# Developing pre-industrial baselines from floodplain lake sediment cores to quantify the extent of metals pollution within the Alberta Oil Sands Region

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**

Oil sands mining operations began in 1967, but the onset of a monitoring program to assess water and sediment quality in the Athabasca River watershed began 30 years later. Consequently, no knowledge of pre-industrial, baseline conditions exists upon which current river sediment quality can be compared. This has undermined an ability to determine the relative importance of contaminants supplied by natural processes versus pollution to the Athabasca River by rapid growth of oil sands development. In this study, a paleolimnological approach was used to analyze sediment cores from five flood-influenced lakes located upstream and downstream of oil sands operations within the Alberta Oil Sands Region (AOSR). Loss-on-ignition and organic carbon and nitrogen elemental analyses were used to differentiate periods of strong and weak Athabasca River flood influence. In addition, the temporal changes in concentrations of bitumen-associated metals vanadium (V) and nickel (Ni) were explored at each lake. A pre-industrial baseline was developed using pre-1967 sediment concentrations of V and Ni, normalized to aluminum concentration, from lakes in the AOSR to estimate the natural range of variability of these metals. When normalized metals concentrations in recently deposited flood-influenced sediment were compared to the pre-industrial baseline, no evidence of enrichment in the river-derived stratigraphic intervals was detected. However, significant enrichment of bitumen-related metals V and Ni (up to 2- and 1.6-fold above the baseline, respectively) was observed in weakly flood-influenced sediment in the two floodplain lakes located closest to the most active mining operations (< 10 km), indicating local atmospheric pollution. Athabasca River sediment data collected by regional monitoring programs RAMP (1997-2002) and JOSM (2012-2014) were examined in the context of the newly developed baselines and showed enrichment of V (1.2-1.7x baseline) and Ni (1.2-2.0x baseline) at some of the river monitoring sites, usually proximal to tributary outflows. This research indicates that sediment profiles from floodplain lakes along the lower Athabasca provide valuable information as pre-industrial depositional areas of natural sediment metals. Paleohydrological analyses, however, indicate that flood-influence at many of these lakes is declining, coincident with oil sands growth, and so many of the lakes no longer frequently capture flood sediments. Nonetheless, metal-specific baselines using the pre-1967 data can be used to detect enrichment in modern sediments of the floodplain lakes and in river sediment monitoring data, the latter previously criticized for inadequate baseline knowledge, and which also now serves as a foundation for ongoing river sediment monitoring.

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## Dedication

This thesis is dedicated to my father, Christian Klemt. I always strive to be as strong, intelligent, creative, and loving as you were. Although you have not been here to see most of my academic achievements, I know you have been with me through every milestone, including this one.

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# Chapter 1 – Introduction

## *1.1 Background*

The Alberta Oil Sands Region (AOSR) in northern Alberta, Canada, holds the third largest oil reserves in the world and is believed to contain 164 billion barrels of recoverable oil under an area of 142,000 $km^2$ in the Athabasca River, Peace River, and Cold Lake watersheds (CAPP, 2018a). Commercial production in the Alberta oil sands began in 1967 at the Great Canadian Oil Sands plant (Suncor Inc.) and produced 32,000 barrels/day (CAPP, 2018b). Today, production has grown to around 2.8 million barrels of oil per day and is mined via both surface (43%) and in situ (57%) extraction techniques (CAPP, 2018a). These mining activities have a large environmental footprint, covering around 1670 $km^2$ of land in northern Alberta, mostly within the Athabasca River basin (Rooney *et al*., 2012).

Increased oil production in the region has led to concerns surrounding negative effects of mining operations to nearby lake, wetland, and river ecosystems, by processes such as the atmospheric release and deposition of contaminants, which include polycyclic aromatic hydrocarbons (PAHs; Kelly *et al.*, 2009, 2010; Kirk *et al*., 2014; Manzano *et al*., 2016) and metals of concern (Cooke *et al*., 2017), nutrient delivery (Hazewinkel *et al*., 2008; Summers *et al*., 2016, 2017), acidification (Hazewinkel *et al*., 2008; Curtis *et al*., 2010), as well as land disturbance and peatland loss by expansion of the mining activities and related infrastructure (Timoney & Lee, 2009; Schindler, 2010; Rooney *et al*., 2012). Studies that have evaluated atmospheric contaminant deposition in the AOSR have shown elevated deposition of PAHs and metals of concern to the landscape within a 50 km radius of the centre of Athabasca oil sands development at Syncrude's Mildred Lake mine (denoted as AR6 in Kelly *et al*., 2009, 2010),

with the deposition footprint largely following the Athabasca River valley corridor (Kirk *et al*., 2014). This has been demonstrated by several years of measurements made on snowpack investigating the amount of deposition that accumulates on the environment during the winter (Kelly *et al*., 2010; Kirk *et al*., 2014; Manzano *et al*., 2016), and measurements made on lake sediment and peat core samples that capture the ice-free season when these contaminants are deposited directly on the waterbodies within the AOSR (Jautzy *et al*., 2013; Kurek *et al*., 2013; Cooke *et al*., 2017; Shotyk *et al*., 2016b; Zhang *et al*., 2016). During spring snowmelt and rain events, contaminants are moved through the landscape and are eventually deposited in the Athabasca River as well as smaller water bodies and tributaries.

Concerns have been expressed about the effects of mining activities on human and ecosystem health in downstream environments along the Athabasca River (Timoney & Lee, 2009; Schindler, 2010). People in the downstream community of Fort Chipewyan, in the Peace-Athabasca Delta (PAD) - a Ramsar Wetland of International Importance and a UNESCO World Heritage Site - have reported higher than average rates of cancer in recent decades, as well as perceived increased incidence of deformed fish from the Athabasca River (Schindler, 2010; McLachlan, 2014). Clearly, there is a need for improved understanding of the influences of industry on the Athabasca River system.

### *1.2 Environmental monitoring in the Alberta oil sands region*

Monitoring is a systematic process which involves the consistent, repeated observation of a system at set locations and at regular intervals over time to assess current conditions and evaluate trends (Chapman, 1991). Systematic monitoring of surface water and sediment in the AOSR for contaminants first began in 1997 with the incorporation of the industry-funded Regional Aquatics Monitoring Program (RAMP) (Cronmiller & Noble, 2018). This program

involved a multiple-stakeholder Technical Program Committee which included industry partners, local, provincial, and federal government groups, consultants (e.g., Hatfield), environmental groups (e.g., Cumulative Environmental Management Association (CEMA), Wood Buffalo Environmental Association (WBEA)), and First Nations communities along the lower Athabasca River (Cronmiller & Noble, 2018). Monitoring for RAMP included the collection of environmental data from the Athabasca River, its tributaries, the downstream delta, and some ecologically-important lakes and wetlands in the watershed. Environmental data included the collection of water, surface sediment, benthic invertebrates, fish, and climate and hydrologic measurements (Cronmiller & Noble, 2018). Unfortunately, the RAMP program was highly controversial, and criticized for inconsistent sampling and methodology, an inability to detect trends of pollution, and lack of accessibility to their data (Schindler, 2010). In his 2010 critique, Schindler highlighted the need to design a sampling program that can separate industrial from natural sources, while monitoring the various pathways of contaminant deposition. As well, seasonal changes must be addressed to account for increases in delivery of pollutants to aquatic systems from contaminated snow during the spring melt (Schindler, 2010).

Following these criticisms, an oil sands Expert Advisory Panel was established by the federal Minister of the Environment in 2010 to assess the state of monitoring and scientific research in the oil sands region and determine the strengths and weaknesses of the current environmental monitoring program. The Expert Panel identified key weaknesses including the lack of pre-industrial baseline data, lack of transparency, and sporadic and inconsistent sampling methodology, and provided recommendations on how to improve monitoring in the AOSR (Dowdeswell *et al*., 2010). In 2012, the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring was developed to expand and improve current environmental monitoring programs

in the AOSR, including RAMP. As part of this implementation plan, the Joint Oil Sands Monitoring Program (JOSM) was initiated to characterize the state of the environment in the AOSR, assess cumulative effects to the watershed, and develop recommendations for an integrated environmental monitoring program (Cronmiller & Noble, 2018). Working with federal and provincial government groups, RAMP's environmental monitoring activities were fully transitioned to JOSM in 2012 (Cronmiller & Noble, 2018). JOSM continues to work closely with both governments, as well as with industry groups and local stakeholders, to improve communication and provide open and transparent collection and reporting of environmental data across the AOSR.

One of the key recommendations mentioned in reports such as the Oil Sands Advisory Panel Report to the Minister of the Environment (Dowdeswell *et al*., 2010) and the Final Program Report by RAMP in support of JOSM (Hatfield Consultants, 2016) is the need for baseline data that underpins an ability of monitoring programs to quantify the extent of industrial pollution. The 2010 report states that "it is important to establish as rigorously as possible the background or baseline level of pollution, against which any future trends can be assessed" (Dowdeswell *et al*., 2010, p.31). Since RAMP was initiated 30 years after oil sands development began in 1967, no pre-oil sands development environmental baseline exists upon which current river sediment and water quality monitoring data can be compared. Studies and environmental monitoring programs have attempted to address the lack of baseline in various ways. RAMP states on its website that it compared sediment and water quality measurements to "historical, pre-development, and regional baseline values", but no details are provided to what those data are. Most recently in the Final Program Report (Hatfield Consultants, 2016), "baseline" for the Athabasca River was defined as any data collected from locations upstream of oil sands

development as of, or prior to, 2015. Pre-industrial baseline data are crucial to interpreting any environmental monitoring data collected, as increased industrial activity during 1997-2015 renders data from this period inappropriate for use as baseline. This situation is further confounded for the Athabasca River, because the river flows through the naturally bitumen-rich McMurray Formation (McMF) where riverbank erosion, groundwater mixing, natural runoff, and aerial transport provide natural inputs of contaminants to the Athabasca River and surrounding watershed (Headley & McMartin, 2004). To date, only a few studies have attempted to use the RAMP monitoring database to evaluate trends (Evans *et al*., 2016), or to evaluate for evidence of downstream pollution (Wiklund *et al*., 2014), in water and sediment data since monitoring of the Athabasca River and surrounding water bodies began. The inability to distinguish natural from industrial sources of heavy metals continues to undermine our ability to track industry-related change across the AOSR. This study aims to use paleolimnological techniques to generate pre-industrial baseline data on river sediment-metals concentrations and lend insight to the interpretation of Athabasca River-monitoring data. Paleolimnology, the study of physical, chemical, and biological information preserved in lake sediments over time, provides a scientific approach for reconstructing past changes in environmental conditions of lakes (Smol, 1992; Cohen, 2003; Smol, 2009). Analysis of lake sediments can aid in the evaluation of aquatic systems where little to no monitoring data are available, and in areas where levels of contaminants are naturally high, to develop knowledge of pre-industrial baseline conditions (Smol, 1992).

Given the short-term data records in the region, paleolimnological studies can provide means to evaluate long-term trends in contaminant deposition and accumulation in the AOSR. In fact, when developing the new water quality monitoring plan for JOSM in 2011, the report's

authors recognized the importance of paleoenvironmental analyses in the AOSR and stated that "careful paleolimnological sampling and analysis could provide essential information on natural background levels (baseline or reference conditions) of sediment and contaminants transported via the rivers and atmosphere, and to quantify trends over time since the onset of industrial activities" (Wrona & di Cenzo, 2011, p. 65). Previous studies have evaluated regional atmospheric trends in contaminant deposition from paleolimnological analyses conducted at small headwater lakes in the AOSR, but have yet to apply these techniques to river-influenced lakes to determine the extent of river pollution (Jautzy *et al*., 2013; Kurek *et al*., 2013; Cooke *et al*., 2017).

### *1.3 River sediment quality monitoring*

Monitoring of sediment quality in aquatic systems has been highlighted as one of the best ways to assess for evidence of aquatic pollution (Reuther, 2009). Sediment quality influences benthic communities and the chemistry of overlying waters (Peeters *et al*., 2004). Thus, sediment quality is directly linked to the health of aquatic systems. Metals can be released to the environment in both particulate and dissolved form. In rivers, dissolved and particulate metals form complexes with sediment and organic matter in the water due to their low solubility, eventually being deposited in river-bottom sediment (Förstner & Müller, 1981; Reuther, 2009). Depositional areas along the river, such as slow-moving sections of the river or lakes that receive floodwaters, can accumulate the sediments carried by the river over time (Audry *et al*., 2004). The method by which benthic and other aquatic organisms interact with heavy metals in sediments is highly dependant on interactions with sediment and organic matter, which ultimately affects the mobility and bioavailability of the metal (Barton & Wallace, 1979; Peeters *et al*., 2004; Parsons *et al*., 2010).

Sediment sampling as part of the RAMP/JOSM monitoring programs has generally focused on areas of deposition within the Athabasca River and its tributaries, where collected sediments consist mostly of sands, silts, and clays, as opposed to gravels and coarser-grained sediment. Sampling of the mainstem of the Athabasca River as a part of RAMP was discontinued in 2005, as it was not considered representative of a depositional environment where temporal changes could be evaluated (Hatfield Consultants, 2009). It was decided by the RAMP Technical Program Committee that efforts should instead be focused on further depositional reaches of the Athabasca Delta (Conly *et al*., 2002; Hatfield Consultants, 2009). In 2006, RAMP began to collect river sediment samples primarily in conjunction with benthic invertebrate and fish monitoring data, and sampling locations were shifted to the lower end of 'depositional reaches' of the river (i.e., near the Embarras River tributary). In the development of the new water quality monitoring plan for JOSM, focus on sediment sampling in the Athabasca River was transitioned to suspended sediments, tied in with understanding hydraulic behaviour of the river and how that can play a role in the transport of contaminants (Wrona & di Cenzo, 2011). River-bottom sediment in depositional areas continues to be collected as a part of JOSM in conjunction with benthic invertebrate monitoring.

The Athabasca River floods most often in the spring, when water levels are highest and erosional events transport natural bitumen downstream (Conly *et al*., 2002). As well, a large influx of contaminants to the river from polluted snowmelt occurs. Studies of particulate and dissolved metals and PAHs in the Athabasca River by Kelly *et al*. (2009, 2010) show highest dissolved concentrations in river water near, and immediately downstream of, oil sands development, which has been interpreted as a consequence of oil sands pollution. But, since metals and PAHs preferentially adsorb onto particles, measurements of particulate and sediment

metals concentrations are needed to improve assessment of river pollution. Recently, the new JOSM monitoring plan suggested paleolimnological sampling of floodplain lakes, back-eddy zones, and deltaic sediments as a method to target depositional areas for pre-industrial river sediment and contaminant levels (Wrona & di Cenzo, 2011).

### *1.4 Paleolimnological applications in assessing pollution*

Many approaches have been developed to assess the anthropogenic contribution of metal accumulation in lacustrine systems using sediment cores. Most commonly used approaches include the calculation of an enrichment factor (EF), excess flux, also known as anthropogenic flux ($\Delta F$), and/or a geoaccumulation index ($I_{geo}$) (e.g., Müller, 1969; Audry *et al*., 2004; Balogh *et al*., 2009; Boës *et al*., 2011; Kurek *et al*., 2013; Wiklund *et al*., 2014; Wang *et al*., 2015; Cooke *et al*., 2017). An enrichment factor quantifies the ratio of the normalized concentration or flux of an element of interest in samples deposited since development relative to values before development (e.g., Audry *et al*., 2004; Boës *et al*., 2011), and has been used to assess enrichment above pre-industrial levels in the AOSR (Kurek *et al*., 2013; Wiklund *et al*., 2014; Cooke *et al*., 2017). Flux measurements evaluate the product of elemental concentration to the sedimentation rate and have been applied to lake systems in the AOSR to evaluate anthropogenic excess flux of PAHs and metals (Kurek *et al*., 2013; Cooke *et al*., 2017). Measurements of flux are beneficial when evaluating flood-influenced systems as they account for the sedimentation rate. Other common methods that have not yet been applied to lakes in the AOSR include the geoaccumulation index ($I_{geo}$), which is a method of determining qualitatively the scale of pollution intensity to determine the degree of anthropogenic influence (e.g., Müller, 1969; Audry *et al*., 2004; Wang *et al*., 2015). $I_{geo}$ values are calculated using pre- and post-contaminant concentrations and compared to the $I_{geo}$ table, where a value of $> 5$ indicates the site is "very

strongly polluted" and a value < 0 is "unpolluted." As well, some evaluations of anthropogenic metal enrichment in lakes have used stable isotopes of metals (i.e., Pb) to evaluate the anthropogenic enrichment factor, using a two-component isotope mixing model to differentiate sources of natural and atmospherically deposited metals (Boës *et al*., 2011).

### *1.5 Paleolimnology in the AOSR*

Paleolimnological assessments of spatial and temporal patterns of change in PAH and heavy metal deposition have been performed at several lakes within the AOSR (Hazewinkel *et al*., 2008; Curtis *et al*., 2010; Jautzy *et al*., 2013; Kurek *et al*, 2013; Summers *et al*., 2016, 2017; Cooke *et al*., 2017). Theses studies all focused on elevated, headwater lakes that do not flood by the Athabasca River and so were used to track changes in deposition via the atmosphere. A study by Kurek *et al*. (2013) showed increased deposition of PAHs via the air since the 1980s within the 50 km radius defined by the Kelly *et al*. studies (2009, 2010), coincident with increases in oil sands development. Analyses of the $\delta^{13}C$ signatures of PAHs in sediment cores from lakes within the 50 km radius have demonstrated a shift away from petroleum-derived PAHs to those associated with unprocessed bitumen, aiding our understanding of modern source pollution in the AOSR (Jautzy *et al*., 2013). Analysis of temporal trends in airborne metal deposition to near-, mid-, and far-field lakes in the AOSR by Cooke *et al*. (2017) reported no metal enrichment beyond 50 km, and a recent decrease in V and Pb, attributed to improvements in mining technologies. This study combined data across lakes, using decadal periods to better analyze spatial differences across the landscape (Cooke *et al*., 2017).

Paleolimnological studies that tackle multiple-stressors on lakes in the AOSR have been increasing in prevalence in recent years, due to the recognition that understanding additive effects of stressors is needed to determine effects on biological endpoints (Lima & Wrona,

2018). Using food-web bioindicator taxa, a study looked at the relative influences of atmospheric deposition and climate change trends in increased primary production, and demonstrated high vulnerability of these shallow, boreal lakes are to the combined effects of warming and industrial activities (Summers *et al.*, 2017). The research that has been conducted in the AOSR shows that paleolimnological studies have been quite successful in identifying large-scale anthropogenic influences, atmospheric pollution, ecological response to industrial activity and spatial patterns of deposition in the AOSR. These types of studies, however, have generally avoided using floodplain systems due to the added complications of riverine additions to interpreting the atmospheric signal. As well, because the sedimentation rate in these systems is variable, and there is very little organic matter present in the lakes, conventional radioisotope dating techniques can be difficult to apply and interpret, which is why multiple lines of evidence (i.e., $^{137}$Cs and $^{210}$Pb) are needed. Floodplain lakes, however, provide a unique opportunity to investigate temporal trends in Athabasca River sediment quality and potentially disentangle natural and anthropogenic sources of contaminants in the river. Indeed, a key research opportunity lies in the application of paleolimnology at flood-influenced lakes along the Athabasca River to address concerns over river pollution that is missing from the literature. There has been much speculation about what gets deposited in the Athabasca River, but there has yet to be a systematic study that incorporates baseline knowledge to identify the extent of industrial pollution of the river.

