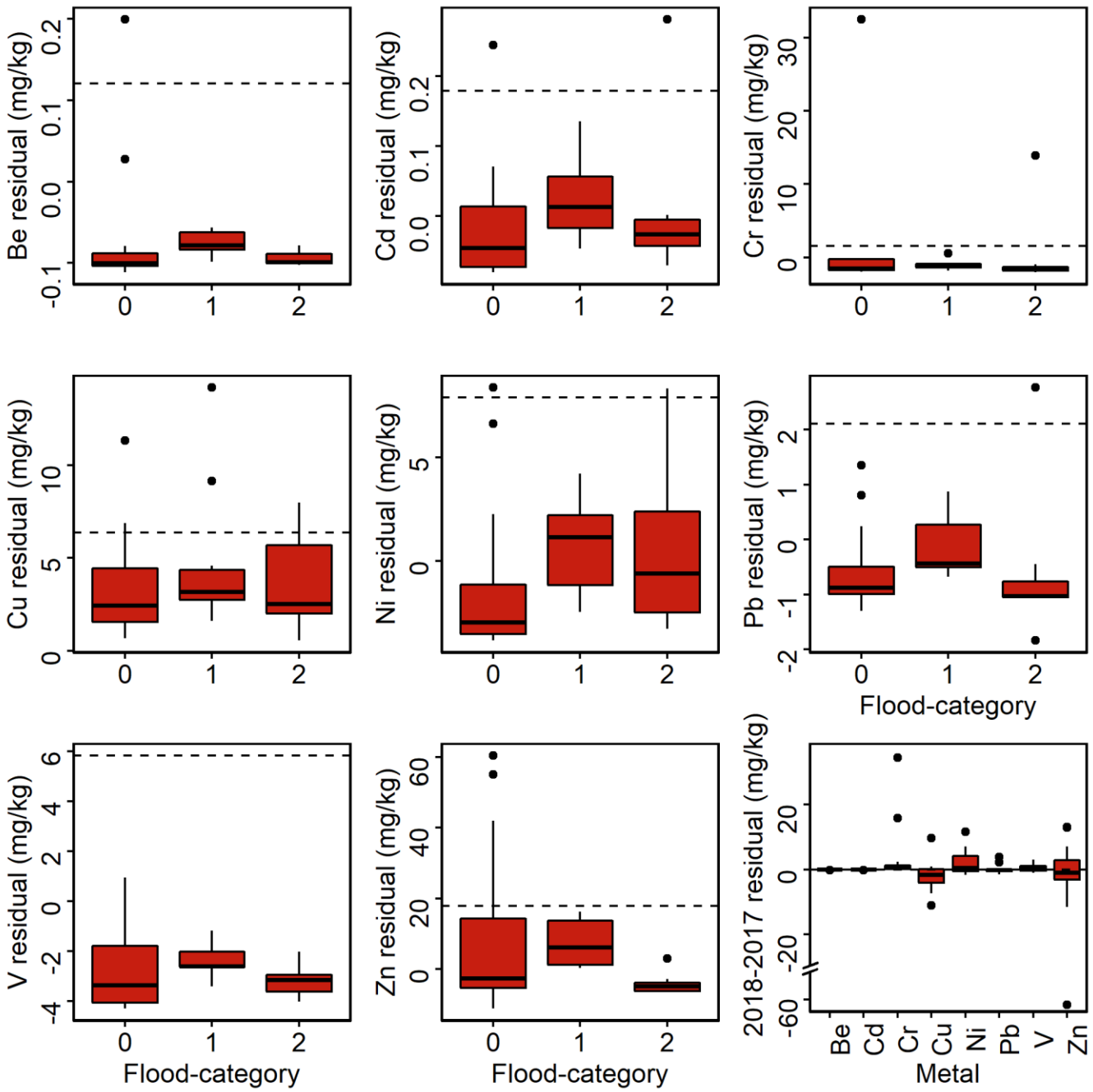

Fig. 9. First 8 panels of boxplots show the distribution of residual concentrations of metals from pre-1920 baselines in biofilm-sediment mixtures collected from lakes across the Athabasca sector of the Peace-Athabasca Delta in 2017 and 2018. Lakes are categorized by flood-category, where "0" represents lakes that did not flood in 2017 nor 2018 (n = 6), "1" represents lakes that flooded in 2018 but not in 2017 (n = 5), and "2" represents lakes that flooded in both 2017 and 2018 (n = 4). Dashed lines indicate the enrichment threshold, which represents the residual concentration metal corresponding to the upper 95% prediction interval for a metal residual at an Al value of 1000 mg/kg based on pre-1920s baselines for the Athabasca sector. Last panel of boxplots shows the residual differences between study years, calculated by subtracting the 2017 concentration from the 2018 concentration for each lake.

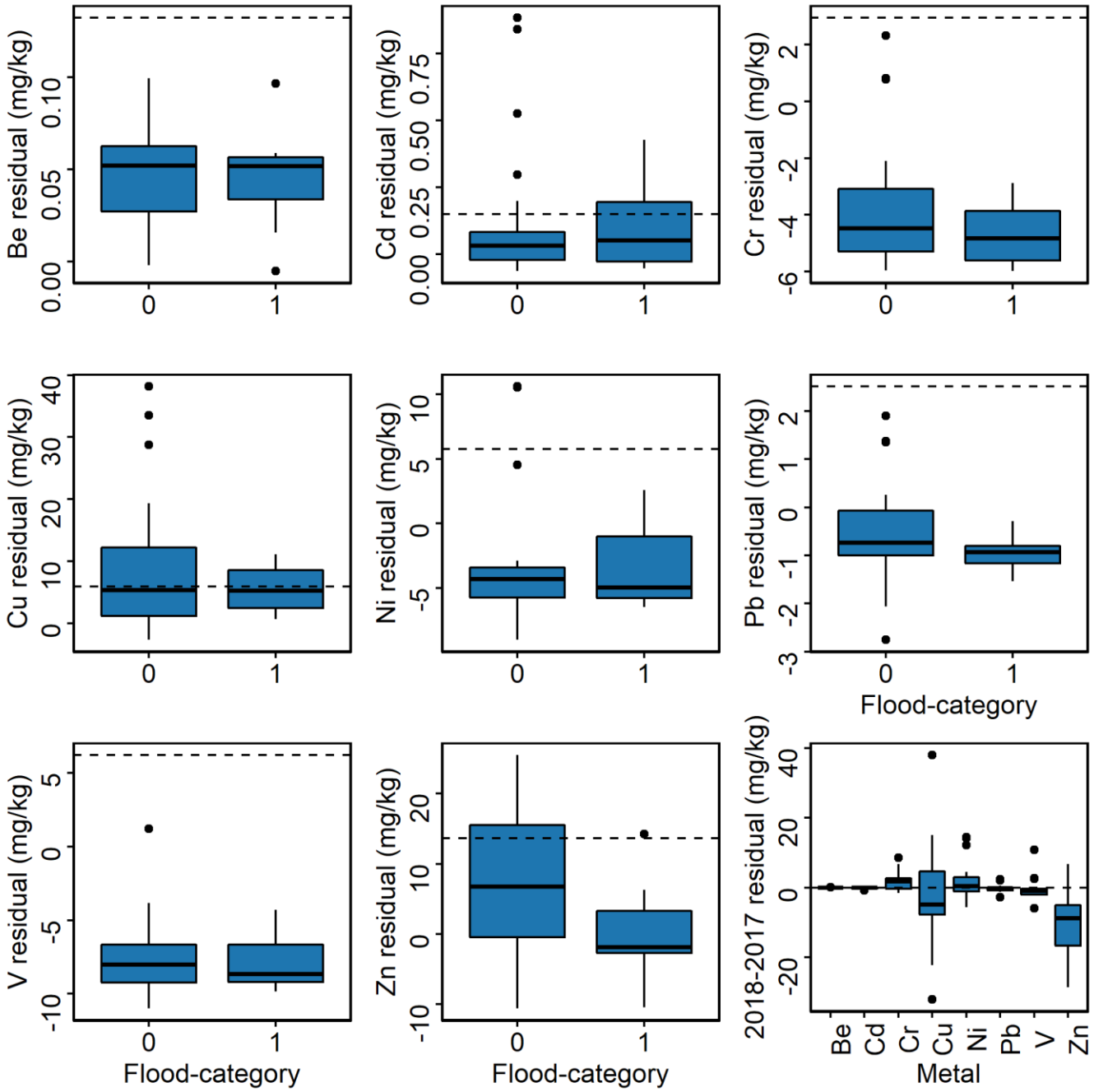

Fig. 10. First 8 panels of boxplots show the distribution of residual concentrations of metals from pre-1920 baselines in biofilm-sediment mixtures collected from lakes across the Peace sector of the Peace-Athabasca Delta in 2017 and 2018. Lakes are categorized by flood year, where "0" represents lakes that did not flood in 2017 nor 2018 (n = 11) and "1" represents lakes that flooded in 2018 but not in 2017 (n = 5). Dashed lines indicate the enrichment threshold, which represents the residual concentration of metal corresponding to the upper 95% prediction interval at an Al value of 1000 mg/kg based on pre-1920s baselines for the Peace sector. Last panel of boxplots shows the residual differences between study years, calculated by subtracting the 2017 concentration from the 2018 concentration for each lake.