### *1.6 Paleolimnology in floodplains*

Paleolimnological studies analyzing metals have successfully been conducted in river-influenced systems in northern Canada and around the world (e.g., Balogh *et al*., 1999, 2009; Audry *et al*., 2004; Brock *et al*., 2010; Wiklund *et al*., 2014; MacDonald *et al*., 2016; Lintern *et*

*al*., 2016b; Ota *et al*., 2017). Paleolimnological assessment of river-transported sediment deposits allows for time-trend analysis of metals and identification of concentrations elevated above pre-industrial background levels that may be attributable to river pollution. This approach has proven to be effective in assessing river pollution using sediment cores from floodplain lakes (e.g., Audry *et al*., 2004; Wiklund *et al*., 2014; MacDonald *et al*., 2016), billabongs/oxbow lakes (e.g., Lintern *et al*., 2016b), and reservoirs (e.g., Balogh *et al*., 1999, 2009) in areas outside the AOSR. This approach was used downstream of the AOSR, in floodplain lakes in the Peace-Athabasca Delta at the terminus of the Athabasca River (Wiklund *et al*., 2014). Pre-industrial baselines were developed from metals analyses of river-supplied sediments deposited before onset of industrial development. Surface sediments collected by RAMP from 2001-2013 were assessed for pollution relative to the baselines and no enrichment was detected (Wiklund *et al*., 2014). Similar research in the Slave River Delta used sediment cores to analyze the various pathways and sources of heavy metals to a flood-influenced lake (MacDonald *et al*., 2016). Researchers found an increase in arsenic concentration coinciding with the onset of gold processing at Giant Mine in Yellowknife, NWT, indicating that this technique can be useful in detecting airborne pollution from industrial sources when the paleohydrological conditions are taken into consideration.

Sedimentary environments of flood-influenced lakes are more complicated than those of isolated lakes because contaminants may be supplied by both river flood-waters and atmospheric pathways. River flood events influence the relative contributions of allochthonous (river-derived inorganic sediment, typically organic matter-poor and metal-enriched), and autochthonous (lake-derived sediment, typically organic matter-rich and metal-poor), sediment present in a floodplain lake at a given time. As well, it is more difficult to date cores accurately by $^{210}$Pb methods, as

rapid deposition of river-borne sediments can depress $^{210}$Pb activity in sediment core intervals and make it difficult to identify the depth at which background (or supported) $^{210}$Pb activity is reached. A key component in analyzing flood-influenced systems is to distinguish river-derived / allochthonous sediment from lake-derived / autochthonous sediment to draw conclusions about what the river has contributed to the lake system. For example, Lintern *et al.* (2016a,b) studied a contaminated billabong (oxbow lake) in Australia and identified flood deposits by two methods. The first assessed changes in sediment characteristics within the core using four common characteristics of flood sediments: presence of laminations, high magnetic susceptibility, smaller particle size, and low occurrence of organic matter (Lintern *et al*., 2016a). The second method is a calculation of Flood Signal Strength (FSS), which quantifies the likelihood that a sample is fluvial in origin using the number of flood-characteristics that are met as well as the magnitude of these properties: high magnetic susceptibility and inorganic matter, sediment particle size, and enrichment of elements more common in the catchment as opposed to local soils (Lintern *et al*., 2016a). In assessing the hydrologic history of a flood-influenced lake in the Slave River Delta, NWT, Brock *et al.* (2010) used a combination of physical, geochemical, and biological proxies to assess flood periods by comparing measured values to the characteristics of a flood deposit sample collected near the lake from a flood event in 2005. Bulk organic carbon ($C_{org}$) and nitrogen (N) elemental content and isotopic signatures ($\delta^{13}C_{org}$, $\delta^{15}N$), carbon-to-nitrogen ratios (C/N), as well as moisture and organic matter contents were measured. These were compared to diatom assemblages, including those indicative of high (*Navicula libonensis, Rhopalodia gibba*) and low (*Achnanthes lancelata var. frequentissima, Achnanthes minutissima, Navicula pupula, Nitzschia amphibia*) river influence. Most studies analyzing floodplain lakes have additionally validated their reconstructed flood history by comparing it to historical records captured by river

discharge gauges upstream of the floodplain lake (Wolfe *et al*., 2008a,b; Lintern *et al*., 2016a; Brock *et al*., 2010; Ota *et al*., 2017).

One main factor, especially when considering river-influenced systems, is the need to account for the influence of variations in grain size on sediment metals concentrations, as metals preferentially partition onto fine-grained sediments like silt and clays (Wiklund *et al*., 2014). One way to do this is by normalizing metal concentrations to a lithogenic element. Geochemical normalization is important for flood-influenced systems due to the fluctuations in energy of the river, which generates variations in grain-size of the sediment being carried (Wang *et al*., 2015). Floodplain lakes generally receive a primarily fine-grained fraction from the river, as the river water must travel a distance across the land and the energy of the river dissipates when flooding these systems (Wiklund *et al*., 2014). Common lithogenic elements used in geochemical normalization include aluminum, lithium, rubidium, scandium, titanium, and zirconium (Audry *et al*., 2004; Boës *et al*., 2011; Wiklund *et al*., 2014; Wang *et al*., 2015). The normalizing agent chosen usually reflects the local geology, to best represent the "natural" geogenic level of a metal of interest (Audry *et al*., 2004; Boës *et al*., 2011; Wiklund *et al*., 2014).

### *1.7 Metals of concern*

Accumulation of metals of concern in the environment from anthropogenic sources (mining, smelting, etc.) has historically been a key consideration for monitoring mining-impacted areas around the world (e.g., Davis *et al*., 1983; Renberg, 1987; Ek & Renberg, 2001; Salonen *et al*., 2006; Jernström *et al*., 2010). Heavy metals are classified as elements that possess a high density and atomic weight (Tchounwou *et al*., 2012). The toxicity of heavy metals depends on factors such as dose, method of exposure, and chemical species, as well as the characteristics (e.g., age, genetics, etc.) of specific individuals (Tchounwou *et al*., 2012). Due to

their high degree of toxicity, heavy metals such as arsenic, cadmium, chromium, lead, and mercury have been classified by the United States Environmental Protection Agency (US EPA) as some of the most dangerous for human health, as some bioaccumulate (e.g., mercury), are toxic even at extremely low concentrations (e.g., arsenic), and can be classified as carcinogenic (Tchounwou *et al*., 2012).

The US EPA lists priority pollutants in the Clean Water Act (2014) that includes many contaminants particularly toxic to aquatic organisms and humans, including many organic compounds, as well as heavy metals such as antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). Kelly *et al*. (2010) detected elevated levels of the above 13 elements in snowpack within 50 km of a central location within the AOSR. A similar spatial extent was determined by Kirk *et al*. (2014) for mercury in snowpack within the AOSR. Based on the spatial pattern of contaminant deposition, it has been suggested that longitudinal patterns of priority pollutant concentrations in the Athabasca River are a result of aerial deposition of metals from industry and subsequent transport during snowmelt and rain events (Kelly *et al*., 2009, 2010). A few studies have even linked a large portion of airborne pollution to airborne petroleum coke (petcoke) dust and unprocessed bitumen, by analyzing lake sediment cores and living moss and peat cores in the AOSR (Jautzy *et al*., 2015; Shotyk *et al*., 2016b; Zhang *et al*., 2016). Currently, oil sands companies store vast quantities of petcoke on site in large piles, making it susceptible to re-distribution by winds (Alberta Energy Regulator, 2014).

Bitumen in the AOSR is highly enriched in metals like vanadium (V), nickel (Ni), iron (Fe), and titanium (Ti), which make them good geochemical tracers of oil sands contamination (Hodgson, 1954; Jack *et al*., 1979; Jacobs & Filby, 1983). Vanadium is a common transition

metal, usually found at low concentrations in the environment, however it is elevated in carbonaceous sediments such as those found in the Alberta oil sands McMF (Schiffer & Liber, 2017). In fact, V concentrations in crude oil can range from 150-290 mg/kg. Following the bitumen upgrading process, V is removed and concentrated in petcoke, a by-product of this process, reaching concentrations of 1,000 mg/kg or higher (Schiffer & Liber, 2017). The most mobile and bioavailable form of the V ion is V(V), which forms oxyanions ($H_2VO_4^-$ and $HVO_4^{2-}$). These oxyanions mimic phosphate anions ($H_2PO_4^-$ and $HPO_4^{2-}$) in the environment due to their structural similarities and compete for uptake in plant and animal cells (Schiffer & Liber, 2017). This also makes V(V) the more toxic ionic form of V as it can inhibit phosphate-metabolising enzymes (Schiffer & Liber, 2017). Until as recently as May 2016, no federal water quality guidelines existed for V for the protection of aquatic life, despite being highly enriched in bitumen and bitumen by-products (Schiffer & Liber, 2017). Currently, the federal freshwater guideline is 0.12 mg V/L for freshwater, but no AOSR or province-specific guidelines exist for acute and chronic exposure for multiple species (ECCC, 2016). A more thorough investigation in V toxicity on four model organisms led by Schiffer & Liber (2017) found that the chronic HC5 toxicity level, which is the hazardous concentration to the most sensitive 5% of species tested, should be 0.05 mg V/L. Leaching of V from petroleum coke, which can exceed 1 mg/L, can have a detrimental effect on the more sensitive cladoceran and diatom species that are prevalent in northern Alberta freshwater systems, and can affect the survivability of regionally important fish species such as *Pimephales promelas* (Schiffer & Liber, 2017).

### *1.8 Study Objectives*

The lack of pre-industrial, baseline, sediment metals data for the Athabasca River in the AOSR impedes ability to detect and quantify the magnitude of river pollution, since the natural

range of variation is unknown. Studies of contaminants in the regional snowpack show clear evidence of atmospheric pollution at least within a 50 km radius of AR6, but we do not know if this leads to discernable pollution of the Athabasca River (Kelly *et al*., 2009, 2010; Kirk *et al*., 2014). Despite monitoring of river-bottom and suspended sediment metals in the Athabasca River by programs like RAMP and JOSM since 1997, these data have yet to be used successfully to evaluate origin or trends in river contaminant concentrations. To address these knowledge gaps, we require both pre- and post-industrial measurements of river contaminant concentrations. The upstream-downstream study design in Kelly *et al*. (2009, 2010) showed that contaminant concentrations are higher within and downstream of oil sands development compared to upstream locations, but without pre-industrial baseline information we cannot know for sure if this spatial pattern has long existed due to erosion of bitumen in shoreline exposures, or has arisen as a result of the release of contaminants by industry via air, surface water, and groundwater.

I hypothesize that this critically missing knowledge can be investigated through the establishment of metal baselines from sediment profiles of flood-influenced, river-proximal lakes in the AOSR using paleolimnological approaches. Paleolimnological work can extend and enhance current monitoring records to develop much needed baselines to adequately assess the extent of industrial pollution. Thus, the objectives of this study are 1) to establish pre-1967 Athabasca River baseline concentrations of bitumen-indicator metals V and Ni using lakes that have historically received river floodwaters in the AOSR; 2) to assess if temporal changes in deposition of these metals have occurred at the study lakes coincident with oil sands development; and 3) to use the V/Al and Ni/Al baselines to evaluate and interpret post-industrial RAMP/JOSM river-bottom and suspended sediment monitoring data for evidence of pollution.

Results from this study will lend insight into future applications of this model to place modern river sediment monitoring data in a long-term context.

## Chapter 2 – Methods

### *2.1 Site descriptions: Alberta oil sands region*

In the Athabasca River watershed, most of the bitumen is located within the McMurray Formation (McMF; Conly *et al*., 2002). The McMF is a natural and diffuse source of metals and PAHs to the river, with several outcrops visible along the banks of the Athabasca River and the Clearwater River, a major tributary upstream of the oil sands (Conly *et al*., 2002). Downstream of Fort McMurray, the steep banks along the Athabasca River gradually begin to open and flatten into a floodplain. Floodplain lakes were chosen based on their proximity to the river and by assessing the extent of the floodplain on Google Earth imagery. Five floodplain lakes were used in this study, two located upstream and three located downstream of major oil sands mining operations (Figure 1). Lake IDs were developed using the lakes' river distances (in km) upstream (Up) or downstream (Down) from AR6 along the Athabasca River, the central location within the AOSR used by Kelly *et al*. (2009, 2010) (Table 1).

**Table 1. Lake and sediment core information for Athabasca River floodplain lakes located upstream (Up 17, Up 10) and downstream (Down 1, Down 26, Down 58) of central oil sands operations (AR6) in Alberta, Canada. (*) denotes the core chosen for analyses.**

| Lake ID | Distance from central oil sands activities (river km) | Distance from lake to river (m) | Lake Depth (m) | Difference in elevation river to lake (m) | Core lengths (cm) |
|---|---|---|---|---|---|
| AR Up 17 | 17 | 140 | 1.4 | 4 | HC1: 43 *<br>HC2: 30 |
| AR Up 10 | 10 | 730 | 4.7 | 4 | HC1: 61<br>HC2: 62 * |
| AR Down 1 | 1 | 140 | 0.6 | 3 | HC1: 55<br>HC2: 54 * |
| AR Down 26 | 26 | 72 | N/A | 2 | HC1: 42 *<br>HC2: 39 |
| AR Down 58 | 58 | 87 | 1.3 | 1 | HC1: 38<br>HC2: 45 * |

N/A = shallower than the probe detection limit of 0.5 m

The floodplain lakes vary considerably in dimension (Table 1). Lake Up 17 is a relatively long (1,339.5 m), narrow (48.5 m), shallow (1.4 m) lake that appears to be part of a former river channel (Figure 2). Former river scars around Up 17 also show the pathway where river floodwaters likely enter the lake, washing in from the southern tip of the old meander. Lake Up 17 is beside some reservoirs adjacent to Highway 63, which appear to have been constructed in 2010 (Google Earth). The lake is situated ~140 m from the river's edge and is elevated ~4 m above the Athabasca River. In comparison, lake Up 10 is larger (approx. 1,810.4 m long x 138.8 m wide), deeper (4.7 m), and is located directly across the river from the Millennium Mine (Figure 2). Although upstream of AR6, the lake sits at the bottom of an incline, atop of which the Mildred Lake Mine is located. Lake Up 10 is farther inland, ~730 m from the river, with a ~4 m difference in elevation.

Lake Down 1 is a small (approx. 1,024.6 m long x 98.3 m wide), shallow lake (0.6 m) (Figure 2). This first downstream lake is located directly across from the Mildred Lake mine and ~600 m downstream of the outlet from the Steepbank River tributary, which cuts through exposures of bitumen from the McMF in a highly altered landscape. There is a ~3 m elevation difference between lake Down 1 and the Athabasca River. Lake Down 26 is a very small (approx. 78.4 m long x 24.2 m wide), shallow (<0.5 m) pond (Figure 2). This downstream lake is located very close to the river (~72 m), with a difference in elevation of ~2 m, indicating that this lake system is highly susceptible to receiving river floodwaters. Down 26 is ~9.93 km and ~5.93 km downstream of the Muskeg and MacKay River tributaries respectively, of which the Muskeg cuts through the industrialized Muskeg River Mine area. The farthest downstream lake, Down 58, is also a small (approx. 484 m long x 55.0 m wide), shallow (1.3 m) lake (Figure 2). With a distance from the river of ~87 m and a difference in elevation of ~1 m, this lake is highly flood-

influenced. Photographs of the study lakes show that the surface areas have shrunk, and water levels have declined in most of the lakes over time (Figure 2). Shrubs and macrophytes are abundant along the shoreline and extend across the bottom of most of the shallower lakes.

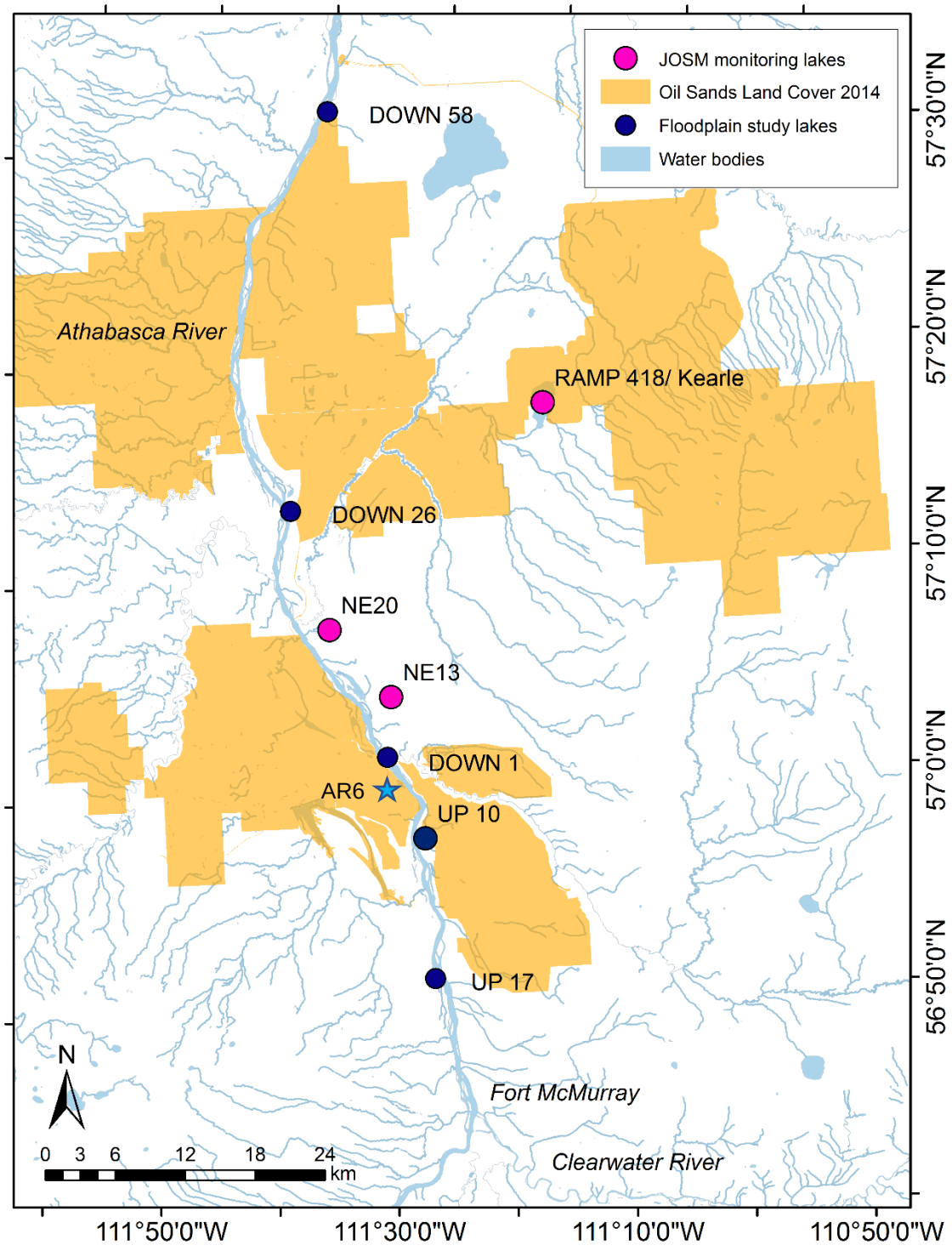


**Figure 1. Site map of the Athabasca oil sands region with floodplain study lakes Up 17, Up 10, Down 1, Down 26, and Down 58, as well as select JOSM monitoring lakes NE 13, NE20, and RAMP 418/Kearle. The oil sands land cover as of 2014 (source: RAMP) is outlined in orange, and waterbodies are blue. The blue star denotes location of AR6 (Kelly *et al.*, 2009, 2010). Map courtesy of Casey Remmer, 2018.**


**Figure 2. Photographs of the floodplain study lakes taken in October 2016 (Up 17, Down 1, Down 26, Down 58) and in July 2017 (Up 10). The pink diamond indicates the approximate coring location at each of the floodplain lakes.**

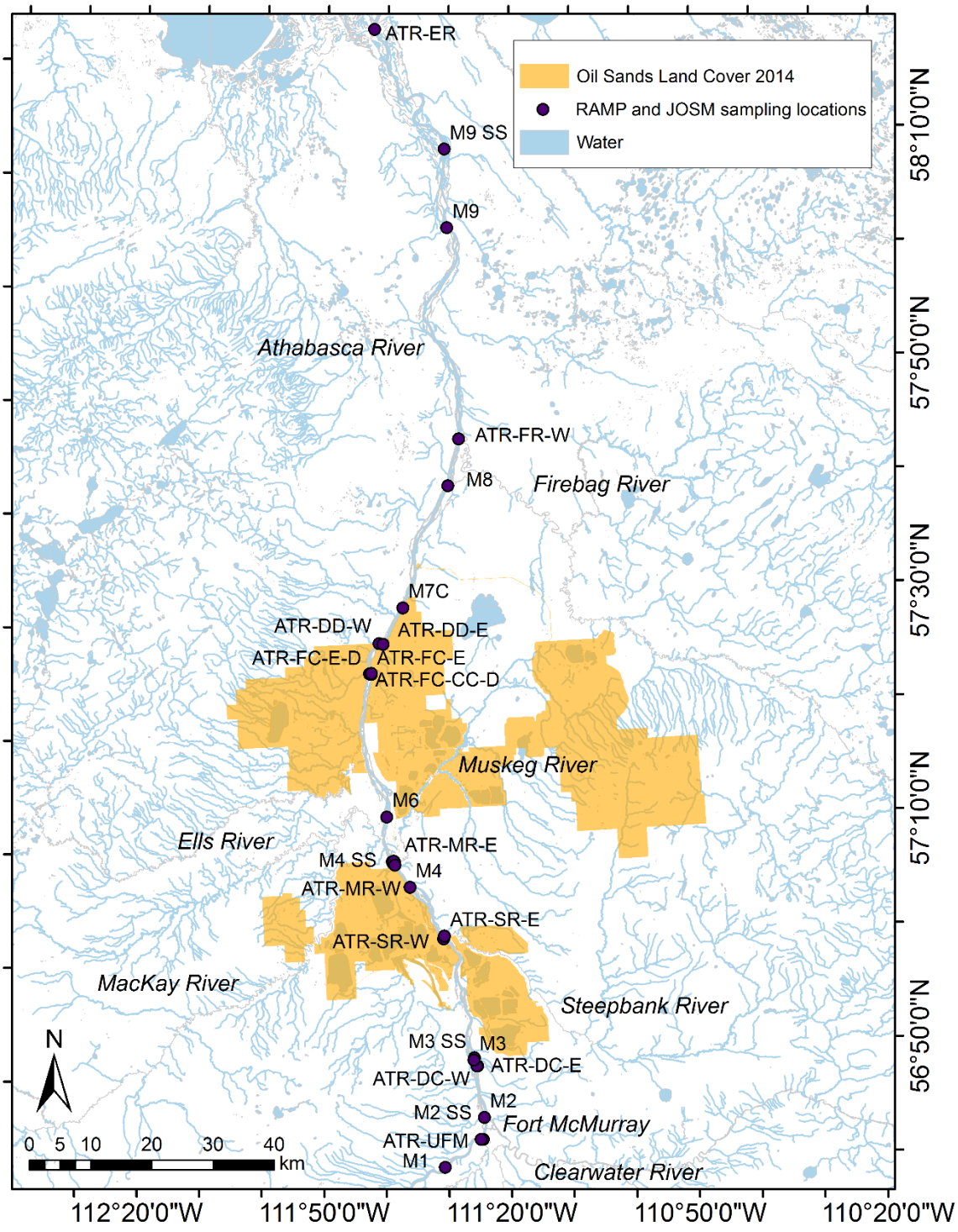


**Figure 3. Site map of the RAMP and JOSM sediment monitoring locations in the Athabasca oil sands region. RAMP sites begin with the signifier ATR (for Athabasca River) and the JOSM sites begin with the signifier M (for Mainstem) (see Table A3). JOSM suspended sediment sites are indicated by SS after the site name. Site M0 is not shown as it is > 50 km kilometers upstream of Fort McMurray. The oil sands land cover as of 2014 is outlined in orange (source: RAMP), and waterbodies are blue. Map courtesy of Casey Remmer, 2018.**

## *2.2 Field methods*

### *2.2.1 Sediment core collection*

Sediment cores were collected from lakes Up 17, Down 1, Down 26, and Down 58 in October 2016, and from lake Up 10 in July 2017. Two sediment cores were collected from each lake using a hammer-driven gravity corer (Glew, 2002). Sediment coring was performed from a helicopter on floats, and the cores were taken from a central deep-water location within each lake. Cores were transported to a field base in Fort McMurray where they were sectioned within 24 hours of collection into 1.0-cm intervals using a vertical extruder (Glew, 1988). Samples were stored in Whirl-Pak® bags, kept in the dark, and refrigerated at 2-4°C.

Limnological measurements were taken to assess the depth, temperature (ºC), pH, dissolved oxygen concentration (%), turbidity (FNU), and specific conductivity (µS/cm) of water at each lake using a YSI probe (YSI ProDSS) (Table A3, Appendix A). The longitude and latitude of the sampling locations were recorded using a GPS device (Table A1, Appendix A).

### *2.2.2 RAMP & JOSM Athabasca River sediment collection*

Metals concentrations data collected by the RAMP and JOSM monitoring programs were used in this study to evaluate post-development river bottom and suspended sediment for evidence of pollution above pre-1967 V/Al and Ni/Al baselines generated from floodplain lake sediment cores. From 1997-2002, river-bottom sediment was collected by RAMP monitoring agencies using 2-4 grabs from a 6” x 6” Ekman dredge and homogenized in a pan before sampling to ensure a representative sample (Hatfield Consultants, 2009). Sediment was collected from various locations along the Athabasca River, usually from depositional areas near the

mouth of major tributaries to the river in conjunction with water quality sampling locations on the east and west banks of the river (Figure 3) (Hatfield Consultants, 2009).

JOSM river-bottom samples were collected as a grab sample from near-shore gravel and sand habitats (Wrona & di Cenzo, 2011). River-bottom sediment for RAMP and JOSM were both collected in autumn in conjunction with benthic invertebrate sampling, as that is considered the period of highest macroinvertebrate abundance and diversity. Bulk suspended sediment samples were collected for JOSM with a passive sampler via continuous flow centrifugation (Wrona & di Cenzo, 2011). River-bottom surficial samples provide information on sediment conditions at the bed-water interface, which are of relevance to benthic organisms and fish during early life stages (Wrona & di Cenzo, 2011). Information on suspended sediment is essential in understanding river contaminant loadings, as many contaminants, such as metals, partition strongly to the fine fraction of sediments, with resulting effects on the health of aquatic and benthic species in the river (Wrona & di Cenzo, 2011). These river-bottom and suspended-sediment samples were evaluated for metals enrichment using the V/Al and Ni/Al baselines developed in this study.

Sediment metals concentrations data from river-bottom samples (RAMP) and river-suspended sediment samples (JOSM) were downloaded from their respective online databases ("Sediment Quality", 2015; "Sediment Quality Mainstem", 2016). River-bottom sediment metals concentrations data collected for JOSM were received from Dr. Joseph Culp (Environment & Climate Change Canada / Wilfrid Laurier University) who is affiliated with the JOSM benthic invertebrate sampling program in the AOSR. Available RAMP data span from 1997 – 2002, and JOSM data from 2012 – 2014. Additional information on the RAMP and JOSM sampling programs, including the study design, sample locations, and lab processing procedures can be

found in the RAMP Technical Design and Rationale report (Hatfield Consultants, 2009) and the Phase 1 Lower Athabasca Water Quality Monitoring Plan (Wrona & di Cenzo, 2011), or the annual RAMP and JOSM monitoring reports (e.g. "Joint Canada/Alberta", 2015; Hatfield Consultants, 2016).

### *2.2.3 Additional Athabasca River sediment collection*

To supplement the river monitoring data collected by RAMP and JOSM with additional data from recent years, river sediment samples were collected during lake coring trips in 2016 and 2017. Samples of recently deposited surficial river sediment were collected from exposed sandbars and shorelines of the Athabasca River at two locations downstream of oil sands activities and one location upstream (October 2016 and July 2017). Following the spring flood in 2017, a sediment sample was also collected from an inland deposit of flood-transported sediment at a location upstream of AR6, in a known area of flooding based on flood maps generated by Alberta Environment & Parks (2017). This sample was collected to evaluate the sediment characteristics of Athabasca River "flood sediment," as it could be indicative of the type of sediment deposited in AOSR floodplain lakes.

### *2.2.4 JOSM sediment core collection*

Sediment core metals concentrations data collected from small, headwater AOSR lakes NE13, NE20, and RAMP 418/Kearle as a part of the JOSM monitoring program, and published in Kurek *et al*. (2013), Summers *et al*. (2016), and Cooke *et al*. (2017), were used in conjunction with data from this study's floodplain lakes to construct the pre-industrial baselines (Table A1). The floodplain lake data captures metals concentrations at the high end of the range (> 10,000 ug/g Al), but does not overlap with lower concentrations in coarser surficial river bottom

sediments of the RAMP and JOSM programs. The AOSR headwater lake sediment data were explored and found to be useful in extending the range of metals concentrations at the low end (< 10,000 ug/g Al) since the lakes appear to share a common geological source of V, Ni, and Al (see Chapter 3).

The headwater lake sediment cores used in the Cooke *et al*. (2017) AOSR paleolimnology metals study were collected as part of the JOSM program between 2011-2014. Cores were sectioned at 0.5-cm intervals for the first 20 cm, below which they were sectioned at 2-cm intervals. Metals were analyzed at the National Laboratory for Environmental Testing (Burlington, Canada) using the aqua-regia method of sediment-metal extraction (Cooke *et al*., 2017). Further information on sediment metals analysis can be found in Cooke *et al*. (2017). Additionally, detailed information on JOSM sediment core collection and dating can be found in Summers *et al*. (2016) and Kurek *et al*. (2013).

## *2.3 Sediment core analyses (Physical and geochemical proxies)*

### *2.3.1 Loss-on-ignition*

Loss-on-ignition (LOI) analysis is a method used to sequentially measure the content of water, organic matter, carbonate ($CaCO_3$), and mineral matter in lake sediments (Heiri *et al*., 2001). LOI analyses were performed on every 1.0-cm section of sediment from each core from the floodplain lakes using ~0.5 g of wet sediment. Sediment samples were first placed in pre-weighed porcelain crucibles and heated in an oven at 90°C for 24 hours, after which they were removed and placed in a desiccator for no less than 2 hours, and then weighed to determine the water content (% wet weight). Samples were then placed in a furnace at 550°C for 2 hours, then removed and placed in a desiccator for 24 hours, following which they were weighed to analyze for the organic matter content in the sediment (% dry weight). Lastly, the samples were once

again placed in the furnace, this time at 950°C for 2 hours, after which they were placed in a desiccator for 24 hours, and then weighed to determine the amount of carbonate (% dry weight) present in the sample. Mineral matter content (% dry weight) was calculated by dividing the post-950°C sediment weight by the post-90°C sediment weight. Following LOI analysis on both cores from each lake, one core was selected for further analyses (Table 1).

### *2.3.2 Organic carbon and nitrogen elemental and isotope analysis*

Organic carbon and nitrogen elemental content and stable isotope ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ can aid in differentiating lake-derived from river-derived sediment (Meyers & Teranes, 2002). Higher C/N ratios are generally associated with flood events, as they bring in more terrestrial-derived organic matter (vascular plants), whereas lower C/N ratios are associated with lake-derived organic matter (algae and aquatic plants) (Meyers & Teranes, 2002).

The carbon isotope composition of sediment is a valuable proxy for determining organic matter sources, as well as changes in lake productivity and nutrient availability over time (Meyers & Teranes, 2002). The ratio of $^{13}C/^{12}C$ can help determine lake productivity, as algae ($C_3$ plants) preferentially take up $^{12}C$, which reduces the amount of $^{12}C$ in the dissolved inorganic carbon (DIC) and provides a signature in algal-derived organic matter that is around 20‰ lighter than the original DIC (Meyers & Teranes, 2002). Algal organic matter can have a very similar carbon isotopic signature to other $C_3$ plants in the surrounding watershed, but has a distinct isotopic signature compared to $C_4$ land or water plants (Meyers & Teranes, 2002). Nitrogen isotope composition of sediment is another proxy for past changes in lake productivity, as well as to differentiate organic matter sources (Meyers & Teranes, 2002). The $\delta^{15}N$ value of dissolved $NO_3^-$, the most readily available form of dissolved inorganic nitrogen for plants and algae, is

more enriched relative to the dissolved inorganic nitrogen that most land plants utilize (Meyers & Teranes, 2002).

Carbon and nitrogen elemental and stable isotope compositions were measured on one core from each floodplain lake at each 1.0-cm interval. A representative sediment sample (~5 g) was placed into 50 mL test tubes. Samples were then acidified with ~45 mL of 10% hydrochloric acid (HCl) for 24 hours to remove carbonate carbon from the sample, with the first two hours spent in a 60 ºC water bath to accelerate the reaction. After 24 hours, once the sediment had settled, the acid was aspirated off from above the sediment and the samples were rinsed with deionized (DI) water. Samples were repeatedly allowed to settle, aspirated, and rinsed until the pH became equivalent to that of the DI water being used. The samples were then freeze dried and sieved at 500 µm to obtain the fine fraction of the sediment and eliminate any coarse debris. Subsamples of the fine fraction (~1-20 mg) were analysed at the University of Waterloo Environmental Isotope Laboratory (UW-EIL) using an elemental analyzer interfaced with a continuous-flow isotope-ratio mass spectrometer (CF-IRMS). This device produces $CO_2$ through an on-line connection, which it delivers to the detector for analysis (Teffera *et al*., 1996).

### *2.3.3 Sediment metals concentrations*

Metals analyses were completed on every 1.0-cm sub-section of a sediment core from each floodplain lake. For each sample, ~1.0 g of freeze-dried sediment was sent to ALS Canada Ltd. (Waterloo, Ontario), a Standards Council of Canada (SCC) accredited laboratory, for analysis of a suite of metals. Sediments were acid digested using $HNO_3$ and HCl prior to sample analysis by inductively coupled plasma mass spectrometry (ICP-MS) following method 200.2/6020A outlined by the United States Environmental Protection Agency (US EPA, 1998). This method is only a partial digest, to dissolve all environmentally available metals, but not

those that are bound within the crystal structure of the sediment, as is recommended by the Canadian Interim Sediment Quality Guidelines (CCME, 2001). This is the same method of analysis used in determining sediment-metals concentrations in the AOSR headwater lakes analyzed by Cooke *et al*. (2017). Quality assurance and control involved the analysis of blank and duplicate samples every 20 cm, and for duplicate measurements of a sample, the average value was used for further analyses. A suite of 34 metals were analyzed by ALS, however metals targeted for interpretation were V, Ni, and Al. In Alberta oil sands bitumen and petroleum coke, V and Ni are enriched relative to other geological sources of river sediment and are therefore considered oil sands indicator metals (Gosselin *et al*., 2010; Wiklund *et al*., 2014). These elements have also been found to be more elevated in snowpack near oil sands operations (Kelly *et al*., 2010; Kirk *et al*. 2014). Additionally, Ni is considered a priority pollutant by the EPA's Clean Water Act (US EPA, 2014).

To assess for evidence of metal enrichment in the sediment cores, a geochemical normalization procedure was used to account for the influence of variation in grain size in the sediment (Loring, 1991). During the time captured by a lake sediment core, floods can introduce variation in the grain size of sediment deposited (Kersten & Smedes, 2002; Wiklund *et al*., 2014). Metals have low solubility in water and therefore adsorb to (or partition onto) particle surfaces. Since smaller grain sizes have a higher surface to mass ratio, they also possess a higher concentration of metals. Due to these processes, normalization is needed to compare among samples within a lake sediment core and among sites. Metals were normalized to aluminum (Al) concentrations, a common lithogenic element used in sediment normalization (Cooke *et al*., 2017; Wiklund *et al*., 2018). Previous studies in the AOSR have used geochemical normalizers Al (Cooke *et al*., 2017), Li (Wiklund *et al*., 2014), and Th (Shotyk *et al*., 2014, 2016a, 2016b).

The use of Al as a lithogenic normalizer within the zone of aerial deposition in the AOSR does present a challenge, as it too becomes enriched in the environment due to oil sands activities (Kelly *et al*., 2010; Kirk *et al*., 2014; Blais & Donahue, 2015; Cooke *et al*., 2017). Due to this, a normalizing agent such as Li or Th, which may be less mobilized by dust would normally be a better alternative. In this study, Al was primarily chosen to explore the RAMP dataset, which did not analyze a complete suite of metals, and therefore lacked an alternative normalizer. Increased Al in post-industrial samples can result in a reduced ability to detect contamination by V and Ni and could lead to errors of omission when concluding there is no contamination when, in fact, V and Ni are elevated. Therefore these consequences were considered when analyzing post-industrial V:Al and Ni:Al concentrations.

### *2.3.4 Sediment core chronologies*

The sediment age-depth relationship for lakes Up 17, Up 10, Down 1, and Down 26 were developed for one core from each lake using gamma ray spectrometric determination of $^{210}$Pb and $^{137}$Cs activity. For each sample analyzed, ~3-4 g of freeze-dried sediment was tightly packed into pre-weighed, plastic SARSTEDT polypropylene tubes to a standard height of 3.5 cm. A thin silicone disc (Supelco®) was placed on top of the sediment, followed by 2 Ton Clear Epoxy resin (Devcon®) to a height of 1 cm. Samples were then left for a minimum of 14 days to allow $^{222}$Rn and its decay products in the sample to equilibrate with $^{226}$Ra prior to analysis of $^{210}$Pb, $^{214}$Bi, and $^{214}$Pb activity. Samples were analyzed for radioisotope activity using the WATER lab's Ortec co-axial HPGe Digital Gamma Ray Spectrometer (Ortec GWL-120-15). $^{210}$Pb activities measured were decay-corrected to the coring date for the core taken at each lake, as well as corrected for density (total sediment and bag weights for each sample) (Schelske *et al*., 1994). Chronologies were developed using a Constant Rate of Supply (CRS) model, where the

activities of $^{214}$Pb and $^{214}$Bi were used to estimate the level of supported $^{210}$Pb activity in the sediment (Robbins, 1978; Appleby, 2001). Standard methods were used to determine the depth of the core where total $^{210}$Pb activity is equal to the supported activity (Binford, 1990). $^{137}$Cs activity was also measured throughout the cores to validate the $^{210}$Pb CRS chronology, or in the case of limited $^{210}$Pb data, to develop the chronology (i.e., at Down 26). For lake Down 58, a chronology was not developed but the depth of maximum measurable $^{137}$Cs was used to estimate the age at that depth. This was determined by relating the peak $^{137}$Cs activity to be the maximum fallout of nuclear testing in the northern hemisphere, which occurred around 1963 (Appleby, 2001).

### *2.4 Data analysis (numerical & statistical)*

To interpret past variations in V and Ni concentrations in the sediment cores, pre-industrial baselines were developed. The pre-industrial period was set as the time prior to 1967, when major oil sands operations began in the AOSR (Gosselin *et al*., 2010). AICc model selection was used to test whether a linear or log-linear relationship would provide a significantly better fit for the data, due to potentially different binding affinities of Al, V, and Ni for different particle sizes of sediment. AICc values were calculated using the AICcmodavg (Mazerolle, 2016) and MASS packages (Ripley, 2018) in 'R' software, version 3.5.1. Pre-industrial baselines were established using linear relations between pre-1967 metal concentrations and the normalizing metal (Al). Data used in baseline development were from floodplain lakes Up 17, Up 10, Down 1, and Down 26, and headwater lakes NE13, NE20, and RAMP 418/Kearle lake (see Chapter 3). 95% prediction intervals (P.I.) were determined and plotted about the linear regressions to define the natural range of variation of individual sediment samples. Post-1967 floodplain lake sediment and RAMP and JOSM river-monitoring metals concentrations data

were evaluated relative to this baseline. If greater than 2.5% of the data points deposited after 1967 plot above the 95% P.I., this was deemed as indicative of pollution (Loring, 1991; Kirsten & Smedes, 2002; Wiklund *et al*., 2014; MacDonald *et al*., 2016). Error bars using the mean precision calculated for replicate sediment samples in PAD lakes, and processed by ALS Canada (Edmonton) for Wiklund *et al*. (2014), were applied to the post-industrial data to evaluate the range of variability that might be expected.