2.4. Discussion

Biofilm-sediment mixtures have long been explored as monitors for metal pollution (Pederson and Vaultonburg, 1996; Ramelow et al., 1987, 1992), and here we demonstrate a novel application of this medium with reference to baseline metals concentrations estimated from pre-industrial (pre-1920) lake and river sediments. Analysis of biofilm-sediment mixtures accrued in lakes of the PAD shows little to no evidence to support that river floodwaters are a contemporary pathway of metals enrichment above the baseline concentrations, which aligns with results from previous paleolimnological studies based on analyses of lake sediment cores and surface sediments (Kay et al., 2020; Owca et al., 2020; Wiklund et al., 2014). The few occurrences of metal enrichment above the range of pre-1920 variability (15/80 groups) are primarily associated with lakes that did not receive floodwaters (11/15 occurrences). Furthermore, the occurrences of metal enrichment are about two-fold more common in the Peace sector (9/32 groups or 28.1%) than the Athabasca sector (6/48 groups or 12.5%) despite that the Athabasca River, but not the Peace River, traverses through a region of oil sands surface mining.

Our assessment of enrichment is contingent on well-defined enrichment thresholds. Strong baseline linear relationships, demonstrated by adjusted R-squared values greater than 0.85 for all baselines except Cr and Ni in the Athabasca sector, indicate that the natural range of variability is well characterized. Due to minimal flare in 95% PIs even at low Al concentrations, the Al concentration selected for enrichment threshold calculations was of no notable consequence on assessment of enrichment. For example, the same groups of lakes were designated as enriched when an Al concentration of 5000 mg/kg versus 1000 mg/kg was used to calculate enrichment thresholds. Furthermore, a group of lakes was designated as enriched even if only one lake in the group, excluding outliers, had a residual metal concentration greater than the enrichment threshold. These features lend confidence to the sensitivity of our calculated enrichment thresholds and approach for assessing enrichment.

The study design was able to discern the role of river floodwaters on metal enrichment because it incorporated measurements from a year with minimal flooding (2017) and a year with a spring ice-jam flood event that inundated many lakes in the Athabasca sector (2018; Remmer et al. 2020a). This provided opportunity to compare inter-annual differences in residual concentrations of metals in lakes that did not flood in either year (“negative control”), lakes that flooded in 2018 but not 2017 (“treatment”), and lakes that flooded in both years (“positive control”). Statistical outcomes, namely, non-significant interaction terms between the two factors (study year and flood-category), indicate the

inter-annual differences in residual metals concentrations are similar among the control groups and the treatment groups. Statistical test outcomes also demonstrate that residual metals concentrations do not differ significantly among lakes that flooded in none, one or both or the study years, as illustrated by the substantial overlap of values in flooded versus non-flooded lakes (i.e., flood-category '0' vs. flood-category '2', Fig. 9; flood-category '0' vs. flood-category '1' in 2018, Fig. 8), and values in lakes that flooded in 2018 with previous measurements in 2017 when they were not flooded (i.e., 2017 vs. 2018 in flood-category '1', Figs. 7, 8). An additional strength of the study design was inclusion of some spring-flooded lakes that also flooded in summer of 2017 and 2018, so supply of metals during summer flow was captured in this study.

More than one occurrence of enrichment is discernable only for metals Cd, Cu and Zn, and primarily in non-flooded lakes where the artificial-substrate periphyton samplers accrued organic-rich biofilm-sediment mixtures. Thus, enrichment of these metals is not caused by river floodwaters and more likely reflects active intracellular uptake by periphytic biota in the absence of flooding (Fig. 11). In support of this inference, it is known that photosynthetic organisms concentrate Cu and Zn within organelles to a greater degree than all other metals measured in this study (Blaby-Haas and Merchant, 2012; Epstein, 1965; Rodriguez and Ho, 2018). Evidence from other studies have shown biofilm-sediment mixtures accumulate Cu and Zn to a greater degree than sediment (Kumari and Maiti, 2020; Ramelow et al., 1992). Furthermore, photosynthetic organisms transport non-essential Cd using non-specific divalent metal transporters, which results in Cd uptake during biomass accrual (Blaby-Haas and Merchant, 2012; Rodriguez and Ho, 2018; Hill et al., 2000). Owca et al. (2020) demonstrated that surface sediments collected from the same lakes in the same years did not exhibit enrichment in Cd, Cu, and Zn. Hence, active biological uptake by periphytic biota appears to complicate comparisons of these three metals between organic-rich biofilm-sediment mixtures accrued in non-flooded lakes and baselines constructed using sediment deposited in flood-prone lakes. However, accumulation of Cu, Zn, and Cd in biota at the base of aquatic food webs is an important finding to inform potential risks to ecosystem health. Fortunately, for Cd and Zn, these results do not compromise ability to assess metal enrichment in biofilm-sediment mixtures in flooded lakes.

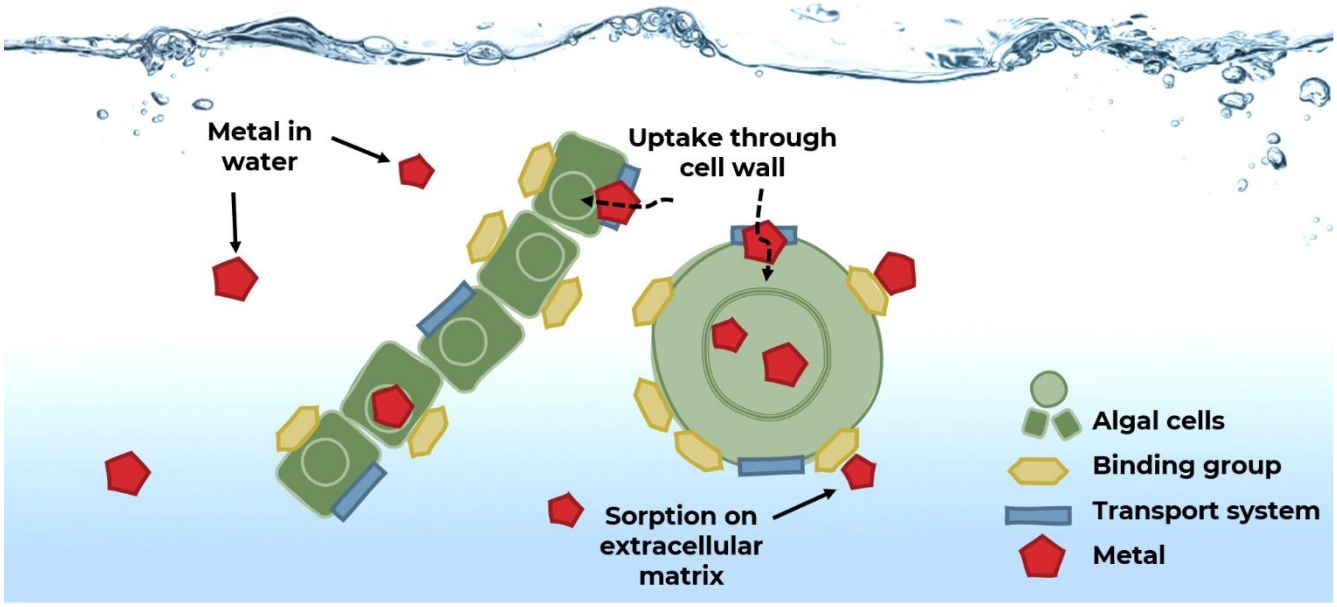

Fig. 11. Schematic depicting pathways of metal uptake and biosorption by algae (adapted from Nguyen et al., 2020).

Improved understanding of pathways of metal accumulation in biofilm-sediment mixtures would provide helpful context for additional interpretation of results from this study. Prior studies have shown environmental factors, such as pH, temperature, and presence of other ions in solutions, exert control on metal bioavailability and subsequently impact on metal uptake by periphytic biota (Meylan et al., 2003; Zabochnicka-Świątek and Krzywonos, 2014). Resulting information could help to explain the observed decrease in Zn from 2017 to 2018 in flooded and non-flooded Peace sector lakes.

Biofilm-sediment mixtures are a viable approach for 'real-time' monitoring of enrichment of metals in flooded lakes (Be, Cd, Cr, Ni, Pb, V, Zn) and non-flooded lakes (Be, Cr, Ni, Pb, V) of the PAD given the alignment of their metal-Al concentrations with pre-1920 baselines. Comparison to sediment-derived pre-industrial baselines is a novel application of biofilm-sediment mixtures, and provides critical context for interpretation of pollution in a landscape where contaminants are supplied by natural processes as well as potentially by industrial releases to the environment. Ability to inform about enrichment in biota at the base of aquatic food webs and to control the duration of biofilm accrual, by setting the time of deployment and retrieval of the artificial-substrate samplers, complements assessments based on analysis of surficial sediment from lakes with inherent variation and uncertainty of their sediment accumulation rates (Owca et al., 2020). This research directly addresses a recommendation for strategic

environmental assessment included in the WBNP Action Plan by providing information about metals supplied by river floodwaters after they flow through a heavily industrialized area (WBNP, 2019), and provides a monitoring framework to consider for future implementation across lakes of the PAD.

To optimize a monitoring program for lakes in the PAD, we recommend deploying artificial substrate samplers at the beginning of the ice-free season (i.e., mid-May) to capture potential effects of spring ice-jam floods. Dual sampling of surface sediment and biofilm-sediment mixtures is ideal for reliable monitoring of both biologically active (Cd, Cu, Zn) and biologically inert (Be, Cr, Ni, Pb, V) metals. Preference for monitoring may be given to flood-prone lakes in the Athabasca sector as they are most vulnerable to potential pollution from upstream oil sands mining. However, we recommend that monitoring also include non-flooded lakes in the Athabasca sector, and flooded and non-flooded lakes in the Peace sector which are unlikely to be affected by AOSR oil sands mining, to serve as informative benchmarks for determination of metals enrichment by oil sands mining and processing activities. The approach developed here may be adapted for implementation at other lake-rich and floodplain landscapes, but will require firm understanding of baseline metals concentrations against which metals concentrations in biofilm-sediment mixtures can be compared. Among the many options for characterizing baseline concentrations, we advocate for analysis of metals concentrations in samples from lake sediment cores deposited prior to possible pollution by anthropogenic activities of concern.

2.5. Conclusions

This research explored roles of river flooding on enrichment of metals of concern at the base of food webs in lakes of the PAD. Assessment of contemporary metals concentrations in biofilm-sediment mixtures in lakes of the PAD relative to pre-industrial (pre-1920) concentrations of metals in lake sediment demonstrate no substantial enrichment of oil sands-derived metals concentrations supplied by Athabasca River floodwaters. The absence of marked metals enrichment in flooded lakes, as well as the lack of difference in enrichment among lakes of different flood status, provide evidence that oil sands industrial metals pollution is not detectable at the base of food webs in lakes of the PAD. Results presented here demonstrate that biofilm-sediment mixtures are useful media for monitoring contemporary concentrations of metals, and complement an existing monitoring framework relying on contemporary concentrations of metals in surface sediment in the PAD (Owca et al., 2020).

Linking timing of flooding with timing of metals accumulation is a distinct advantage of artificial substrate samplers, but is contingent on routine isotope monitoring of hydrological conditions, as was

performed throughout the study years of this research (Remmer et al., 2020b). Alternately, oxygen isotope composition of aquatic cellulose synthesized by periphytic algae present in biofilm-sediment mixtures may also be used to track lake water balance and hydrological processes during the period of accrual (Savage et al., in review). This possibility, along with other possible metrics indicative of ecological integrity that can be gleaned from biofilm-sediment mixtures (e.g., algal community composition, biomarkers related to metal-stress, deformed diatom cells; Lavoie et al., 2012; MacDonald et al., 2012; Millie et al., 1993), may provide additional opportunities for long-term aquatic ecosystem monitoring.

Chapter 3: Conclusions

3.1. Key findings and relevance of research

Comparison of metals concentrations in biofilm-sediment mixtures relative to pre-industrial concentrations in sediment identifies little to no enrichment of metals associated with oil sands development in lakes of the PAD supplied by Athabasca River floodwaters. This finding aligns with the growing body of other lines of evidence that oil sands activities in the AOSR have not resulted in pollution of downstream lakes in the PAD (Hall et al., 2012; Kay et al., 2020; Owca et al., 2020; Wiklund et al., 2012, 2014). The two-year, spatially comprehensive dataset of metals concentrations in biofilm-sediment mixtures from across broad hydrologic gradients in the PAD provided a unique opportunity to assess roles of river floodwaters on metals enrichment. Widespread flooding in 2018 that was most pronounced in the Athabasca sector of the PAD lent well to evaluation of metals enrichment at lakes where potential for AOSR oil sands pollution has been of greatest concern. In contrast, minimal flooding in 2017 was suitable for benchmark comparisons with non-flooded lakes which did not receive river-supplied material, including potential contaminants. Multivariate testing of metals concentrations in flooded versus non-flooded lakes revealed that Athabasca River floodwaters do not contribute to metals enrichment. However, enrichment above the natural range of variability was observed for Cd, Cu, and Zn in non-flooded lakes, which suggests bioconcentration of these biologically active metals in organic-rich biofilm-sediment mixtures.

This study demonstrated the utility of a novel monitoring framework that compares metals concentrations in biofilm-sediment mixtures to pre-industrial lake sediment. Previous monitoring approaches involving biofilm-sediment mixtures have tended to rely on intracellular metals concentrations in the biotic component of the mixture to approximate bioavailable metals in the environment (e.g., Behra et al., 2002; Lavoie et al., 2012; Leguay et al., 2016). The application developed here instead took advantage of entrapped suspended sediments in biofilms, which generally enables analogous comparisons between Al-normalized metals concentrations in biofilm-sediment mixtures and sediment. Confidence in relating Al-normalized biologically inert metals (Be, Cr, Ni, Pb, V) between these two media, including those related to oil-sands development (Ni, V; Hodgson, 1954; Jack et al., 1979; Jacobs and Filby, 1983), is supported by prior studies which demonstrated correspondence between metals concentrations in biofilm-sediment mixtures and surface sediment (Pederson and Vaultonburg, 1996; Ramelow et al., 1987, 1992). Confidence is also imparted by

consistency of findings based on analysis of surface sediment (Owca et al., 2020) and those based on biofilm-sediment mixtures (this study) collected from the same sites and during the same years. A key benefit of this monitoring framework is that it includes information on pre-disturbance conditions, and thus provides a temporal perspective on metals enrichment in the PAD.

Effective monitoring programs are capable of quantifying environmental changes since onset of anthropogenic disturbance, which is contingent on rigorous characterization of baseline conditions (Dowdeswell et al., 2010; Lindenmayer and Likens, 2009, 2010; Smol, 1992; Wrona and di Cenzo, 2011). This principle guided our development of a monitoring framework in the PAD, which compared metals concentrations in biofilm-sediment mixtures with pre-1920 concentrations from lake sediment cores to measure enrichment above the natural range of variability. It is intended that this framework be used in tandem with a formerly established surface sediment monitoring approach (Owca et al., 2020) to effectively quantify enrichment of metals in both abiotic and biotic environmental media to advance goals of the WBNP Action Plan (WBNP, 2019).