Enrichment factors (EF) were used to assess the magnitude of regional anthropogenic pollution of metals in sediments deposited after 1967 (in the study lakes and RAMP/JOSM river-bottom surficial sediments and river suspended sediments), following methods widely employed by other studies in the AOSR (Wiklund *et al*., 2012; Kurek *et al*., 2013; Cooke *et al*., 2017) and elsewhere (e.g., Müller, 1969; Audry *et al*., 2004; Balogh *et al*., 2009; Boës *et al*., 2011). The EF is generally expressed as a ratio of the measured normalized concentration of a metal at a specific sediment depth ($X_i$) to the concentration that is expected based on its relationship with the normalizing metal, in this case aluminum ($Al_i$), prior to industrial activity (Equation 1). This relationship was evaluated using the pre-industrial V/Al and Ni/Al baselines developed in the previous section. Values of EF above 1 identify enrichment of the metal concentration above values expected from the pre-industrial relationship.

$$EF = (X_i/Al_i)/(X_{pre\text{-}1967}/Al_{pre\text{-}1967}) \quad \text{(Equation 1)}$$

For the EFs, an upper 95% EF P.I. was calculated for each metal of concern using the average of three points from the V/Al and Ni/Al baseline upper P.I. and following Equation 1. Statistical analyses on the trends observed in the enrichment factors over time were conducted using ‘R’ software, version 3.5.1.

The nonparametric Mann-Kendall trend test was used to assess the strength and direction of association between metals concentrations and time in floodplain lakes Up 17, Up 10, Down 1, and Down 26 (Ho: no trend; Ha: monotonic trend (upward or downward)), with the 'Kendall' package (v.2.2) (McLeod, 2011). Time series of the lakes' temporal enrichment factors were configured using the 'zoo' package (v.1.8-3) (Zeileis *et al*., 2018). The Mann-Kendall trend test assessed if there were statistically significant increasing or decreasing monotonic trends of metal enrichment in the time series defined by a core from these lakes. To evaluate the occurrence of directional trends in the metals concentrations over time, breakpoint linear regressions were used. The 'segmented' package (v.0.5-3.0) was used to determine if and when breakpoints occur in normalized V and Ni concentrations (Muggeo, 2017). Two breakpoints were assumed for the linear relationships and a three-segmented model was used. This assumption was based on observations of the EF graphs for lakes with significant increasing trends over time, where an increase was observed (breakpoint 1) followed by a plateau or decrease (breakpoint 2).

Excess flux (also known as anthropogenic flux, $\Delta F$) can be used to detect the extent to which the supply rate of the metal of interest to the floodplain lake has become elevated above the pre-industrial baseline. Therefore, excess flux measurements were only calculated for lakes where there was significant "excess" observed above the V/Al and Ni/Al baselines. To calculate the flux of anthropogenically-enriched metals to the lake, the calculated enrichment factor ($X_{EF}$) is multiplied by the dry mass sedimentation rate (g $cm^{-2}$ $yr^{-1}$) and the raw concentration of the metal measured at a specific interval depth ($X_i$). Excess flux measurements were also corrected for sediment focusing, to allow for the quantification of the atmospheric deposition of anthropogenically-derived metals. The 'adjusted excess flux' ($\Delta F_{adj}$) is developed using the sediment focus factor (FF), following Muir *et al*. (2009). FF is calculated for all $^{210}Pb$ dated

cores by dividing the measured $^{210}$Pb flux to the $^{210}$Pb flux predicted for the core based on the latitude of the lake site and therefore varies for each core (Table E6).

$$\Delta F = ((X_{EF}-1)/(X_{EF}))*(\text{dry mass sedimentation rate}*10)*(X_i) \quad \text{(Equation 2)}$$

$$\Delta F_{adj} = \Delta F / FF \quad \text{(Equation 3)}$$

## Chapter 3 - Results and Interpretation

### *3.1 Sediment core chronologies & paleohydrology*

The $^{210}$Pb activities in the sediment cores from lakes Up 17, Up 10, Down 1, and Down 26 decline downcore, but with marked variability (Figure 4). This is typical of flood-influenced lakes, where episodic influxes of river-supplied sediment with low $^{210}$Pb activity depress activities of atmospheric deposition of $^{210}$Pb to the lake bottom. At lake Up 17, total $^{210}$Pb activity is relatively constant in the upper 4 cm, rises to a peak at 10 cm (137.68 Bq/kg) and declines markedly between 10 and 18 cm depth, after which values continue to decline more gradually to background (or the supported $^{210}$Pb value = 33.37 Bq/kg ± 4.16, 1 SD) at 40-41 cm (34.86 Bq/kg ± 5.70, 1 SD) (Figure 4). The sedimentation rate is relatively rapid (avg. = 0.2356 g $cm^{-2}$ $year^{-1}$). Periods of lower radioisotope activity and high mineral matter content in the sediment core from lake Up 17 correspond to periods of rapid sedimentation, and likely represent periods of strong flood influence (Figure 5). The highest peak in sedimentation dates to 1944 ± 20 years, which corresponds to the highest flood recorded in Fort McMurray in 1936 (Winhold & Bothe, 1993). Other spikes in sedimentation rate date to 1976 ± 9 years, 2013 ± 0.9 years, and 2016 ± 0.3 years, and likely correspond to the Fort McMurray floods in 1977, 2013, and 2016, respectively (Winhold & Bothe, 1993; Sturgess, 2014; Giovannetti, 2016) (Figure 4, Up 17 sed. rate panel). Radiocesium activity is constant for the top 22 cm (1.2-8.2 Bq/kg) and rises to a distinct peak at 28-29 cm depth (39.62 Bq/kg ± 1.09, 1 SD), which corresponds to a $^{210}$Pb-based CRS date of 1963 (± 13.7 years, 2 SD). The CRS model determined the basal date of the core to be ~1897 CE (± 25 years, 2 SD).

Total $^{210}$Pb activity in the core from lake Up 10 decreased rapidly with depth below the surface of the core (278.81 Bq/kg) and reaches background (55.75 Bq/kg ± 12.50, 1 SD) at 12-13 cm (46.44 Bq/kg ± 5.87, 1 SD), with a marked decline (trough) between 2 and 3 cm depth (Figure 4). The sedimentation rate is lower and less variable (0.0214-0.0507 g cm$^{-2}$ year$^{-1}$) at Up 10 than at Up 17, but a discernible peak in sedimentation in the uppermost 3 cm corresponds to the trough in activity observed in the $^{210}$Pb profile (Figure 4). Radiocesium activity remains constant for the uppermost 6 cm before rising to peak at 9-10 cm (31.21 Bq/kg ± 1.06, 1 SD), which corresponds to the $^{210}$Pb-based CRS date of 1963 (± 14.8 years, 2 SD). Linear extrapolation to the base of the core (62 cm) using the CRS model generates a basal date of ~955 CE (± 135 years, 2 SD).

At lake Down 1, total $^{210}$Pb activity declines from 128.42 Bq/kg at the surface of the core and reaches background (31.52 Bq/kg ± 3.48, 1 SD) at 27-28 cm depth. Despite some variability at the bottom of the core, values below 27 cm remain within 1 SD of the supported values, as estimated from $^{226}$Ra activities, suggesting that background levels are reached by 27-28 cm depth (38.61 Bq/kg ± 6.80, 1 SD). This variability in activity near the bottom of the core corresponds to variability in sedimentation rate in the early 1900s when the lake was more flood-influenced (Figure 4), as indicated by relatively high mineral matter content (~69-87%) (Figure 5). A distinct peak in sedimentation rate is observed at an estimated age of 1931 ± 36.3 years (2 SD), which likely corresponds to the 1936 Fort McMurray flood (Winhold & Bothe, 1993). Activity of $^{137}$Cs is variable at the top of the core, but forms a discernible peak (30.63 Bq/kg ± 0.8956, 1 SD) at 20-21 cm depth, before declining gradually after 24 cm. Assuming this cesium peak corresponds to 1963, the year of peak above-ground nuclear bomb testing, it corresponds within the range of error of the date determined by $^{210}$Pb dating and the CRS model (1973 ± 11 years, 2

SD). A basal date of ~1807 CE (± 47 years, 2 SD) was determined for the core using the CRS dating model with extrapolation.

In the core from lake Down 26, total $^{210}$Pb activity declines slightly from the top of the core (157 Bg/kg) to a narrow range of values (43.6-25.5 Bq/kg) from 8 cm to the bottom of the core. In highly flood-influenced systems, re-worked sediment from the river banks dilutes the $^{210}$Pb activity, masking the atmospheric $^{210}$Pb signal and creating the nearly constant measured $^{210}$Pb. The high sedimentation rate (0.1666 g cm$^{-2}$ year$^{-1}$) determined for the core and the high mineral matter content (76-88%) throughout the core support this assertion of a strongly flood-influenced lake (Figure 5). A distinct $^{137}$Cs peak (5.44 Bq/kg) was measured at 16-17 cm (Figure 4). Average $^{137}$Cs values measured above and below this peak are lower, spanning a range of 0.46-4.57 Bq/kg. The $^{137}$Cs activities are considerably lower at this lake than the previous lakes, which is consistent with the more rapid deposition of river-supplied sediment to this system, and makes dating by $^{210}$Pb activity impossible. This peak in measured $^{137}$Cs activity was used to estimate the 1963 stratigraphic horizon (± 5.9 years, 1 SD). The subsequent chronology was developed using the average calculated sedimentation rate for the lake (0.1666 g cm$^{-2}$ year$^{-1}$) and cumulative dry mass at 1963 (416.60 g), and extrapolated down-core to a basal date of ~1817 (± 21.5 years, 1 SD).

Similarly, Down 58, a strongly flood-influenced lake system with very high mineral matter content (~83-91%) was not able to be dated using $^{210}$Pb techniques as the $^{210}$Pb is generally at or slightly above background activity (39.3-48.1 Bq/kg) signifying high sedimentation rate diluting the atmospheric $^{210}$Pb fallout. Measurable $^{137}$Cs activity was detected in the core to the basal depth of 45 cm (2.33 Bq/kg), with the highest value measured at 34.5 cm (4.07 Bq/kg) (Table D5, Appendix D). We can thus infer that at a depth of 34.5 cm in lake Down

58, the sediment is likely no older than 1963, but may be as young as 1952, the start of above ground nuclear testing which led to anthropogenically-induced atmospheric Cs fallout. This assumes no downward mobility in $^{137}Cs$ - a valid assumption, since Cs is less mobile in organic-poor sediments.

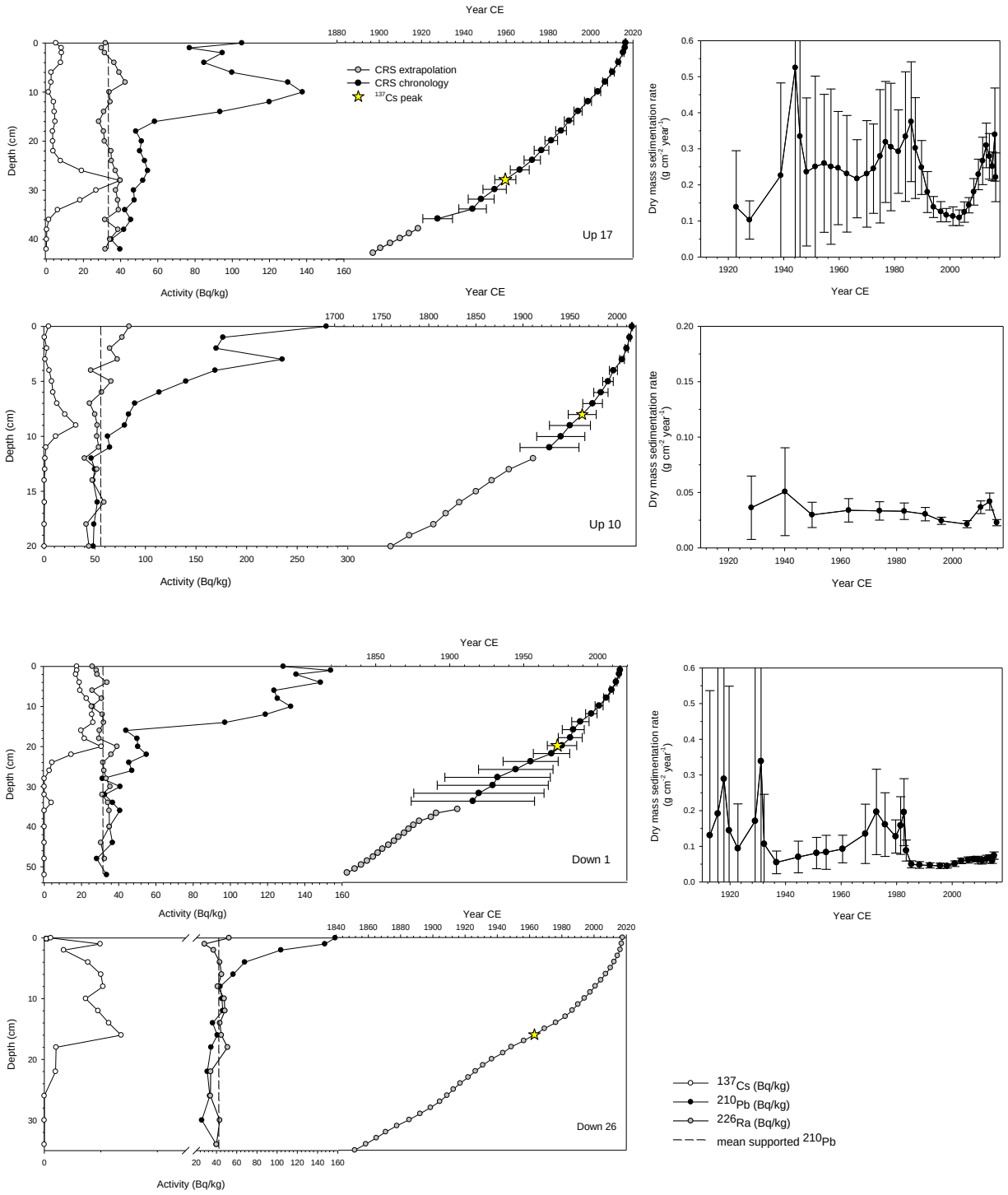


**Figure 4. Activities profiles of radioisotopes $^{210}$Pb (black circles), $^{137}$Cs (open circles), and $^{226}$Ra (dark grey circles) in Bq/kg for sediment cores from lakes Up 17, Up 10, Down 1, and Down 26. The age-depth relationship is also plotted for each graph, with extrapolation using the CRS model (light grey circles) and the $^{137}$Cs peak indicated by a yellow star. Sedimentation rate is presented in the right panels. Error bars represent 1 standard deviation. Note: low $^{210}$Pb values at Down 26 prevented the calculation of varying sedimentation rate (0.1666 g cm$^{-2}$ year$^{-1}$).**

### *3.2 Temporal trends in sediment composition and inferred paleohydrology*

High sediment mineral matter content is interpreted in these floodplain lakes as indicative of strong influence of river flooding that supplies rapid influx of inorganic suspended river sediment. Conversely, intervals of relatively high organic matter content occur when river flood influence is less and in-lake productivity increases. We observed that most of the sediment cores possess high mineral matter content (> 75%) throughout their profiles, identifying that these lakes have generally been strongly flood-influenced, as was the aim of the study design. The exception is lake Down 1, where organic matter content is more variable with core depth (Figure 5). Here, an interval of relatively high organic matter content (24-42%) during ~1840-1912 is followed by an interval of lower organic matter content (9-27%) during ~1915-1983. After ~1985, organic matter content increased to 24-43%, with coincident increase in organic C and N content (18-22% and 1.3-1.9% respectively; Figure 5, see also Figure B3).

Uppermost sediments in lakes Up 17, Up 10, and Down 26 also show marked decline of mineral matter content (from > 75% to ~40-70%) after ~1990 (Up 10) and ~2014 (Up 17, Down 26; Figure 5). An interval of reduced mineral matter content was also observed in lake Up 17 between ~1995 and 2008. These declines in mineral matter content coincide with the rise of organic matter (from < 20% to ~20-47%), and organic C (7-25%) and N content (0.7-2.7%) (Figure 5, see also Figures B1, B2, and B4). The mineral matter content in the core from lake Down 58 is the most consistent, ranging from 82-91% over the length of the core (Figure 5). This suggests that this lake has consistently had the strongest flood influence among the study lakes.

Comparisons of fluctuations in organic matter, mineral matter, and organic C and N content profiles in these lake systems to chronological proxies (lake sedimentation rates and

radioisotope activity-depth relationships) were used to identify periods of stronger and weaker flood-influence. Periods of stronger flood influence generally have higher mineral matter content, depressed $^{210}$Pb activity, and increases in sedimentation rate (e.g., Up 17). During periods of weaker flood influence, organic matter and organic C and N content are higher, indicating more in-lake productivity that is less frequently diluted with an influx of inorganic river sediment. Observational notes taken when sectioning the cores also offer insight into changes in mineral matter and organic matter content associated with flood-influence. Sediment deposited during intervals of higher mineral matter content (periods of higher flood influence) consisted of grey, dense, clay- and silt-rich sediment, whereas intervals of lower mineral matter content (periods of lower flood influence) had a higher content of black, organic-rich sediment, occasionally with pieces of partially-decomposed reeds and other macrophytes.

### *3.3 Temporal variations in metals concentrations*

Stratigraphic profiles demonstrate that sediment metal concentrations of Al, V, and Ni in all lakes are strongly and positively correlated in all five floodplain lakes and vary in concert with temporal variations in the inferred changes in paleohydrology. In general, stratigraphic intervals of stronger flood-influence (higher mineral matter content) correspond with relatively higher sediment concentrations of Al, V, and Ni concentrations, and intervals of weaker flood-influence (lower mineral matter content) correspond with lower concentrations of these metals (Figure 6). However, a few exceptions to the trend of stronger flood-influence corresponding with higher sediment metals concentrations are observed at lakes Up 10 and Down 1. At lake Up 10, a peak is observed in V concentration just before the lake begins to become less flood-influenced in ~1973. Here, V concentration appears to increase to a larger extent than Al concentration (Figure 6). Similarly, at lake Down 1, during the less flood-influenced period that

began in ~1983, a peak in V and Ni concentrations is observed when Al concentrations decline (Figure 6).