3.2. Recommendations

The lack of evidence for enrichment of metals via fluvial pathways in contemporary lake samples does not alleviate the need for continued monitoring efforts in the PAD. There are remaining uncertainties surrounding sequestration and remobilization of contaminants known to have been deposited from atmospheric emissions in a localized area surrounding the AOSR (Kelly et al., 2009, 2010; Kirk et al., 2014). Anthropogenic climate change is altering natural and anthropogenic processes, such as hydrological regimes and carbon cycling, which may initiate remobilization of legacy contaminants in the catchment and increase metal loading to the Athabasca River with potential to be delivered to downstream lakes of the PAD (Bacardit and Camarero, 2010; Macdonald et al., 2005; Pelletier et al., 2021; Whitehead et al., 2009). As oil sands industry continues to operate and grow (CAPP, 2019), metals concentrations could increase in the future relative to the current situation, possibly presenting greater risk of exposure of contaminants to humans and wildlife. It is therefore recommended that systematic, long-term sampling of biofilm-sediment mixtures and surface sediment be employed to detect potential early warning signals of metals enrichment in lakes of the PAD.

Dual sampling of biofilm-sediment mixtures and surface sediment is recommended over selection of just a single medium because each approach has unique advantages that compensate for the principal limitation of the other approach. For example, biological activity in organic-rich biofilm-sediment

mixtures leads to disproportionate accumulation of Cd, Cu, and Zn relative to sediment, indicating that assessment of enrichment of these biologically active metals above baseline due to oil sands activities should be restricted to surface sediment sampling. However, quantifying enrichment of Cd, Cu, and Zn in biofilm-sediment mixtures is otherwise useful to compare enrichment of these metals between the two media and thus demonstrate the degree to which metals are bioconcentrated at the base of food webs in lakes relative to sediment supplied to lakes via the Athabasca River. As a contrasting example, opportunistic sampling of freshly deposited surface sediment flood layers may not always be logistically possible following a flood event, whereas biofilm-sediment mixtures invariably capture potential signals of the influence of river flooding on metals accumulation in aquatic biota and suspended sediments because of their controlled accrual time. Thus, collection of biofilm-sediment mixtures may be prioritized in flood-prone lakes of the Athabasca sector, which are most vulnerable to potential flood-derived contamination from upstream AOSR mining activities. Overall, complementary sampling of these two media ensures ability to confidently assess contamination of the suite of 8 metals (Be, Cd, Cr, Cu, Ni, Pb, V, Zn) relative to baseline levels and address ongoing concern for the potential of the Athabasca River to deliver oil sands-derived contaminants to flood-prone lakes in the Athabasca sector.

Ability to explore effects of flooding on enrichment of metals is contingent on determination flood status coincident with timing of biofilm-sediment accrual and/or collection of surface sediment. Flood status of lakes may be based on water isotope compositions, specific conductivity, and field observations, as was done throughout the study period of this research (Remmer et al., 2020b). Alternatively, oxygen isotope composition of aquatic cellulose synthesized by biota within biofilm-sediment mixtures may be used to track lake water balance and infer presence of flooding during the accrual period (Savage et al., in review). We recommend that metals monitoring continue to be paired with water isotope tracer monitoring to assess possible impacts of climate warming and river regulation on lake hydrological processes, as well as potential pollution releases from upstream industrial and municipal sources on water quality. Collectively, these monitoring strategies address the recommendation from the WHC to "expand the scope of monitoring and project assessments to encompass possible individual and cumulative impacts on […] the PAD" (WHC/IUCN 2017, p. 4).

Measurement of metals in biofilm-sediment mixtures accrued on artificial substrate samplers represents only a small fraction of valuable monitoring information that can be gleaned from this complex medium. In fact, measurement of additional indices could broaden the scope of monitoring to include assessment

of ecological responses to metals exposure. For example, indices that may be indicative of adverse metal effects on algae include perturbations of diatom communities (Genter and Lehman, 2000; Morin et al., 2012; Sabater, 2000), production of chemical biomarkers related to metal-stress (Lavoie et al., 2009; Le Faucheur et al., 2005), and the presence of deformed diatom cells (Falasco et al., 2009). Alternately, we have previously emphasized the environmental relevance of characterizing metals accumulation in biofilm-sediment mixtures as they form the base of aquatic food webs. However, there is opportunity to further refine this perspective by characterizing subsequent metals transfer to a higher trophic position through sampling of invertebrate grazers and/or fish from lakes (Cain et al., 2011; Munger and Hare, 1997; Xie et al., 2010). Because transmission of metals through the food web may depend on limnological conditions specific to the region (Cui et al., 2012), studies of trophic transfer are warranted in the PAD. Apart from metals monitoring, biofilm-sediment mixtures may also be used to measure photosynthetic pigments and thus track spatiotemporal patterns of variation in algal community composition and abundance (Millie et al., 1993; Hall et al., 1999; Leavitt and Hodgson, 2001; Thomas et al., 2013). Pigments within the accrued biofilm-sediment mixtures featured in this study were quantified using High Performance Liquid Chromatography and briefly explored, but further analysis of these data was deemed beyond the scope of the thesis (Appendix D). Evidently, artificial substrate samplers offer opportunity to simultaneously monitor a range of ecological and environmental quality metrics, which make them attractive as a tool for long-term aquatic ecosystem monitoring.

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Appendices

Appendix A: Study site locations

Table A1. Locations of river bank sites from which pre-1920 sediment was collected in July 2019.

Site ID	Latitude	Longitude
Athabasca river bank 1	58.397	-111.525
Athabasca river bank 2	58.385	-111.518
Peace river bank 1	58.923	-111.619
Peace river bank 2	58.936	-111.638
Peace river bank 3	58.950	-111.707

Table A2. Locations of lakes from which biofilm-sediment mixtures were collected (n = 49 in 2017; n = 42 in 2018).

Lake	Lat	Long	Sampling Year
PAD1	58.806	-111.243	2017 & 2018
PAD2	58.835	-111.319	2017 & 2018
PAD3	58.833	-111.284	2017
PAD4	58.843	-111.401	2017 & 2018
PAD6	58.812	-111.387	2018
PAD8	58.812	-111.356	2017 & 2018
PAD12	58.956	-111.329	2017 & 2018
PAD13	58.948	-111.375	2017 & 2018
PAD14	58.933	-111.428	2017
PAD15	58.950	-111.507	2017
PAD16	58.882	-111.401	2017 & 2018
PAD17	58.872	-111.428	2017
PAD18	58.896	-111.36	2017 & 2018
PAD19	58.442	-111.629	2017 & 2018
PAD20	58.419	-111.592	2018
PAD21	58.369	-111.569	2017
PAD22	58.397	-111.499	2017 & 2018
PAD23	58.390	-111.445	2017 & 2018
PAD24	58.394	-111.360	2017
PAD26	58.420	-111.270	2017
PAD27	58.436	-111.262	2017
PAD30	58.510	-111.517	2017 & 2018
PAD31	58.496	-111.518	2017 & 2018
PAD32	58.497	-111.443	2017 & 2018
PAD33	58.420	-111.440	2017 & 2018
PAD36	58.466	-111.251	2017 & 2018
PAD38	58.418	-111.123	2018
PAD39	58.465	-111.186	2018
PAD40	58.508	-111.191	2017
PAD50	58.859	-111.889	2017 & 2018
PAD52	58.877	-111.75	2017 & 2018
PAD53	58.772	-111.649	2018
PAD54	58.870	-111.578	2017 & 2018
PAD57	58.829	-111.594	2017 & 2018
PAD58	58.830	-111.552	2017 & 2018
PAD62	58.372	-111.851	2017
PAD64	58.954	-111.775	2018
PAD65	58.897	-111.775	2017 & 2018
PAD66	58.970	-111.492	2017
PAD71	58.563	-111.881	2018

M1	58.448	-111.015	2018
M2	58.418	-110.914	2017 & 2018
M3	58.431	-110.973	2017 & 2018
M5	58.502	-110.793	2017
M6	58.533	-110.794	2017 & 2018
M7	58.436	-111.047	2017 & 2018
M8	58.399	-111.804	2017 & 2018
M9	58.328	-111.822	2017
M10	58.289	-111.792	2017 & 2018
M11	58.550	-111.333	2017 & 2018
M12	58.556	-111.413	2017
M14	58.571	-111.52	2017 & 2018
M15	58.881	-111.257	2017 & 2018
M16	58.894	-111.209	2017
M17	58.903	-111.322	2017 & 2018
M18	58.906	-111.289	2017 & 2018
M19	58.885	-111.323	2018

Appendix B: Raw metals concentrations in the biofilm-sediment mixtures

Table B1. Raw concentrations of metals in biofilm-sediment mixtures accrued in 2017.