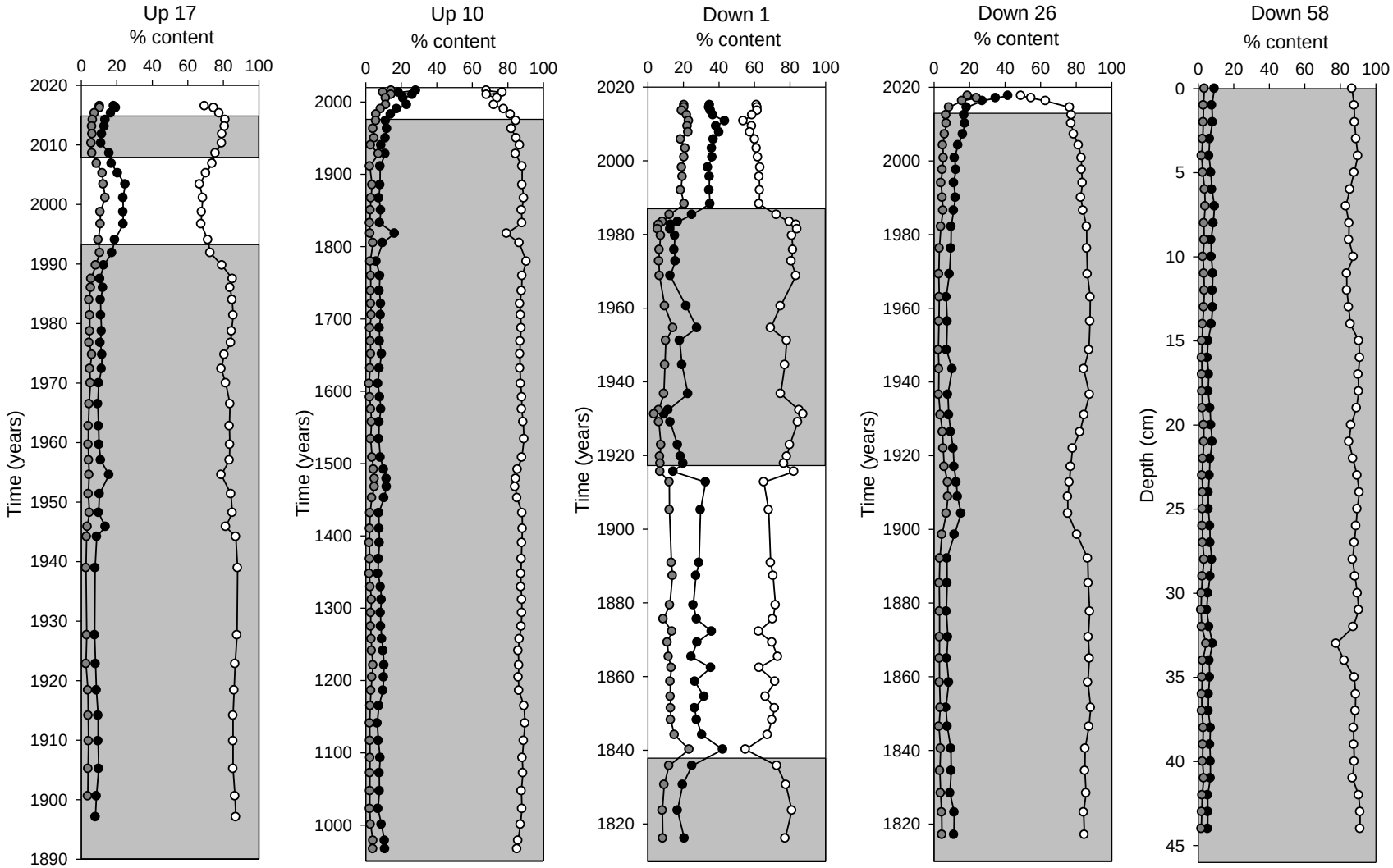


**Figure 5. Stratigraphic profiles of organic matter (black circles), mineral matter (white circles), and organic carbon (dark grey circles) content in sediment cores from lakes Up 17, Up 10, Down 1, Down 26, and Down 58. Lakes are arranged in sequence from upstream to downstream. Shaded areas represent strongly flood-influenced sediment intervals.**

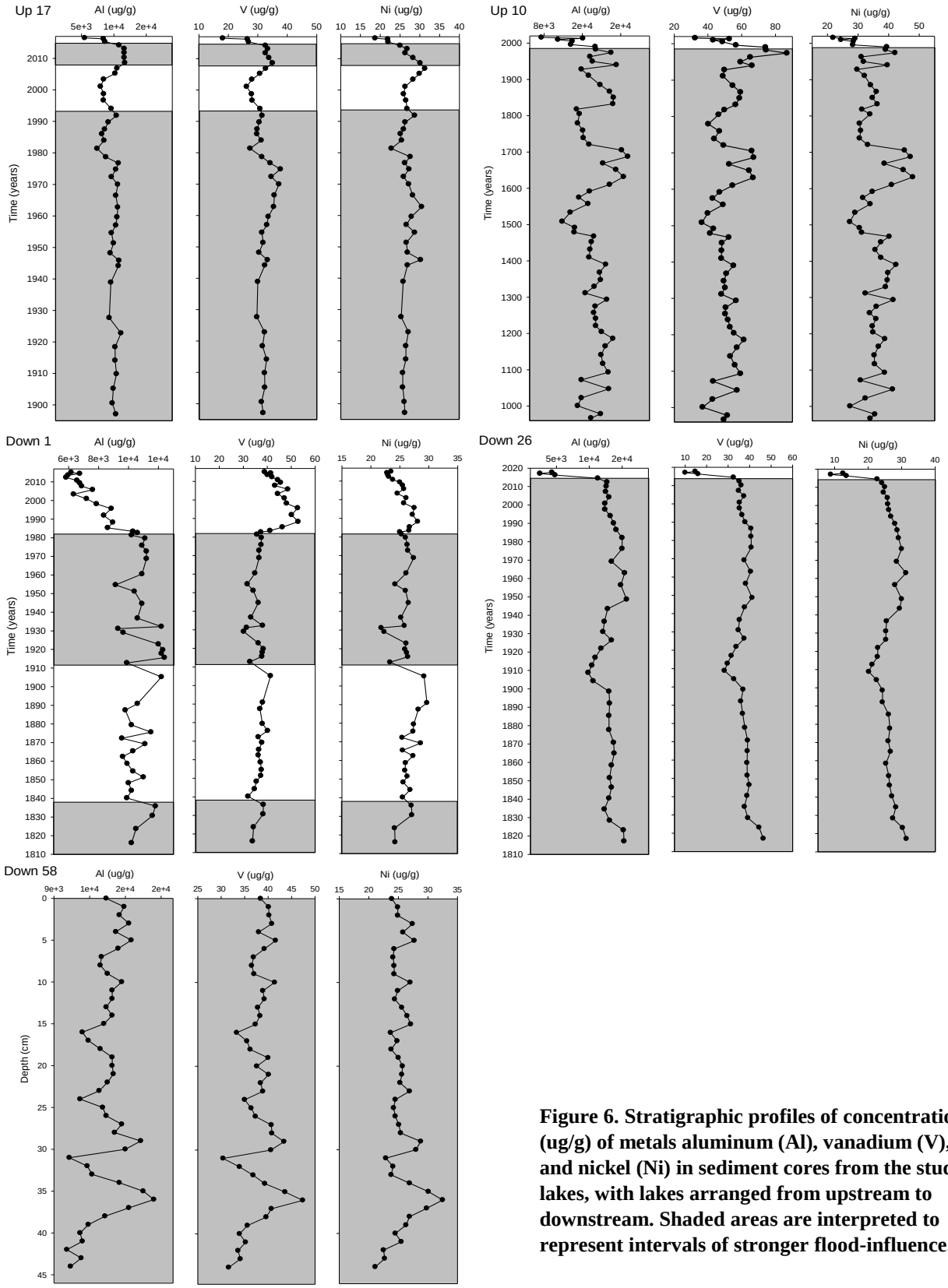


**Figure 6. Stratigraphic profiles of concentrations (ug/g) of metals aluminum (Al), vanadium (V), and nickel (Ni) in sediment cores from the study lakes, with lakes arranged from upstream to downstream. Shaded areas are interpreted to represent intervals of stronger flood-influence.**

### *3.4 Developing a regional pre-industrial baseline*

For the floodplain lakes where sediment core chronologies could be established (Up 17, Up 10, Down 1, and Down 26), pre-industrial (pre-1967) linear relations and 95% prediction intervals were determined for concentrations of the two metals of concern (V, Ni) with respect to the normalizing agent Al. As expected, concentrations of both V and Ni follow a distinct positive linear relation with Al in these samples because the ratios of V and Ni to the normalizing agent Al is relatively constant prior to 1967 (Figure 7, A & B). Due to observations of deviations in the pre-1967 data above and below the V/Al and Ni/Al baselines that appeared slightly biased, and potentially underestimating Al in the mi-range, and V and Ni at the extreme ends (Figure 7), AICc model selection tested the hypothesis that a log-linear model would be a better fit for the data. The linear model had the highest support (Tables E1 and E2, Appendix E).

Lakes Up 17, Up 10, and Down 26 are all strongly flood-influenced prior to 1967 (Figure 5). Lake Down 1 is the only lake where a pre-1967 period of weaker flood-influence is observed, and these samples are not readily distinguished from the other strongly flood-influenced sediments in Up 17, Up 10, and Down 26 (Figure 5; Figure 7, A & B). The strong linear relationships observed for all the sediment core samples, regardless of the status of flooding, shows that pre-industrial V/Al and Ni/Al relations do not differ between periods of strong and weak flood influence. This is likely because the geological source is the same whether it is flood-supplied sediment or remobilized former flood-supplied sediment from the local lake catchment. Weakly flood-influenced samples also likely still contain sediment related to flood events and so still have some use in assessing river sediment metals concentrations. Therefore, all of the pre-industrial sediment data were utilized in baseline construction, regardless of whether the sediment is strongly flood-influenced or not.

The floodplain lakes we sampled adjacent to the Athabasca River provide a good pre-industrial baseline for sediments with Al concentrations ranging from 10,000-25,000 µg/g. Up 17 and Down 1 sediments plot near the lower end of the range (10,000-13,000 µg/g) in a cluster, whereas sediments from Up 10 and Down 26 capture the mid- to higher-end (10,000-25,000 µg/g) (Figure 7, A & B). The sediment samples from the study lakes, however, do not include values at the low end of the range of sediment Al concentration (< 10,000 µg/g). Notably, Athabasca River river-bottom and suspended sediment samples collected by the RAMP and JOSM monitoring programs have much lower concentrations of Al (< 10,000 µg/g), V, and Ni compared to sediments of the floodplain lakes, likely because the sediment is coarser grained than what is deposited in the floodplain lakes. Thus, the gap of floodplain lake sediment values at the low end of the plot requires that the linear regression is extrapolated outside the range of measured values to assess the low Al content RAMP and JOSM samples for evidence of pollution. This increases the uncertainty for evaluation of the RAMP/ JOSM data, as well as other potential test samples with Al concentrations < 10,000 µg/g.

To expand the range of concentrations of Al and the metals of concern (V, Ni) to include Al concentrations < 10,000 µg/g, the use of pre-1967 sediment core data from three small, shallow (mean depth 2.1 m) lakes (NE13, NE20, and RAMP 418/Kearle) located 10-35 km from AR6 were explored (published in Cooke *et al*., 2017) (Figure 3). Sediments of these headwater lakes, located in the AOSR and within the Athabasca River watershed, possess lower concentrations of Al (< 10,000 µg/g) and, correspondingly, lower concentrations of V and Ni with metal-Al ratios similar to the floodplain lake sediments; thus, they capture lower portions of the linear relations (Figure 7, C & D). Sediments from lakes NE13 and NE20 have Al concentrations < 1,000 µg/g and plot near the origin of the V/Al and Ni/Al scatterplots. At lake

RAMP 418/Kearle Al concentrations are between 2,000-4,000 µg/g. Although a gap (~5,000-10,000 µg/g) remains between the floodplain study lakes and the AOSR headwater lakes, the linear relations are now well-anchored at the lower end of the concentrations and both the floodplain and AOSR data are readily captured by the same linear relations (Figure 7, C & D).

The pre-industrial baselines characterizing V/Al (Eqn. 3) and Ni/Al (Eqn. 4) relations, established using pre-1967 sediment metal concentrations from floodplain lakes Up 17, Up 10, Down 1, and Down 26 and AOSR headwater lakes NE13, NE20, and RAMP 418/Kearle (V/Al: $R^2 = 0.9632$; Ni/Al: $R^2 = 0.9332$) (Figure 7, C & D) can be expressed as follows:

$$[V]\ \mu g/g = 0.0026*([Al]\ \mu g/g) + 4.8712 \quad \text{(Equation 4)}$$

$$[Ni]\ \mu g/g = 0.0016*([Al]\ \mu g/g) + 6.8138 \quad \text{(Equation 5)}$$

Sediment from both floodplain and headwater lakes follow close along the same linear relations and pass close to the origin (V/Al and Ni/Al), indicating that both datasets have similar V/Al and Ni/Al ratios, which suggests that similar parent geological materials for both floodplain and headwater lakes are the source of these pre-industrial metals in the surrounding AOSR. The crossplots in Figure 7 (C & D) show that samples from each of the headwater lakes vary over quite a narrow range of values, whereas the floodplain lake samples vary over a much wider range of values. This illustrates how natural inputs of metals to non-flooded lakes are quite consistent in the headwater lakes, in comparison to the periodic flooding and non-flooding intervals at the floodplain lakes, which results in a wider range of metal concentrations from the variation in energy conditions of river floodwaters and consequently particle sizes.

The 95% prediction intervals about the regression line, developed as per methods in Wiklund *et al*. (2014), define the natural range of variation of V and Ni concentrations relative to Al concentration for individual lake sediment samples in the AOSR prior to possible pollution from oil sands development (Figure 7, C & D). If unpolluted, 95% of individual sediment samples would be expected to fall within the 95% P.I.s. If > 2.5% of the test samples fall above the upper 95% P.I., this could identify a new enriched source of materials possibly due to pollution from industrial activities.

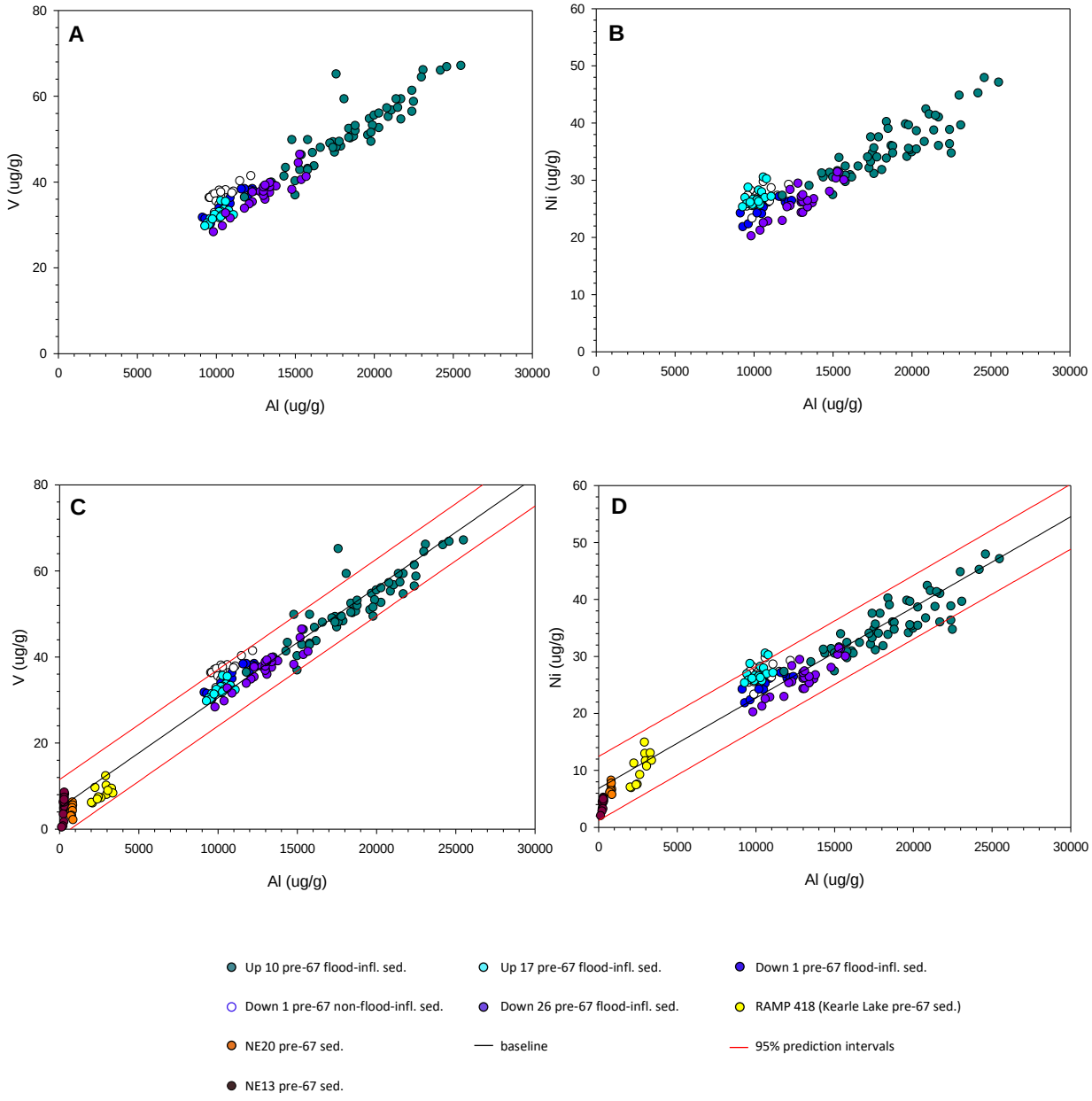


**Figure 7. Crossplots showing the relations between sedimentary concentrations of Al and V (left column, A & C) and Al and Ni (right column, B & D) in pre-1967 floodplain lake sediment from lakes Up 17 (light blue), Up 10 (green), Down 1 (dark blue), Down 26 (purple), with the open circles denoting less-flood-influenced sediment from Down 1. Pre-1967 headwater lake sediment from lakes NE13 (dark red), NE20 (orange), and RAMP418/ Kearle (yellow) were added to the floodplain lake data (C: V/Al, D: Ni/Al). The linear regression line (black line) and the 95% prediction intervals (red) are based on pre-1967 sediments from all the lakes listed.**

### *3.5 Assessment for V and Ni pollution*

Sediments deposited in the study lakes after onset of oil sands development in 1967 were plotted on the established pre-1967 regional baseline to evaluate for evidence of V and Ni enrichment. For V, post-1967 sediment samples at lakes Up 17, Down 26, and Down 58 all plot within the 95% P.I.s, indicating no evidence of enrichment (Figure 8). This includes during both the strongly and weakly flood-influenced periods at lakes Up 17, which overlap substantially, and at Down 26, where the values for strongly and weakly flood-influenced sediment samples follow the same linear relation but are distinctly lower for the weakly flood-influenced sediments, likely due to dilution of organic matter. For lakes Up 10 and Down 1, however, there is clear indication of V enrichment above baseline in the less flood-influenced sediments, indicating an additional source of the metal to these lakes, which lie within a 10 km distance from AR6 (Figure 8). As seen in Figure 9, both Up 10 and Down 1 are located in an area of high airborne V net loading (572-715 µg/$m^2$) as measured in snowpack samples from February-March 2011 and 2012 across the AOSR (Kirk *et al*., 2014). For lake Down 1, this is evident in the data from 1983-2015 (30% of post-1967 sediment samples), which cluster distinctly above the upper 95% P.I. At lake Up 10, there is evidence of enrichment above baseline from 1974-2016 (88% of post-1967 sediment samples), but the data here are more dispersed. V concentrations of post-1967 sediment samples that plot above the baseline for Down 1 and Up 10 do not exceed the CCME guideline of 120 ug V/g, however, some samples do exceed the chronic hazardous HC5 concentration of 50 ug V/g. Schiffer & Liber (2017) suggest that this new benchmark should act as an interim guideline for protection of aquatic life in the AOSR until appropriate, region-specific water quality guidelines are developed.

On the Ni/Al baseline, no enrichment is observed in post-1967 flood-influenced or less-flood-influenced sediment from lakes Up 10, Down 26, and Down 58, as all data plot within the 95% P.I.s (Figure 10). Enrichment of Ni, clustering just above the upper 95% P.I., is observed for Up 17, and Down 1 (14% and 26% of each lake's post-1967 data points, respectively). This enrichment is observed in recent, less flood-influenced sediments at Down 1, likely reflecting a different source of Ni to the lake, as observed for V at this lake (Figure 8). For lake Up 17, marginal enrichment in some flood-influenced sediments is observed, but since they are upstream of major industry this is likely attributed to airborne oil sands pollution, or inputs to the river from the upstream, urban center of Fort McMurray or other upstream industries. Overlap between strongly and weakly flood-influenced sediments is evident at Up 17. The CCME does not have a guideline for freshwater sediment concentrations of Ni for the protection of aquatic life and has determined that this value needs to be assessed on a site-specific basis, since background values of Canadian freshwater sediments can range from 2 to 50 mg/kg dry weight (Moore and Ramamoorthy, 1984; CCME, 2015). Since there currently are no Canadian oil sands-specific guidelines for the toxicology of Ni in AOSR freshwater sediment, the worst-case scenario chronic HC5-50 threshold value of 94 mg Ni/kg determined in Vangheluwe *et al*. (2013) was used to evaluate the sediment taken in these lakes, but all values including those enriched above the Ni/Al baseline fall well below that concentration.