Lake	Al (mg/kg)	Be (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	V (mg/kg)	Zn (mg/kg)
PAD1	189.00	0.03	0.07	0.60	5.00	0.46	0.06	1.12	22.30
PAD2	1020.00	0.07	0.95	2.45	14.70	1.64	5.38	6.38	31.50
PAD3	322.00	0.02	0.10	1.02	22.20	0.78	2.54	2.95	20.00
PAD4	605.00	0.05	0.39	2.13	30.50	3.04	5.68	4.28	34.50
PAD8	867.33	0.06	0.19	2.79	6.59	1.09	4.93	3.48	17.50
PAD12	1160.00	0.08	0.32	2.30	11.40	1.60	6.20	9.38	38.90
PAD13	236.00	0.09	0.26	1.16	8.24	1.34	4.11	1.70	20.40
PAD14	1055.10	0.15	0.18	2.19	6.55	1.38	4.44	4.89	21.70
PAD15	1690.00	0.09	0.37	3.61	8.91	1.76	5.65	5.94	26.10
PAD16	2550.00	0.13	0.26	4.35	14.50	3.05	6.82	9.58	34.50
PAD17	331.00	0.06	0.47	1.79	36.50	3.68	4.22	2.18	35.00
PAD18	2100.00	0.09	0.68	6.10	38.40	3.07	8.40	6.70	39.00
PAD19	6345.00	0.35	0.22	9.49	14.25	6.99	16.45	16.65	45.30
PAD21	6480.00	0.36	0.23	9.85	11.70	5.61	14.20	16.80	54.40
PAD22	489.00	0.06	0.05	0.93	3.00	0.88	2.61	2.89	11.30
PAD23	893.00	0.08	0.17	1.81	10.20	2.07	4.57	3.88	24.10
PAD24	1360.00	0.06	0.09	2.07	24.20	1.71	5.07	4.31	20.00
PAD26	749.00	0.05	0.18	1.67	13.30	1.34	3.38	2.59	18.60
PAD27	302.00	0.02	0.06	0.82	3.55	0.59	1.79	1.56	7.41
PAD30	302.00	0.02	0.05	0.61	2.30	0.46	4.04	1.05	5.80
PAD31	2220.00	0.13	0.11	3.20	5.17	1.82	8.93	6.68	14.03
PAD32	2990.00	0.17	0.19	5.14	18.90	3.71	7.82	9.94	32.40
PAD33	533.00	0.04	0.09	0.70	8.40	1.06	2.90	2.43	14.20
PAD36	318.00	0.03	0.06	1.15	4.62	0.95	5.42	1.69	14.20
PAD40	7650.00	0.40	0.14	10.30	9.10	4.95	14.20	19.80	41.50
PAD50	345.00	0.02	0.08	0.88	3.29	0.64	4.16	1.60	9.84
PAD52	200.00	0.01	0.04	0.79	13.10	0.67	4.33	6.87	13.90
PAD54	4810.00	0.34	0.54	9.70	21.70	5.17	17.60	18.40	58.00
PAD57	3150.00	0.14	0.18	5.21	6.40	2.59	9.10	10.50	32.20

PAD58	6770.00	0.40	0.39	11.10	13.30	6.18	16.70	19.60	72.70
PAD62	4540.00	0.28	0.46	8.08	12.10	4.48	17.50	12.30	40.40
PAD65	254.60	0.02	0.08	1.13	7.37	0.80	3.42	4.83	19.51
PAD66	345.00	0.02	0.06	0.59	2.46	0.37	5.68	1.55	5.30
M2	6400.00	0.61	0.45	11.30	12.40	6.97	22.80	21.00	84.30
M3	570.00	0.03	0.07	1.29	4.82	0.73	2.07	2.11	10.20
M5	2670.00	0.23	0.11	4.94	5.37	2.36	12.70	8.73	31.10
M6	136.00	0.01	0.16	0.34	6.59	0.34	1.07	0.56	69.60
M7	224.33	0.03	0.04	0.87	4.65	0.52	1.80	1.91	14.70
M8	2430.00	0.15	0.09	3.73	6.16	2.11	5.85	7.16	17.60
M9	2830.00	0.15	0.16	4.80	20.10	3.53	9.80	9.30	36.00
M10	6330.00	0.36	0.37	9.90	18.40	5.18	12.80	16.10	44.60
M11	38.00	0.01	0.02	0.05	0.72	0.09	0.54	0.26	3.60
M12	257.00	0.02	0.05	0.49	2.44	0.44	1.77	1.05	5.60
M13	8050.00	0.44	0.23	11.50	11.40	6.50	15.60	21.40	44.40
M14	1430.00	0.08	0.40	2.29	7.67	1.18	3.37	5.06	13.20
M15	1650.00	0.11	1.02	4.41	15.00	2.89	7.11	7.01	38.20
M16	503.00	0.07	0.63	2.05	16.60	2.75	7.55	3.20	36.00
M17	146.00	0.01	0.12	1.25	8.09	0.55	1.63	1.20	5.50
M18	111.00	0.01	0.14	0.49	6.23	0.28	1.04	2.77	4.90

Table B2. Raw concentrations of metals in biofilm-sediment mixtures accrued in 2018.

Lake	Al (mg/kg)	Be (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	V (mg/kg)	Zn (mg/kg)
PAD1	84.90	0.01	0.11	7.25	19.90	0.41	12.00	0.58	14.80
PAD2	361.00	0.03	0.15	1.85	18.60	0.61	4.57	2.67	19.60
PAD4	521.00	0.03	0.03	3.72	8.04	2.98	3.84	2.78	5.20
PAD6	30300.00	1.32	1.79	216.00	330.00	84.80	58.40	100.00	409.00
PAD8	850.00	0.05	0.05	1.73	11.08	0.69	9.42	3.12	11.85
PAD12	2480.00	0.13	0.14	10.40	7.39	1.89	23.10	10.50	27.50
PAD13	392.00	0.12	0.13	24.70	13.60	1.53	NA	3.26	32.60
PAD15	5150.00	0.26	0.26	10.30	21.70	4.69	12.00	17.50	35.90
PAD16	2190.00	0.11	0.13	7.06	7.16	5.01	5.12	8.13	20.00
PAD18	3580.00	0.27	0.16	6.40	8.90	1.61	5.92	8.51	29.70
PAD19	769.00	0.09	0.11	1.88	2.45	1.02	7.21	3.61	28.70
PAD20	237.00	0.03	0.09	1.55	2.06	0.40	9.01	2.81	14.80
PAD22	2411.50	0.14	0.19	6.04	6.91	2.51	10.83	9.07	21.70
PAD23	434.00	0.04	0.08	1.84	2.37	1.86	3.83	2.76	25.25
PAD30	5440.00	0.29	0.19	8.50	11.10	3.57	19.20	14.70	31.70
PAD31	3250.00	0.17	0.10	5.77	7.90	2.61	8.98	10.30	19.40
PAD32	2450.00	0.17	0.27	4.48	6.91	2.55	10.40	8.44	36.50
PAD33	552.00	0.04	0.03	1.19	1.02	0.47	1.90	1.80	4.80
PAD36	639.00	0.06	0.08	2.02	3.57	1.08	9.56	3.50	12.20
PAD38	5800.00	0.30	0.16	9.00	9.88	4.18	9.83	14.30	37.20
PAD39	1500.00	0.09	0.43	9.99	13.20	2.58	5.64	5.69	28.40
PAD50	3340.00	0.15	0.16	13.10	5.93	2.08	25.00	20.10	21.90
PAD52	99.40	0.01	0.07	2.42	1.63	2.61	1.14	0.69	6.90
PAD53	1220.00	0.07	0.15	10.90	3.93	4.47	3.77	4.20	15.30
PAD54	4620.00	0.25	0.68	8.79	11.70	3.76	19.70	15.90	43.50
PAD57	673.00	0.03	0.12	2.12	40.00	0.90	4.01	2.64	18.30
PAD58	4710.00	0.24	0.31	10.50	7.73	4.25	12.10	16.90	40.30
PAD64	1260.00	0.07	0.11	4.27	4.55	1.13	10.80	5.28	15.60
PAD65	391.00	0.03	0.11	1.67	15.10	1.82	3.53	2.11	20.00