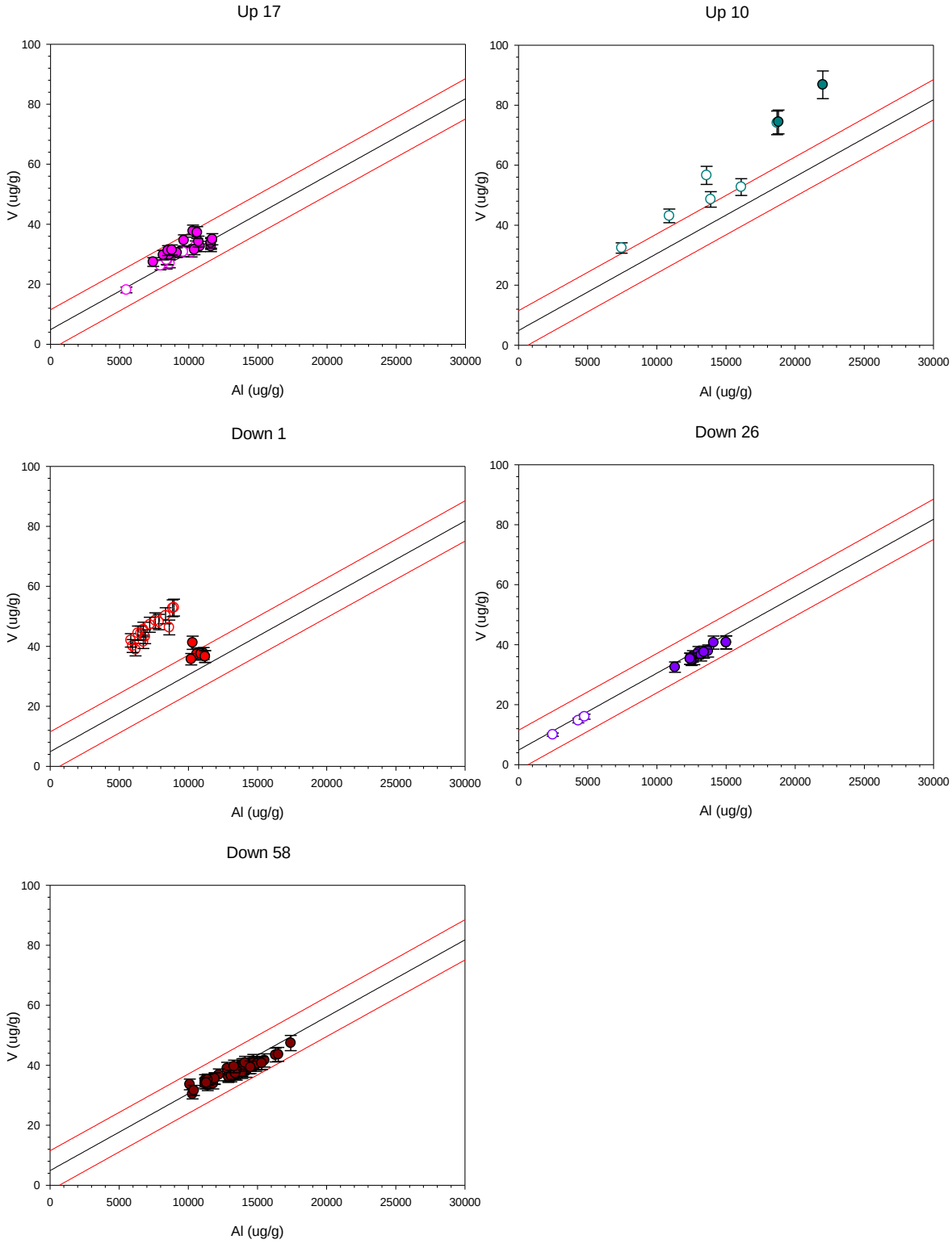


**Figure 8. Crossplots assessing Al-normalized V concentrations in sediments deposited in the study lakes since 1967-onset of oil sands development (circles) relative to the pre-industrial baseline (black line) and 95% prediction intervals (red lines). Closed circles: flood-influenced sediment intervals; Open circles: less-flood-influenced sediment intervals. Error bars are from the mean % precision of V calculated from ALS-analyzed duplicate lake sediment samples 200 km downstream (Wiklund *et al*., 2014).**

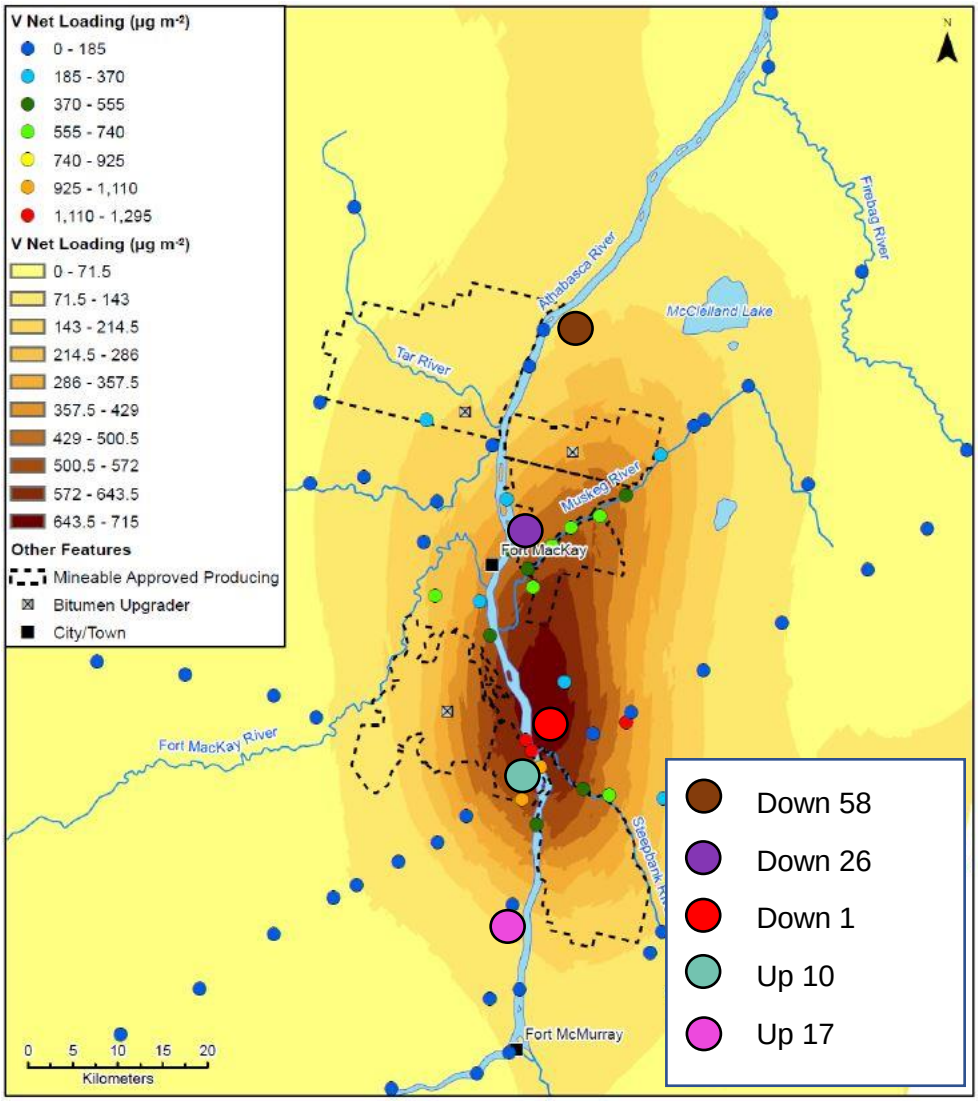


**Figure 9. Map of the AOSR mining region showing locations of the study floodplain lakes Up 17, Up 10, Down 1, Down 26, and Down 58, superimposed on a vanadium net loading map to the snowpack in winter of 2012 (adapted from Figure S6: Kirk *et al*., 2014).**

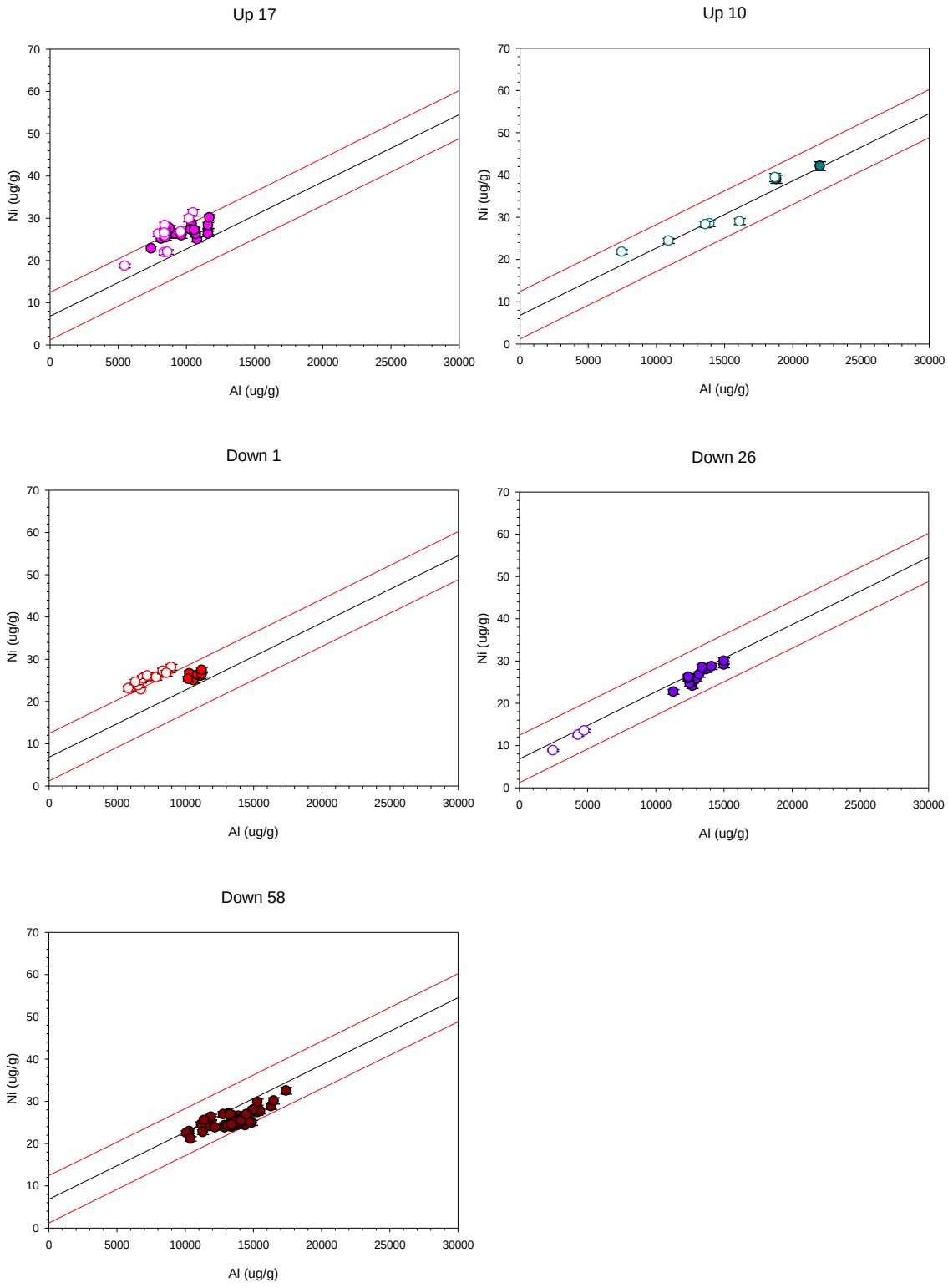


**Figure 10. Crossplots assessing Al-normalized Ni concentrations in sediments deposited in the study lakes since 1967-onset of oil sands development (circles) relative to the pre-industrial baseline (black line) and 95% prediction intervals (red lines). Closed circles: flood-influenced sediment intervals; Open circles: less-flood-influenced sediment intervals. Error bars are from the mean % precision of Ni calculated from ALS-analyzed duplicate lake sediment samples 200 km downstream (Wiklund *et al.*, 2014).**

### *3.6 Evaluating regional river sediment monitoring data for evidence of pollution*

Athabasca River-bottom V and Ni data collected by RAMP and JOSM, as well as suspended-sediment data from JOSM, were evaluated using the pre-1967 V/Al and Ni/Al baselines (Figure 11). Nearly all the river-bottom sediment and the suspended-sediment samples follow the V/Al linear relation, plotting within the 95% P.I.s. Two RAMP samples out of the 75 RAMP/JOSM combined Athabasca River-bottom samples (2.7%) have values that fall above the baseline (site IDs: ATR-SR-W (Oct. 2000), ATR-MR-E (Oct. 2000)) (Figure 11A). This is very close to the 2.5% threshold, which indicates that the V present in the post-1967 Athabasca River sediment samples are only slightly above the expected range of natural (pre-industrial) variability.

The majority of the river-bottom sediment and suspended-sediment Ni data plot within the 95% P.I.s for the Ni/Al baseline. The normalized concentrations of Ni in the Athabasca River sediment samples (suspended and bottom sediments) follow a slightly steeper Ni/Al relation than the pre-industrial baseline, which is particularly apparent for the JOSM river-bottom samples. Five of the 75 river-bottom sediment samples (6.7%) collected by RAMP (site IDs: ATR-DC-E (Oct. 2000), ATR-SR-E (Sept. 2002), ATR-SR-W (Sept. 2002)) and JOSM (site ID: M7C (Sept. 2012, 2014)) plot above the 95% P.I.s (Figure 11B). Suspended sediment samples collected along the lower Athabasca River cluster near the upper 95% P.I., with 8 out of the 25 samples (32%) above the upper 95% P.I. (site IDs: M0 (Sept. 2012; and Feb., June & Sept. 2014), M2 (Sept. 2012, 2013), M3 (Sept. 2012, 2013)) (Figure 11B). This is higher than the 2.5% threshold, indicating that there is evidence of enrichment of Ni in post-1967 Athabasca River sediment. Exposed river-bottom sediment collected in 2016 and 2017 during coring excursions, and the

flood deposit sample collected after the spring flood in 2017, follow closely along the baseline linear regression for the V/Al and Ni/Al relationships.

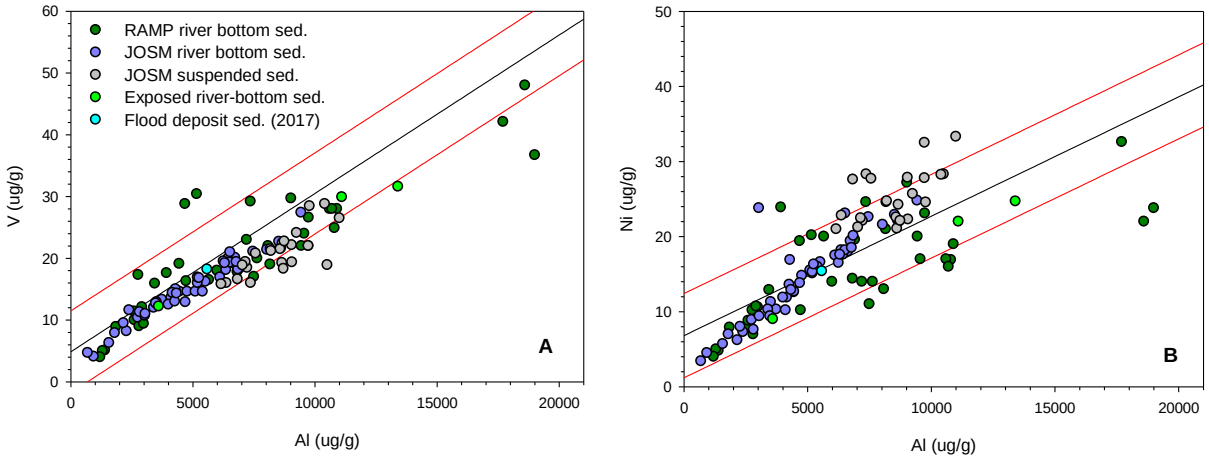


**Figure 11. Scatterplot of post-1967 Athabasca River sediment vanadium (A) and nickel (B) concentrations versus aluminum concentrations in the Athabasca River sediment samples collected by the Regional Aquatics Monitoring Program (RAMP) and the Joint Oil Sands Monitoring Program (JOSM). Exposed river-bottom sediment and a flood deposit sample collected during this study (2016, 2017) are also shown. Samples are plotted relative to the V/Al and Ni/Al linear regressions (black line) and 95% prediction intervals (red lines) from Figure 7.**

### *3.7 Enrichment factor and excess flux analyses*

To quantify temporal trends in sedimentary V and Ni concentrations, enrichment factors (EF) were calculated for floodplain lakes where a chronology was developed: Up 17, Up 10, Down 1, and Down 26. Enrichment factors were also calculated for RAMP/JOSM samples to quantify enrichment of samples that plot outside the upper 95% P.I. on the baselines. In Figure 12 below, a line is drawn at an EF of 1, which indicates no enrichment, and the upper 95% P.I. corresponding to the upper 95% P.I. of the baseline metal-Al linear regression is shown. This 95% P.I. for the EFs represents the same relationship between the linear regression and the 95% P.I. calculated for the baseline, indicating the natural range of variation.

A significant trend of increasing V EFs from the 1960s to 2016 was observed at both Up 10 and Down 1 (Mann-Kendall trend test, $p < 0.05$, Figure 12, Table 2). At Up 10, EFs of V increased to 1.4x above the baseline beginning in the 1970s and remained elevated until ~1995 when the EF began to decline. At Down 1, V increased rapidly to a doubling above the baseline beginning in the early 1980s (breakpoint at 1982, $p < 0.05$, Figure E3 (Appendix E)), after which values levelled out but remained high (breakpoint at 1986, $p < 0.05$, Figure E3 (Appendix E)). Of the EFs calculated for V in the RAMP and JOSM Athabasca River sediment samples, only four RAMP river-bottom sediment samples plotted outside the 95% P.I. (~1.2-1.7x baseline, Figure 12). These river-bottom samples were collected in October 2000 (ATR-MR-E and ATR-SR-W) and September 2002 (ATR-DC-E and ATR-SR-W), at depositional environments located near the Muskeg River (MR), Steepbank River (SR), and Donald Creek (DC) tributary mouths (Figure 12).

A significant trend of increasing Ni EFs above baseline was detected at Down 1 (Mann-Kendall trend test, $p < 0.05$, Figure 12, Table 3). EFs of Ni increased to 1.45x above baseline

beginning during the same 1980s period identified for V at this lake and then levelled out in recent years (breakpoints at 1982 and 1986, $p < 0.05$, Figure E4 (Appendix E)). While no significant temporal trend was detected at Up 17 (Mann-Kendall trend test, $p > 0.05$, Figure 12, Table 3), EFs of Ni increased to 1.4x baseline beginning in the late 1970s, before declining back toward baseline starting in the early 2000s. In RAMP river-bottom samples, Ni EFs plotted above the 95% P.I. (~1.3-1.8x baseline, Figure 12) for similar sites where V enrichment was also detected in October 2000 (ATR-MR-E, ATR-SR-W, and ATR-DC-E) and September 2002 (ATR-SR-W, ATR-SR-E). Enrichment was also detected in a depositional area near the Firebag River in September 2002 (ATR-FR-W). Ni EFs calculated for JOSM river-bottom samples displayed enrichment above the 95% P.I.s in September 2012 (M4 and M7C, 1.2 and 2.0x baseline) and 2014 (M7C, 1.3x baseline) (Figure 12). Site M7C is a new JOSM sampling site, established to estimate Athabasca River water and sediment quality downstream of the Ells River and the total mining area, but upstream of the Tar River (Figure 3). Site M4 was also a RAMP sampling location (formerly ATR-MR) on the Athabasca River mainstem, which was designed to capture Athabasca River water and sediment quality downstream of the Steepbank River and Suncor and Syncrude mining operations, and upstream of Fort McKay and the MacKay River (Figure 3). The Ni EFs calculated for several JOSM suspended sediment samples plotted above the 95% P.I. (1.2-1.5x baseline, Figure 12) from samples collected at M0 (Sept. 2012, 2014; Feb. 2014, Jun. 2014), M2 (Sept. 2012, 2013), M3 (Sept. 2012, 2013), and M9 (Oct. 2012). Interestingly, M0, M2, and M3 are all sites located upstream of oil sands operations. Sites M0 and M2 are both upstream of Fort McMurray and considered ‘baseline/reference sites’ for the new JOSM monitoring program. Site M0 is intended to represent the status of the Athabasca River water and sediment quality prior to reaching the oil sands area, and M2 is located

immediately upstream of Fort McMurray (former RAMP site ATR-UFM). Site M3 (formerly RAMP site ATR-DC) is located directly downstream of Fort McMurray and the Clearwater River. Site M9, a new JOSM site located downstream of the Firebag River and upstream of the Embarras River, is the only downstream site that exhibited Ni enrichment.

**Table 2. Results of Mann-Kendall trend tests on the vanadium EF values from sediment cores from lakes Up 17, Up 10, Down 1, and Down 26. The symbols (*) = denotes stat. significance, p<0.05; (+) = upwards trend; (-) = downwards trend.**

| Lake | Up 17 | Up 10 | Down 1 | Down 26 |
|---|---|---|---|---|
| Kendall's tau | - 0.152 | + 0.410 | + 0.420 | - 0.485 |
| Two-sided p-value | 0.158 | $2.62 \times 10^{-6}$ * | $9.42 \times 10^{-6}$ * | $1.25 \times 10^{-5}$ * |
| Kendall Score (S) | - 140 | 774 | 594 | - 401 |
| Denominator (D); tau=S/D | 919.63 | 1887.50 | 1413.39 | 826.30 |
| Variance of Kendall Score | 9687 | 27097 | 17922 | 8385 |
| Timescale | ~1897-2016 | ~966-2015 | ~1816-2015 | ~1817-2017 |

**Table 3. Results of Mann-Kendall trend tests on the nickel EF values from sediment cores from lakes Up 17, Up 10, Down 1, and Down 26. The symbols (*) = denotes stat. significance, p<0.05; (+) = upwards trend; (-) = downwards trend.**

| Lake | Up 17 | Up 10 | Down 1 | Down 26 |
|---|---|---|---|---|
| Kendall's tau | + 0.137 | + 0.014 | + 0.39 | - 0.138 |
| Two-sided p-value | 0.198 | 0.874 | $3.99 \times 10^{-5}$ * | 0.211 |
| Kendall Score (S) | 128 | 27 | 551 | - 116 |
| Denominator (D); tau=S/D | 934.93 | 1885.99 | 1413.90 | 838.20 |
| Variance of Kendall Score | 9750 | 27093 | 17926 | 8448 |
| Timescale | ~1897-2016 | ~966-2015 | ~1816-2015 | ~1817-2017 |

To quantify the increase in deposition rate above the V/Al and Ni/Al pre-industrial baselines, adjusted excess flux ($\Delta F_{adj}$) was calculated. Excess flux was calculated for lakes that showed > 2.5% enrichment (or "excess") above the baselines' upper 95% P.I. (Figures 9 and 10). Since enrichment of V above the baseline was observed at lakes Up 10 and Down 1 (Figure 8), and enrichment of Ni above the baseline was observed at Up 17 and Down 1 (Figure 10), excess flux was calculated for these three lakes. The V $\Delta F_{adj}$ at lake Up 10 peaked at ~16x the baseline in 1973, before declining to an excess of ~4x baseline in ~2015 (Figure 13A). The V $\Delta F_{adj}$ at Down 1, however, steadily increased during the 1980s, peaking at ~17x the baseline in ~2005 when it levelled out (Figure 13A). At both Up 10 and Down 1, $\Delta F_{adj}$ was highest when the lakes were weakly flood-influenced.

The Ni $\Delta F_{adj}$ at lake Up 17 peaked at ~11x the baseline in ~1979 when the lake was strongly flood-influenced, likely associated with the 1977 Fort McMurray flood, and declined after ~1981 when the lake became weakly flood-influenced (Figure 13B). After a decline starting in the 1990s, the Ni $\Delta F_{adj}$ levelled out to a doubling of baseline values. The Ni $\Delta F_{adj}$ at lake Down 1 did not peak as high as the V $\Delta F_{adj}$ observed, reaching an adjusted excess flux of ~6x the baseline in the 2000s, after which values levelled out with no indication of subsequent decline (Figure 13B).

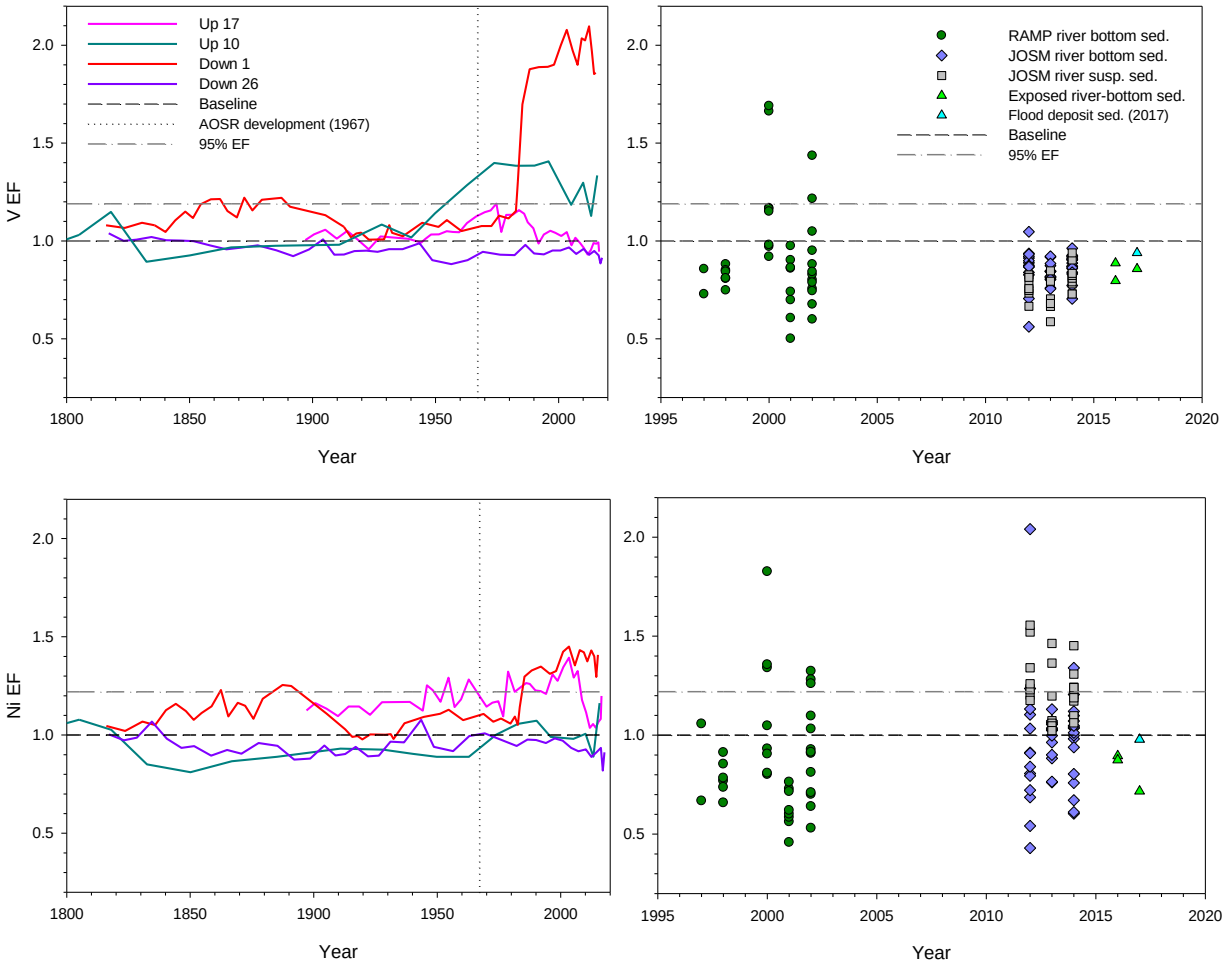


**Figure 12. Enrichment factors for V and Ni at lakes Up 17 (pink), Up 10 (green), Down 1 (red), and Down 26 (purple) in the two left-hand panels. In the right-hand panels, enrichment factors for Athabasca River-bottom sediment monitoring data from RAMP (dark green circles) and JOSM (purple triangles) are plotted beside JOSM suspended sediment data (grey squares), exposed river-bottom samples collected during this study (light green triangles), and a flood deposit sample (light blue triangle). The dashed line at an EF = 1 represents the baseline, and the grey dashed-and-dotted line above it represents the upper 95% prediction interval EF. A dotted line at 1967 represents the start of AOSR development.**

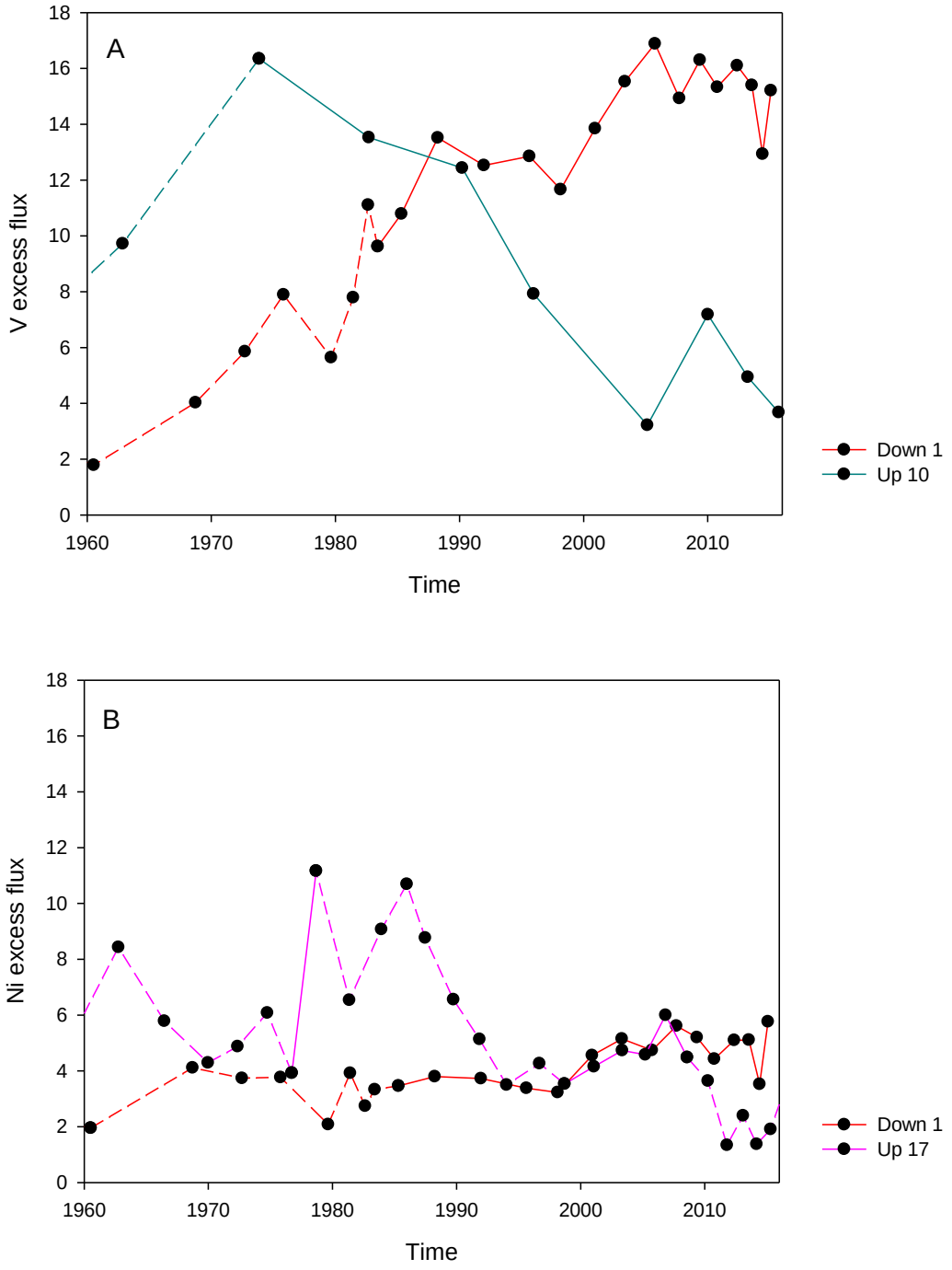


**Figure 13. Adjusted excess flux ($\Delta F_{adj}$) of V (plot A) for lakes Up 10 (green) and Down 1 (red) and Ni (plot B) for lakes Up 17 (pink) and Down 1 (red), from 1960-2017. The solid line connects intervals that are enriched above the upper 95% P.I. on the V/Al baseline. The dashed line represents points that do not display enrichment above the baseline.**

## Chapter 4 – Discussion

The absence of knowledge about the natural range of variation for concentrations of contaminants in Athabasca River water and sediment in the AOSR region before industrial development has made it difficult to determine the extent of river pollution by oil sands mining and processing activities. Such knowledge, however, is essential to disentangle "natural" from industrial sources of contaminants and to detect evidence of pollution. Erosion of natural bitumen exposures continues to contribute loadings of contaminants of concern to the Athabasca River, but industrial pollution cannot be evaluated when these contributions have never been characterized. Development of pre-industrial baselines has been a key recommendation ever since the 2010 Federal Expert Panel report, which proposed that "The natural, pre-development state of the [Athabasca River] waters could be further investigated by analysis of information preserved in sediment profiles that can be obtained from lakes and ponds that are situated in locations prone to river flooding (e.g., along the lower Athabasca River and its tributaries…)." (Dowdeswell *et al*., 2010, p. 32). Here, we demonstrate the use of floodplain lakes as an archive of natural river-sourced metal concentrations to characterize baseline conditions and natural variation, and evaluate their uppermost sediment and Athabasca River sediment monitoring data for evidence of pollution.

### *4.1 Use of floodplain lake sediment cores to develop baseline metal concentrations*

Floodplain lakes provide a useful archive of past river sediment composition because they store and preserve river sediments conveyed by floodwaters in their stratigraphic profiles. The flood-supplied sediments that get deposited in floodplain lakes along the Athabasca River are generally fine-grained, mineral-rich suspended sediments to which metals preferentially adhere. In this study, we show that sediment cores extracted from floodplain lakes provide

dateable, decipherable, stratigraphic profiles of hydrological changes and river-sediment metals concentrations. Despite some challenges (e.g., dating) associated with paleolimnological investigations in floodplain lakes presented by fluctuating sedimentary environments, evidence presented here demonstrates that generating accurate and informative data is possible. Analyses of LOI and elemental organic C and N concentration allowed identification of periods of varying river flood influence. Periods of stronger flood influence in the sediment cores were identified as intervals with clay-rich sediment (small grain size) possessing relatively high mineral matter content and minimal organic matter and C and N content. In comparison, periods of weaker flood influence were identified as sediment intervals with relatively high organic matter and C and N content, and low mineral matter content. These distinguishable sedimentary features allowed for the determination of stratigraphic intervals when each lake was receiving strong influence of Athabasca River floodwaters, from which pre-industrial river sediment could be evaluated.

Despite concerns over the ability to date floodplain lake sediments, developing reliable sediment core chronologies is possible, as demonstrated by the combined application of $^{210}$Pb and $^{137}$Cs dating techniques. Where the $^{210}$Pb signal, primarily used for determining lake sediment ages, was diluted by rapid river sediment deposition during flood regimes, a chronology could be developed or estimated based on peak $^{137}$Cs activity in 1963, the height of above-ground nuclear bomb testing. One lake core could not be dated due to very strong flood influence, which depressed $^{210}$Pb activities to near background throughout the core and prevented detection of the $^{137}$Cs peak. Evidence of $^{137}$Cs found throughout the core, however, suggests the stratigraphic record obtained was likely deposited since the onset of oil sands development, which allowed the core from this lake to be used to test for evidence of industrial pollution. The

close match between peaks in estimated sedimentation rates and known flood events for the Athabasca River at Fort McMurray also increases confidence in the accuracy of the estimated core ages. This comparison is similar to other studies where hydrometric river data was used to identify past flood events in the paleolimnological record (Brock *et al*., 2010; Lintern *et al*., 2016a). The effective dating techniques employed in this study allowed for the determination of the pre- and post-industrial periods in floodplain lake sediment cores, in order to evaluate the natural range of variation of metals.

In evaluating the stratigraphic profiles of metals concentrations in the floodplain lake cores used in this study it was found that sedimentary concentrations of metals associated with bitumen (V, Ni) were strongly and positively associated with Al concentrations. This identified a need to normalize sedimentary V and Ni concentrations to the lithogenic element prior to evaluating the extent of pollution. Since increases in Al supply to the environment by oil sands operations occurs in addition to increases in V and Ni, it has been suggested that this normalization procedure could mask the full impact of oil sands effects on lakes (Blais & Donahue, 2015). Therefore, accumulation rates (excess flux) and enrichment calculations were used to elucidate changes in these metals compared to average pre-industrial accumulation of V and Ni ratios to Al, following Cooke *et al*. (2017). Excess flux calculations evaluate the increased rate of anthropogenic deposition above the pre-industrial baseline using the product of sedimentation rate to V and Ni concentrations, and enrichment factors present the magnitude of increase in concentrations above the pre-industrial baseline. This allowed for the assessment of the extent of pollution to be evaluated using other lines of evidence, to help avoid potential errors of omission due to post-industrial increase in Al.

Pre-industrial baselines (V/Al, Ni/Al) were established following the procedure in Wiklund *et al*. (2014), which used 95% P.I.s to allow detection of samples enriched in V and Ni above the baseline. Pre-1967 metals concentration data were used from floodplain lakes (higher V, Ni, Al concentrations) and headwater lakes (lower V, Ni, Al concentrations). Headwater lakes were incorporated into the baseline in an effort to extend the range of the V/Al and Ni/Al relations, since they follow the same linear relation (V:Al and Ni:Al ratio) as the floodplain lakes, and even weakly flood-influenced pre-1967 intervals from Down 1 show the same relation of V and Ni with Al. The use of headwater lakes on a river-specific baseline is unlike previous studies, where only strongly flood-influenced intervals were used to establish baselines to approximate river conditions (e.g., Wiklund *et al*., 2014; MacDonald *et al*., 2016). However, we suggest that a common geologic source for V, Ni, and Al across the AOSR explains the strong V/Al and Ni/Al linear relations and similar V/Al and Ni/Al ratios among all the lakes, including those outside of the floodplain. Indeed, NE13, NE20, and RAMP 418/Kearle are all located on the bitumen-rich McMurray Formation (Conly *et al*., 2002; Hein & Cotterill, 2006). From analyzing Google Earth and aerial images of the AOSR, it appears as though NE13 and NE20 were also likely part of the river floodplain in the past and, therefore, may contain similar fluvial-derived materials. Prior to industrialization of the region, sediment deposited in these headwater lakes was likely allochthonous, from erosion and runoff of the local McMF catchment. This offers evidence that the regional geology is comparable between the two lake types located in the McMF.

Although the use of headwater lakes on a baseline targeting river floodplain sediment was not originally what was planned in the study design for this project, incorporation of data from these lakes helped to extend the range of metals concentrations so that the values included

in the pre-industrial baselines could overlap with a broad set of river monitoring samples obtained after development of the oil sands. The atmospheric pollution signals detected above the baseline in select floodplain lakes follows temporal trends shown in other research (Kurek *et al*., 2013; Cooke *et al*., 2017), providing evidence in support of this approach. With the addition of pre-1967 data from more geologically-similar lakes in the McMF region of the AOSR, the linear relationship could be further extended to fill in gaps in ranges not covered by the floodplain lakes used in this study (4,000-9,000 µg Al/g). As well, the original study design of this project was based on the upstream-downstream model of river monitoring, to assess river sediment loadings upstream and then downstream of industry. While this model is useful when the primary mechanism of contaminant delivery is river transport, here we saw that this was not the case, and rather aerial transport of contaminants showed a stronger signal in the floodplain lakes. Considering this now, an "inside-outside" monitoring setup, where lakes located inside and outside the 50 km zone of aerial deposition would be better suited for comparison in future studies. Future research could also attempt to target high-energy floodplain lakes (that receive a coarser grain size) along the Athabasca River to fill in the lower end of the linear relationship although they are likely going to be challenging to date using radiometric methods.