M1	269.00	0.02	0.10	1.81	2.81	0.70	2.00	1.65	11.80
M2	3580.00	0.31	0.21	6.98	17.09	4.17	16.63	13.63	82.40
M3	1270.00	0.06	0.06	3.68	3.44	1.05	2.49	3.64	12.30
M6	2010.00	0.10	0.12	37.40	5.47	4.03	4.42	6.93	16.50
M7	136.50	0.01	0.01	0.36	0.60	0.24	2.00	0.62	2.75
M8	1960.00	0.11	0.05	3.21	5.48	1.34	9.67	8.97	7.70
M10	2860.00	0.17	0.22	5.39	6.39	3.33	7.43	9.61	24.10
M11	27.00	0.01	0.01	0.20	0.20	0.12	0.61	0.10	2.60
M14	654.00	0.04	0.07	16.80	6.38	4.37	13.70	2.40	7.50
M15	489.00	0.04	0.16	2.71	5.64	1.06	2.00	3.11	36.10
M17	208.00	0.01	0.05	0.69	1.54	0.55	2.59	0.90	6.20
M18	1960.00	0.10	0.11	4.53	6.32	1.71	6.71	6.60	15.40
M19	691.00	0.05	0.57	6.38	14.50	25.60	4.61	3.34	55.30

Appendix C: Loss-on-ignition data for the biofilm-sediment mixtures

Table C1. Loss-on-ignition results for biofilm-sediment mixtures accrued in 2017.

Lakes	%H2O	%OM	%MM	%CaCO3
PAD1	96.63	23.43	36.17	40.40
PAD2	99.25	74.49	17.88	7.63
PAD3	98.98	58.82	19.80	21.37
PAD4	99.23	63.49	19.96	16.55
PAD8	98.57	66.97	21.99	11.04
PAD12	98.33	57.08	29.57	13.35
PAD13	99.67	82.64	9.49	7.87
PAD14	99.14	55.59	22.78	21.63
PAD15	98.54	54.17	25.29	20.53
PAD16	98.81	24.83	41.10	34.08
PAD17	99.61	72.33	20.83	6.84
PAD18	99.25	73.36	24.76	1.88
PAD19	95.81	37.80	55.66	6.54
PAD21	92.60	42.95	50.75	6.31
PAD22	99.20	76.88	17.60	5.52
PAD23	99.32	80.31	19.69	0.00
PAD24	99.43	80.09	20.55	-0.64
PAD26	99.30	82.11	12.91	4.98
PAD27	97.90	64.74	18.45	16.81
PAD30	98.39	42.37	31.90	25.74
PAD31	96.27	29.80	44.29	25.91
PAD32	99.16	63.31	32.50	4.19
PAD33	98.07	102.31	-34.83	32.51
PAD36	97.63	93.76	4.50	1.74
PAD40	92.54	17.00	72.90	10.10
PAD50	93.63	51.36	33.94	14.71
PAD52	96.52	40.25	29.49	30.27
PAD54	98.74	56.43	38.57	5.00
PAD57	97.22	81.92	12.81	5.27
PAD58	94.30	37.00	59.48	3.52

PAD62	99.32	30.91	49.31	19.78
PAD65	98.31	74.62	13.96	11.42
PAD66	97.77	32.34	32.37	35.29
M2	96.47	51.78	45.31	2.91
M3	98.50	40.82	29.02	30.16
M5	97.13	70.14	27.87	1.99
M6	98.97	86.64	8.04	5.33
M7	97.56	45.96	24.96	29.09
M8	95.39	42.08	30.37	27.55
M9	98.33	51.85	29.74	18.40
M10	98.49	53.97	40.85	5.18
M11	92.63	26.43	35.00	38.57
M12	96.92	22.87	35.46	41.68
M13	95.15	24.65	56.79	18.56
M15	99.24	74.42	21.97	3.61
M16	99.58	81.63	13.51	4.86
M17	99.21	88.64	8.04	3.32
M18	96.72	50.15	23.48	26.37

Table C2. Loss-on-ignition results for biofilm-sediment mixtures accrued in 2018.

Lake	%H2O	%OM	%MM	%MM	%CaCO3
PAD1	99.89	92.13	7.87	4.81	3.06
PAD2	99.57	83.67	16.33	10.89	5.44
PAD3	99.94	82.50	17.50	10.70	6.80
PAD4	99.54	79.77	20.23	13.45	6.78
PAD6	99.99	100.00	0.00	NA	NA
PAD8	99.61	79.85	20.15	17.66	2.49
PAD12	99.33	65.55	34.45	24.57	9.88
PAD13	99.91	79.37	20.63	29.27	NA
PAD14	99.81	65.08	34.92	23.05	11.87
PAD15	99.95	50.72	49.28	41.25	8.03
PAD16	99.86	23.00	77.00	47.08	29.92
PAD17	99.96	88.89	11.11	11.11	0.00
PAD18	99.87	83.00	17.00	7.48	9.52
PAD19	97.25	80.83	19.17	17.87	1.29
PAD20	98.04	72.44	27.56	24.05	3.51
PAD22	99.65	85.92	14.08	12.65	1.44
PAD23	99.58	85.24	14.76	NA	NA
PAD26	99.97	91.30	8.70	-3.13	11.83
PAD30	99.84	39.81	60.19	52.63	7.56
PAD31	99.80	81.82	18.18	12.00	6.18
PAD32	99.77	69.39	30.61	29.22	1.39
PAD33	99.61	44.97	55.03	28.52	26.52
PAD36	99.84	96.26	3.74	1.20	2.54
PAD38	99.87	59.00	41.00	NA	NA
PAD39	99.99	100.00	0.00	0.00	0.00
PAD50	99.74	55.00	45.00	37.52	7.48
PAD52	99.95	67.74	32.26	32.26	0.00
PAD53	99.98	40.00	60.00	60.00	0.00
PAD57	99.27	73.23	26.77	18.19	8.58
PAD58	99.90	59.72	40.28	47.83	0.00
PAD64	99.92	58.18	41.82	12.15	29.67
PAD65	99.75	92.13	7.87	4.04	3.82

PAD66	99.87	37.23	62.77	55.53	7.23
M1	99.89	66.27	33.73	32.10	1.64
M2	99.28	79.83	20.17	19.83	0.34
M3	99.59	64.13	35.87	23.06	12.81
M6	99.97	42.31	57.69	21.08	36.62
M7	99.59	69.39	30.61	16.27	14.34
M8	99.34	73.75	26.25	21.97	4.27
M9	99.88	81.82	18.18	18.18	0.00
M10	99.90	81.67	18.33	11.53	6.80
M11	98.06	31.50	68.50	33.11	35.38
M12	99.96	46.43	53.57	19.57	34.00
M14	99.88	59.04	40.96	NA	NA
M15	99.50	81.92	18.08	16.89	1.19
M17	99.69	77.73	22.27	11.15	11.13
M18	99.90	92.65	7.35	17.35	0.00
M19	99.92	89.29	10.71	NA	NA

Appendix D: High Performance Liquid Chromatography (HPLC) pigment analysis

D.1. HPLC material and methods

For each lake, the filter with subsample for pigment analysis was cut into pieces and added to a 20 mL glass scintillation vial. The filter pieces were completely submerged by 5 mL of extraction solvent (acetone:methanol:water; 80:15:5 by volume) for 24 hours at -20°C. The extract from each sample was then filtered through a polytetrafluoroethylene (PTEE) syringe filter (0.22 µm pore size) to remove impurities, and subsequently dried under inert N_2 gas. Pigments were recovered using 500 µL of injection solution (acetone:ion pairing reagent (IPR):methanol; 70:25:5 by volume), where 0.75 g tetrabutylammonium acetate and 7.7 g ammonium acetate made up IPR solution. High performance liquid chromatographic (HPLC) analysis was performed using a *Waters* HPLC reverse-phased system with a *Symmetry C18* Stainless steel column (4.6 x 75 mm; 3.5 µm particle size), following methods by Mantoura and Llewellyn (1983) and modified by Leavitt et al. (1989). Pigment compounds were separated via gradient delivery of mobile phase A (methanol:IPR, 90:10 by volume) and mobile phase B (methanol:acetone, 73:27 by volume). Sudan II was used as an internal and external standard because it has carotenoid-like absorption characteristics and maintains a consistent position in the chromatographs. Sudan II filled vials were positioned as the first and last sample of the HPLC sequence and Sudan II was also added to periphyton pigments to control for dilution and injection errors. Following methods described in Jeffrey et al. (1997), pigment identification and quantification was performed using a *Waters 2998* Photodiode Array (PDA) detector based on chromatographic mobility (retention time) and spectral characteristics (Leavitt and Hodgson, 2001) relative to known standards. Pigment abundance was expressed in nmol/cm^2 following Equation (1), modified from Leavitt and Hodgson (2001):

(1) Pigment (J) / surface area (biofilm-sediment mixture) = $(A_i / S_j) \cdot (V_t \times 1000 / V_i) \cdot A_p^{-1} \cdot M_j^{-1}$,

where M_j is the molecular weight of pigment J (g/mol), A_i is the peak on the chromatogram (area), S_j is the slope of regression relating area of Sudan II peak versus mass of pure pigment (area/µg), V_t is the total sample volume (µL), V_i is the injection volume (µL), and A_p is the surface area of the shield that accrued biofilm-sediment mixture.

D.2. HPLC pigment data

Table D1. Pigment abundance (nmol/cm^2) in biofilm-sediment mixtures accrued in lakes of the Peace-Athabasca Delta from May to September 2017 and May to September 2018.

Lake	Chlorophyll a	Chlorophyllide a	Pheophorbide a	Chlorophyll c	Chlorophyll b	Pheophytin b	Pheophytin a	β-carotene	Canthaxanthin	Diadinoxanthin	Diatoxanthin	Fucoxanthin	Lutein	Neoxanthin	Violaxanthin
May - September 2017															
PAD2	9.96	0.00	0.01	0.55	4.22	3.62	5.79	0.35	0.08	0.16	0.26	1.47	1.29	0.83	0.12
PAD6	6.55	0.22	0.05	0.07	2.30	1.28	1.40	0.30	0.04	0.34	0.16	0.00	1.41	0.56	0.06
PAD12	20.75	0.00	0.10	1.12	12.48	10.09	32.30	0.67	0.46	1.73	0.73	3.35	4.94	1.66	0.00
PAD13	13.76	0.00	0.00	0.38	3.13	5.30	5.95	0.41	0.45	0.52	0.21	0.85	0.68	0.64	0.00
PAD14	20.57	0.02	0.00	0.25	8.41	5.17	16.57	1.21	0.15	1.24	0.00	1.04	4.13	1.92	0.23
PAD15	14.11	0.02	0.25	0.49	7.17	3.06	14.94	0.59	0.20	0.56	0.00	0.80	3.22	1.23	0.29
PAD16	5.18	0.00	0.07	0.26	1.14	0.72	0.52	0.13	0.04	0.10	0.09	0.48	0.61	0.14	0.21
PAD18	12.89	0.00	0.15	0.52	4.43	1.18	4.43	0.71	0.28	0.89	0.36	1.20	2.19	0.97	0.14
PAD19	50.45	0.32	0.63	1.26	28.99	17.99	45.83	0.71	0.34	2.65	1.53	3.92	9.00	5.45	1.08
PAD21	37.20	0.24	0.03	1.65	12.49	21.19	24.58	1.31	1.63	3.80	0.00	2.26	4.20	3.29	0.36
PAD22	19.88	0.04	0.09	0.30	3.49	0.73	9.00	1.02	0.78	1.12	0.00	0.54	1.46	1.42	0.00
PAD23	70.51	1.27	0.00	1.97	25.41	33.35	12.89	1.61	0.97	2.02	0.72	4.04	7.24	3.71	1.16
PAD24	65.72	2.63	1.10	0.45	36.26	24.99	38.25	1.17	0.50	1.61	0.70	1.66	14.11	6.35	0.91
PAD26	50.17	4.22	0.79	0.42	28.43	8.06	14.11	0.90	0.81	0.88	0.00	0.00	9.30	4.73	1.10
PAD27	26.99	2.99	1.53	0.23	20.20	7.30	17.21	0.25	0.36	0.76	0.51	0.00	10.29	3.85	0.52
PAD30	12.71	0.43	0.18	0.32	3.61	4.73	10.17	0.64	0.49	0.35	0.00	0.92	1.96	0.96	0.00
PAD31	31.59	0.52	0.90	3.21	17.13	11.78	24.95	1.10	0.15	1.12	0.00	7.65	6.17	3.36	0.42
PAD32	18.57	0.93	0.44	1.39	7.65	5.42	9.94	0.30	0.15	1.10	0.18	2.75	3.01	1.52	0.63
PAD33	16.76	0.41	0.10	0.51	5.53	2.62	0.33	0.40	0.08	0.44	0.00	1.53	2.01	1.04	0.09
PAD36	40.41	2.09	0.54	0.30	16.61	10.85	16.24	0.18	0.95	0.61	0.00	0.67	2.23	1.34	0.94

PAD38	2.49	0.00	0.00	0.07	0.89	0.22	0.76	0.16	0.00	0.16	0.00	0.42	0.46	0.14	0.04
PAD39	2.77	0.00	0.00	0.03	0.39	0.17	0.24	0.06	0.02	0.08	0.14	0.19	0.49	0.22	0.00
PAD40	200.66	0.16	0.66	20.11	30.01	34.19	74.32	3.63	1.35	6.43	2.14	59.85	5.55	4.92	0.00
PAD50	47.28	7.87	4.48	1.00	26.80	8.80	27.65	0.50	0.74	0.98	0.00	3.38	9.21	1.81	1.32
PAD52	84.17	1.80	0.00	0.82	25.15	16.83	17.79	1.01	1.45	2.19	0.00	5.62	5.34	2.64	1.56
PAD53	1.27	0.00	0.02	0.01	0.44	0.15	0.30	0.04	0.01	0.03	0.00	0.07	0.13	0.00	0.00
PAD54	29.45	0.08	0.00	1.79	6.72	4.08	6.84	0.77	0.36	1.46	0.72	4.93	1.90	1.27	0.11
PAD57	87.08	7.16	4.21	0.70	47.15	20.17	26.73	0.98	0.77	0.89	0.00	0.00	12.24	7.86	1.07
PAD58	62.80	0.00	0.19	0.58	28.96	19.80	27.13	0.89	1.49	2.42	0.40	2.82	7.52	5.12	1.47
PAD65	17.39	0.35	0.33	0.15	6.83	2.81	2.58	0.33	0.14	0.22	0.07	0.41	1.19	0.91	0.00
M2	69.63	0.25	0.11	2.35	29.50	43.35	18.58	2.44	0.86	1.72	0.45	11.65	6.61	4.03	0.96
M3	13.56	0.07	0.14	0.15	4.14	1.17	2.45	0.65	0.44	2.94	0.00	0.76	0.00	0.94	0.00
M6	1.41	0.00	0.67	0.26	1.37	21.21	35.07	0.71	0.00	4.28	0.00	0.71	0.00	2.00	0.00
M7	16.19	0.18	0.00	0.10	4.63	4.35	3.64	0.51	0.13	0.60	0.00	0.58	1.72	1.11	0.05
M8	94.21	2.18	0.00	3.79	41.85	7.74	49.21	2.28	0.54	2.02	0.00	13.28	15.82	10.96	1.06
M10	15.33	1.26	0.24	0.19	6.68	1.36	0.89	0.32	0.00	0.56	0.00	0.00	2.64	1.20	0.82
M11	52.88	1.45	0.00	7.12	31.56	4.14	1.96	1.19	3.20	8.74	0.00	36.83	13.59	10.78	0.99
M12	5.28	0.00	0.00	0.31	3.30	2.13	1.84	0.30	0.00	0.67	0.00	0.92	0.73	0.28	0.00
M13	43.62	0.00	0.00	8.02	18.15	179.97	52.05	3.84	2.57	6.61	4.45	33.88	6.17	4.33	0.69
M15	10.29	0.00	0.08	0.93	3.82	6.38	9.42	0.66	0.18	0.64	0.39	2.71	1.43	1.10	0.27
M17	97.97	4.29	0.12	0.10	36.82	27.97	8.88	3.41	1.14	2.12	0.49	0.00	16.49	8.24	1.09
M18	40.80	1.58	0.00	0.60	12.54	3.05	4.10	0.36	0.41	1.26	0.39	2.28	6.16	2.46	0.60
M19	5.36	0.00	0.02	0.31	1.83	1.25	1.21	0.13	0.06	0.09	0.01	0.63	0.62	0.27	0.13
May - September 2018															
PAD1	23.49	2.92	2.32	0.00	13.60	2.37	6.26	0.76	0.00	1.09	0.00	0.00	8.62	0.84	0.15
PAD2	67.82	10.36	8.68	0.00	49.16	18.81	30.67	2.07	1.37	2.75	0.00	0.00	20.09	3.59	1.91
PAD3	6.97	0.23	0.00	0.00	3.06	3.96	0.90	0.27	0.00	0.42	0.11	0.82	1.96	1.23	0.00
PAD4	58.54	4.50	4.47	0.00	27.82	4.02	6.44	0.89	0.00	0.85	0.00	0.00	12.94	2.22	0.91
PAD6	1.07	0.00	0.03	0.06	0.10	0.00	0.04	0.04	0.00	0.04	0.14	0.13	0.08	0.01	0.00
PAD8	40.05	0.88	0.58	0.54	10.93	7.66	8.59	1.90	0.31	1.64	0.00	2.62	4.45	2.01	0.22

PAD12	32.20	4.26	1.02	0.36	24.15	10.93	22.62	0.49	0.00	1.37	0.71	0.00	11.70	6.17	1.64
PAD13	3.09	0.00	0.00	0.37	1.98	1.40	3.84	0.26	0.06	0.42	0.00	0.87	0.68	0.32	0.00
PAD15	5.48	0.09	0.30	0.15	1.83	0.31	0.46	0.12	0.00	0.45	0.00	0.69	1.08	0.15	0.00
PAD16	1.29	0.23	0.19	0.10	0.54	0.10	3.59	0.25	0.00	0.12	0.00	0.39	0.44	0.07	0.07
PAD17	12.03	0.06	0.00	0.73	3.51	3.56	2.23	0.23	0.00	0.66	0.12	1.61	0.95	0.62	0.08
PAD18	27.17	0.00	0.00	0.78	7.72	1.95	6.88	1.85	0.28	1.11	0.00	2.86	4.62	2.39	0.30
PAD19	73.25	0.00	5.53	10.01	38.19	35.59	124.87	6.33	0.71	5.02	1.18	41.19	15.07	2.11	0.46
PAD20	59.06	1.49	0.00	2.28	34.13	6.74	64.11	2.32	0.60	1.74	0.62	15.66	10.59	6.25	0.62
PAD22	48.49	2.31	3.76	1.13	21.42	8.91	30.19	1.99	0.77	1.74	0.42	6.01	7.58	1.67	0.36
PAD23	7.44	0.00	0.44	0.12	3.65	0.00	3.18	0.15	0.00	0.25	0.00	0.80	1.63	0.18	0.00
PAD26	2.81	0.00	0.00	0.06	0.93	0.16	0.14	0.09	0.00	0.11	0.10	0.20	0.50	0.17	0.00
PAD30	9.94	0.00	0.00	0.52	2.70	1.66	2.92	0.34	0.05	1.08	0.13	1.39	1.79	0.65	0.05
PAD31	38.31	2.37	0.09	3.16	21.07	4.66	10.35	0.61	0.12	0.63	0.00	1.21	12.35	5.54	0.69
PAD32	28.33	0.31	0.07	0.61	7.78	5.02	25.49	0.35	0.54	0.64	0.22	2.41	0.96	0.75	0.16
PAD33	5.50	0.00	0.00	0.40	5.18	2.51	0.00	0.46	0.17	0.52	0.30	1.10	1.73	0.57	0.12
PAD36	3.76	0.33	0.41	0.00	1.34	0.82	5.16	0.77	0.11	1.23	0.00	0.14	1.02	0.27	0.00
PAD38	8.89	1.69	1.57	0.00	9.19	3.16	0.00	0.15	0.00	0.61	0.00	0.00	3.76	0.45	0.13
PAD39	3.76	0.01	0.00	0.01	2.08	0.66	1.96	0.02	0.00	0.06	0.00	0.00	0.81	0.21	0.03
PAD50	42.60	0.72	0.00	1.05	27.71	17.54	51.45	0.89	0.59	2.34	0.60	4.76	15.39	6.16	1.12
PAD52	1.40	0.00	0.00	0.02	0.73	0.26	0.54	0.06	0.00	0.03	0.00	0.03	0.44	0.13	0.00
PAD53	0.66	0.00	0.00	0.04	0.15	0.00	0.08	0.03	0.00	0.00	0.00	0.17	0.08	0.00	0.00
PAD54	13.54	0.02	0.31	0.22	1.43	1.30	0.00	0.00	0.63	0.62	0.16	0.61	0.83	0.24	0.14
PAD57	14.34	4.77	3.56	0.00	11.46	2.63	7.24	0.21	0.00	0.72	0.00	0.00	8.33	1.04	0.34
PAD58	5.07	0.14	0.00	0.07	3.67	1.71	5.92	0.27	0.00	0.28	0.00	0.28	1.50	0.53	0.09
PAD64	10.79	0.14	0.14	0.09	4.12	0.66	5.74	0.18	0.23	1.12	0.60	0.48	2.53	0.83	0.00
PAD65	31.13	1.46	0.96	1.49	25.96	7.82	23.08	0.86	0.22	2.18	0.00	0.00	16.21	6.39	0.56
PAD66	2.55	0.08	0.05	0.15	1.49	0.23	5.30	0.00	0.07	0.38	0.16	0.84	1.22	0.26	0.23
M1	0.15	0.99	0.56	0.49	0.11	0.00	0.00	0.00	0.00	0.86	0.00	1.09	0.00	0.00	0.00
M2	4.59	0.95	1.03	0.59	7.86	8.81	20.47	0.39	0.23	0.00	0.00	1.84	3.38	0.44	0.18
M3	38.02	7.01	6.90	0.75	37.41	33.20	44.47	1.38	0.30	1.94	0.00	0.00	18.09	1.81	1.28

M5	13.16	0.82	1.28	0.00	9.38	3.04	10.98	0.26	0.17	0.23	0.00	0.45	3.60	0.39	0.13
M6	0.89	0.00	0.06	0.22	0.34	0.33	1.16	0.04	0.00	0.12	0.00	0.47	0.13	0.00	0.00
M7	60.30	8.56	4.12	0.36	36.60	5.22	54.92	0.45	0.19	2.04	0.00	0.00	18.39	6.01	1.36
M8	8.61	0.00	0.00	1.19	10.97	11.38	39.90	1.70	0.16	0.00	0.61	4.28	5.49	3.06	0.64
M9	23.37	0.00	0.00	0.27	13.28	4.72	8.05	0.19	0.12	0.00	0.00	0.39	5.71	0.34	0.00
M10	9.46	0.34	0.18	0.26	10.76	7.29	22.58	0.35	0.11	1.04	0.00	0.79	5.71	1.75	0.63
M11	85.76	22.07	10.73	6.83	48.45	34.07	47.44	2.76	5.90	7.10	0.81	20.37	28.38	5.85	3.57
M12	0.50	0.05	0.12	0.04	0.26	0.27	1.03	0.03	0.00	0.00	0.00	0.14	0.22	0.00	0.01
M14	5.47	0.00	0.00	0.68	2.44	1.99	7.71	0.25	0.08	0.88	0.25	1.69	1.32	0.54	0.05
M15	0.76	3.12	7.43	1.52	4.12	4.21	4.69	0.17	0.07	2.52	0.00	1.66	9.81	0.42	1.07
M17	62.09	5.41	2.62	0.52	43.80	15.62	34.96	0.21	1.08	1.28	0.00	0.00	0.00	5.92	15.35
M18	14.20	0.61	0.00	0.16	10.08	3.43	12.00	0.35	0.08	0.86	0.00	0.61	5.58	2.54	0.00
M19	1.35	0.01	0.03	0.06	0.45	2.05	3.49	0.02	0.05	0.00	0.00	0.27	0.52	0.16	0.00