This study generated pre-industrial data that can, for the first time, be used to evaluate Athabasca River sediment samples deposited within the AOSR since the onset of development for evidence of pollution. The method for evaluating river sediment in floodplain lakes that was used in this study is comparable to other studies which have conducted paleolimnological work in other flood-influenced aquatic basins, including the analysis of a floodplain lake in the Slave River Delta (NWT, Canada; Brock *et al*., 2010) and oxbow lakes along the Yarra River (Australia; Lintern *et al*., 2016a,b). These studies examined lakes that receive periodic

floodwaters and defined periods of flooding using a multi-proxy approach. Both the Brock *et al*. (2010) and Lintern *et al*. (2016a,b) studies treated flood periods in lake sediment as a binary variable (i.e., flooded vs. not flooded). A similar method to differentiate flooding periods was used in this study, however sections of the core were indicated as either "strongly" or "weakly" flood-influenced, to acknowledge that there is some portion of the sediment that is not entirely either river- or lake-derived. Treating flooding as a binary variable can prevent fully capturing the variability in the mixing of autochthonous and allochthonous sediment when a system floods. In other instances, flooding should be treated as a continuous variable assessing the various proportions of sediment from each source especially for lakes highly susceptible to flood events. One way to address this challenge in the future is through the development of a sediment mixing model. Mixing models have been used to estimate source proportions in aquatic environments, usually involving tools like isotope tracers to track lake food web dynamics and sediment source fingerprinting (e.g., Bird *et al*., 2010; Zigah *et al*., 2012; Stock *et al*., 2018). The development of a mixing model to evaluate river sediment proportions was not possible in this study, as the attempted use of river sediment (coarse-grained, metal-poor, organic-matter poor) as an end member was not representative of the floodplain river flood sediment (fine-grained, metal-rich, organic-matter poor). Hydrologic gradients exert a large amount of control on the composition of sediment at depositional areas along rivers, such as floodplain lakes. River flood events influence the relative contributions of allochthonous and autochthonous sediment present in a floodplain lake at a given time, dictating variations in sediment grain size and metal concentrations. When Al values for the lakes and RAMP/JOSM river sediment samples were plotted relative to organic C values, some of the strongly flood-influenced, metal-rich lakes (e.g., Down 58) were more depleted in organic matter than the river samples, making the river end-member not applicable to

these lakes (Figure B6, Appendix B). If end members can be better determined, this could be a highly effective future tool to tease apart allochthonous and autochthonous contributions to lakes in the Athabasca River floodplain.

### *4.2 Evaluating the extent of pollution to the Athabasca River*

The Athabasca River is vulnerable to multiple sources of exposure to anthropogenic contaminants from oil sands industrial operations, mainly in the forms of direct aerial deposition within a 50 km radius of AR6, contaminants supplied via snowmelt runoff and river ice processes during breakup, and surface runoff to the river from intense rain events. The potential inputs of contaminants to the Athabasca River, particularly from contaminated snowmelt, have elevated concerns for human and ecosystem health in downstream, depositional reaches of the river. Historically flood-influenced lakes that capture episodic floodwaters from the Athabasca River were used to assess if metal enrichment above natural, baseline conditions, can be detected in stratigraphic sequences of the sediment when the lakes were strongly flood-influenced. At the downstream Athabasca River floodplain lakes (Down 26 and Down 58) that remained strongly river-influenced throughout most of the time captured by their respective sediment cores (high mineral matter content, low organic content, low/variable $^{210}$Pb), there was no evidence of post-industrial enrichment of V or Ni above the pre-industrial baseline in Athabasca River supplied sediment. Down 58 has remained strongly and consistently flood-influenced over the length of the sediment core, likely due in part to its proximity to the river and low elevation in comparison to the other lakes. Analyses of the core from this lake, which likely captured entirely post-industrial sediment based on $^{137}$Cs radiometric activity measured at the base of the core, did not detect any enrichment of V or Ni. Until 2014, Down 26, another small lake system proximal to the river, had remained consistently river-influenced, and no post-industrial enrichment of V or

Ni was detected. Post-1967 sediment at these floodplain lakes falls very closely along the pre-industrial Al-normalized baseline for V and Ni, suggesting no evidence of pollution of Athabasca River sediment at these downstream locations.

The Athabasca River sediment V and Ni baselines developed in this study provide a unique ability to assess river sediment samples obtained by monitoring programs in the region for evidence of pollution. Monitoring in the region has been criticized for its inability to detect pollution or evaluate trends, but with the method of baseline development shown here this is now possible. The post-1997 RAMP/JOSM river sediments evaluated in this study represent depositional areas of the river from upstream of Fort McMurray to the Embarras River. The V and Ni concentrations in the RAMP/JOSM samples plot at the lower end of both the V/Al and Ni/Al baselines, overlapping with the pre-1967 headwater lake concentration data. Most of the river sediment samples plot along the linear relationship observed with the V/Al and Ni/Al baselines, showing that the river samples have similar metal ratios. It is expected that the river samples, which are coarser than the fine-grained, silty sediments primarily received by the floodplain lakes, would naturally have lower concentrations of metals.

Results from this study demonstrate how sampling of both river bottom sediment and suspended sediment are valuable indicators of river sediment enrichment. Of the downstream sites that show enrichment outside the range of natural variation, most are located near tributary mouths (Steepbank, Ells, Muskeg), where they are in direct and frequent contact with exposures of bitumen (Conly *et al*., 2002; Conly *et al*., 2007) and pass directly through a heavily altered landscape, and therefore may be more representative of the tributary itself than of the Athabasca River as a whole. The detection of > 2.5% of samples above the 95% P.I.s could either identify that these sites have been polluted in recent years, or the pre-industrial baselines developed from

4 floodplain lakes adjacent to the Athabasca River mainstem and 3 headwater lakes within the AOSR are unable to provide adequate baselines for sediments conveyed by the smaller tributaries where these samples were collected. As well, due to differences in energy between the Athabasca River and its tributaries, it is likely that the grain size of sediment brought from these tributaries is smaller, less coarse, and therefore more metal-rich, as they are slower moving river systems. Spatial patterns observed for ΣPAHs in the Athabasca River and its tributaries (including the Steepbank and Muskeg Rivers) have been reported previously for RAMP samples, where the highest concentrations were observed to be near exposed bitumen beds (Evans *et al*., 2016). Depositional areas, like those sampled as a part of RAMP, are generally in slow-moving portions of the river where benthic invertebrates live and fish spawn. In fact, weathered bitumen sediments, typical of natural exposures downstream of the Athabasca, Ells, and Steepbank rivers, were found to be toxic to fish native to northern Alberta that were in early development stages (Colavecchia *et al*., 2004, 2006). Canadian interim sediment quality guidelines for V toxicity (120 µg V/L) and the chronic HC5-50 threshold value of 94 mg Ni/L determined in Vangheluwe *et al*. (2013) are currently not exceeded at any of these monitoring sites, however there may be other exceedances of metals (or PAHs) that were not examined in this study. This study was able to take modern river sampling data and place it in a long-term context to evaluate post-industrial signals. Our results show that these depositional areas of the river, that are downstream of oil sands activities and that exhibit enrichment, may require further consideration and analysis of source contributions.

The clear enrichment of Ni in suspended sediment samples at upstream JOSM sites (M0, M2, and M3) indicates that there may be a different geological footprint or river pollution source upstream compared to what is observed farther downstream, as these samples appear to be more

enriched compared to locations downstream of oil sands development. As noted earlier, when plotted on the Ni/Al baseline, the suspended sediment samples follow a steeper trend than that of the baseline linear relationship established using pre-industrial lake data. This additional input at sites M2 and M3 could be from upstream tributaries exposed to natural bitumen exposures, such as the Clearwater River, which contributes more than 60% of the total tributary suspended sediment load to the Athabasca River and passes through the McMF (Conly *et al*., 2002). Kelly *et al*. (2010) found that occasionally there were some particulate and dissolved fractions of water samples from the Athabasca River that had metal concentrations higher than background levels, at distant sites > 50 km away from oil sands activities, similar to observations here. Due to their distant location, they were determined to be "local sources un-related to oil sands mining and processing," and given a background designation. This is evidence that the observed Ni enrichment in the suspended sediment samples from the most distant upstream site M0 (chosen to reflect upstream boundary conditions in the Athabasca River outside the region of oil sands development) is precedented.

Interpretation of Athabasca River sediment monitoring data using these baselines does have its limitations. For example, the time period captured by the river-bottom surface-sediment samples is unknown. The sample may contain sediments deposited over several years, not just the season when it was collected. Some sediment is re-deposited from depositional locations upstream. So, there is uncertainty as to what the surface sediment samples represent, which makes it challenging to draw conclusions about the extent to which oils sands operations have caused pollution of the river. As well, RAMP only has sediment data available from fall sampling, and JOSM has fall river-bottom data, and some fall, winter, and summer suspended sediment data. As is well known, the spring freshet brings an influx of contaminants into the

river from contaminated snowmelt, which is missed if sediment monitoring is not year-round. By adapting the river sediment sampling frequency to capture seasonal differences and major hydrological events (i.e., significant floods), a temporal perspective for river sediment could be better defined and anticipated.

### *4.3 Atmospheric signals of pollution at floodplain lakes*

Declining river discharge and climate warming in northern Alberta have led to changes in the flood regime of the river (Schindler & Donahue, 2006; Wolfe *et al*., 2008a), which has resulted in reduction of flood frequency in recent decades at most of the floodplain lakes used in this study. The transition from strong to weak flood-influence at many of these lakes resulted in a shift from dominantly allochthonous sediment inputs to more autochthonous-generated organic matter. This transition to greater isolation of the basins from the Athabasca River floodwaters occurred at Up 17 after ~1994, Up 10 after ~1990, Down 1 after ~1988, and Down 26 after ~2014. The decline in flood frequency makes these sites unhelpful in assessing recent river pollution, but provided opportunity to evaluate these sites for deposition of aerially-transported pollution at the study sites closest to mining activities.

Results of this study display evidence of V and Ni enrichment above the Al-normalized baseline in weakly flood-influenced sediments at lakes very close to AR6 (within 20 km), suggesting detection of localized atmospheric pollution where flooding became less frequent due to reduction of river discharge. For V, excess flux calculations show a dramatic rise to ~16x baseline in 1973 and ~14x baseline in 1988 for Up 10 and Down 1, respectively (Figure 13A). These results are consistent with the timings of PAH increases recorded at nearby lakes in the AOSR by Kurek *et al*. (2013), which indicated that since ~1970-1980, ΣPAH concentrations have risen sharply. The alignment of these findings with established patterns of increasing air

pollution at lakes that receive no flood influence, suggests the study lakes capture an accurate record of airborne metal pollution for the AOSR.

As oil sands surface mining and bitumen processing activities have improved over time, it is likely that sources of atmospheric pollutants to the landscape have changed as well, as suggested by studies of Jautzy *et al*. (2013), Kurek *et al*. (2013), and Cooke *et al*. (2017). In the early days of oil sands activity (~1978-1993), conveyer belt dust and stack emissions were two predominant sources of metal-associated fugitive dust released to the landscape (Landis *et al*., 2012; Atkinson, 2017). At Up 10, the V excess flux reaches a peak ~16x the baseline $\Delta F_{adj}$ in the early 1970s, and then begins to decline around 1980 to an excess flux of only ~4x baseline $\Delta F_{adj}$ in recent years (Figure 13). The pattern of decreasing V flux at Up 10 is similar to temporal metal patterns detected by Cooke *et al*. (2017). At near-field lakes NE13 and NE20 (< 20 km away from AR6), Cooke *et al*. (2017) observed that V flux ratios rose to 24x the baseline at NE13 in the 1970s and 15x the baseline at NE20 in the 1980s, coincident with increased dust emissions during this time. In recent decades, however, the flux in metals has declined substantially to ~8 at both headwater lakes, which has been attributed to modern improvements in mining technologies such as the addition of electrostatic precipitators on emissions stacks (late 1970s) and decommissioning of the conveyer belts (early 1990s).

Despite these improvements to mining technologies since the 1990s, aerial deposition continues in the AOSR, as demonstrated by the black snow filters presented in Kelly *et al*. (2009) as well as subsequent snowpack studies (e.g., Kirk *et al*., 2014; Manzano *et al*., 2016). Here, it is evident primarily in the V excess flux calculated for post-1983 sediments in the Down 1 sediment record, which continue to be high and above background levels ($\Delta F_{adj}$ peaks ~17x the baseline in 2005 and remains at ~15x baseline in 2015), unlike the recent decline

observed at lake Up 10 (Figure 13) and headwater lakes NE13 and NE20 (Cooke *et al*., 2017). Possible sources of the continuation of airborne deposition to lake Down 1 include wind-blown particulate matter from open pit mining, wind-blown petcoke dust from stockpiling, stack emissions from the process of upgrading bitumen, fine tailings from reclamation sites, land disturbance from mining activities, emissions from vehicles, or dust from activity on haul roads. Zhang *et al*. (2016) suggest that the primary source of modern aerial deposition in the AOSR is petcoke dust, which is heavily enriched in V and Ni. Using a chemical mass-balance model to quantify the contribution of prospective PAH and metal sources to moss and peat contamination in the AOSR, Zhang *et al*. (2016) estimated that mean V and Ni contributions to moss from delayed petcoke as a source were 30% and 21%, respectively. Down 1 is located on the east side of the river, across from stockpiled petcoke dust, and so this may be the origin of the excess V and Ni observed in the lake sediment record.

### *4.4 EF development for establishing a foundation for ongoing monitoring*

The expression of metals concentration data as an enrichment factor allows concentration data to be presented as the magnitude above the pre-industrial baseline, and to present the data in a chronological sequence to identify the timing of changes. This is a distinct advantage over simply expressing the data as a crossplot of the metal of interest normalized to Al. The use of enrichment factors in evaluating river sediments can be a useful tool to add value to using monitoring data in the future. EFs express the data as the number of doublings of the metal concentration above the pre-industrial baseline (EF = 2 = two times higher than baseline), allowing for simple quantification of the extent of pollution. As we show in Figure 12, EFs also allow for the interpretation of sediment samples collected from the Athabasca River for evidence of pollution, including the samples collected by RAMP and JOSM. Since the data can be plotted

by year, trends can be more easily evaluated, providing an ongoing application to interpret monitoring data in the Athabasca River which was not possible before.

# Chapter 5 – Conclusions, Implications, and Recommendations

## *5.1 Summary of findings*

This study examined sediment cores from floodplain lakes located upstream and downstream of major oil sands activities along the Athabasca River in the Alberta Oil Sands Region. Using a paleolimnological approach, pre-industrial levels of bitumen-associated metals V and Ni were evaluated and assessed for post-industrial river and atmospheric pollution. This study is the first paleolimnological investigation into lakes located on the floodplain of the lower Athabasca River within the AOSR, responding to recommendations in the Expert Panel Report (2010) and the JOSM monitoring implementation plan (2011), to specifically target and investigate pre-industrial river-supplied sediment to establish baseline, reference conditions.

Pre-industrial baselines for Athabasca River sediment V and Ni concentrations were developed to detect pollution (i.e., when > 2.5% of samples above the upper 95% P.I.) and to quantify the magnitude of pollution (as EF and $\Delta F_{adj}$ values) since the onset of development. Sediments analyzed from floodplain lakes along the Athabasca River do not show evidence of V or Ni enrichment in post-industrial river-supplied sediment at these sites (Down 26 and Down 58). Flood influence has declined at several of the lakes due to declining river flows in recent decades. Enrichment above the natural range of variation of V in lakes within 10 km of AR6 (Up 10 and Down 1), and enrichment of Ni at lakes Up 17 and Down 1 was present in modern, weakly flood-influenced sediment, indicating local atmospheric deposition. In fact, some upper sediment samples at Down 1 exceed the chronic hazardous HC5 concentration of 50 µg V/g (Schiffer & Liber, 2017). The evidence of continuing V and Ni pollution at Down 1 may indicate localised pollution from nearby petcoke stockpiles at the Mildred Lake Mine, as petcoke is

highly enriched in both V and Ni (up to 1000 mg/kg, or higher), and stores are located nearby, across the river from Down 1.

Enrichment was detected in samples collected by the former monitoring program RAMP, which was criticized for its inability to detect pollution or evaluate trends in the Athabasca River. Elevated levels of V and Ni in RAMP (2000, 2002) river-bottom sediments, and Ni in JOSM (2012, 2014) river-bottom sediments, was detected at key depositional locations along the river, usually near, or downstream of, tributary mouths such as the Steepbank, MacKay, and Ells rivers. Enrichment of Ni in JOSM (2012-2014) suspended sediment is observed mainly at upstream sampling locations, and therefore attributed to natural loadings from the river and its upstream tributaries (e.g., Clearwater River) that contribute a smaller sediment grain size. V and Ni sediment quality guidelines for the protection of aquatic life were not exceeded at any of the river sampling locations. Archived RAMP samples and current JOSM samples can now be evaluated for contaminant enrichment relative to a pre-industrial baseline.

### *5.2 Research significance and implications*

Where pre-industrial measurements of river sediment are unavailable, and the monitoring time frame is too short to detect any trends, inference of baseline conditions using paleolimnological approaches is a valuable tool (Forstner & Müller, 1981; Smol, 1992). Due to the impact of multiple stressors in the AOSR, the determination of baseline or reference conditions for the Athabasca River has proved to be difficult. This study responded to recommendations in the Expert Panel Report on the state of oil sands monitoring, which highlighted the need to better establish pre-industrial baseline conditions in the AOSR and recommended the use of floodplain lakes along the Athabasca River as a means to evaluate future river trends (Dowdeswell *et al*., 2010). The research questions and methodologies used to

outline the research objectives of this study also align with the baseline monitoring goals of the new JOSM program, which was developed in response to the 2010 report. JOSM highlights the need for lake sediment coring and additional paleolimnological analyses to help establish regional and localized baseline conditions, which they acknowledge are a key requirement to evaluate environmental change in the AOSR (Wrona & di Cenzo, 2011). This study is a valuable contribution to knowledge of baseline conditions in the lower Athabasca River floodplain, as it shows that the sediment records from floodplain lakes can be used to assess regional, pre-industrial concentrations of metals in sediment conveyed by the Athabasca River and evaluate the magnitude of post-industrial metals enrichment.

Predictions of future warming in northern Alberta are rising coincident with industrial development (Gosselin *et al*., 2010; Timoney & Lee, 2011). Coupled with expanding industrial activity in the lower Athabasca are threats of reduced snow-pack in the headwaters and other upstream stressors (e.g., agriculture, pulp and paper mills, population growth, etc.), making the lower Athabasca River increasingly vulnerable to ecological degradation (Schindler & Donahue, 2006). The evidence of declining Athabasca River influence was seen in 4 of the 5 floodplain lakes analyzed in this study, which have become increasingly isolated from the river after having been strongly flood-influenced for several decades. This prevents the ability to use recent sediments at these lakes to evaluate for river pollution. Instead, these lakes have become recorders of pollution by aerial pathways, particularly those within 20 km of AR6. Water levels are expected to continue declining in these lakes and this provides incentive to keep monitoring them as an atmospheric archive, upon which to examine the legacy of bitumen mining activities in the AOSR.

This study showed that long term, baseline data from river-influenced lakes can be informative to the interpretation of current river monitoring data. Sample collection by RAMP was done in such a way that trends could not be evaluated (e.g. inconsistent sampling times, locations, methodologies, etc.) (Dowdeswell *et al*., 2010; Gosselin *et al*., 2010). Using the method this study employed, the RAMP/JOSM monitoring database can be utilized to interpret post-industrial metal concentrations against pre-industrial values. This has important implications for JOSM as they work towards developing a more strategic monitoring framework in the AOSR that encompasses an understanding of natural and industrial sources of contaminants and their pathways of release to the environment, and that situates that information in an understanding of decadal from multi-decadal variability.

### *5.3 Future recommendations*

The new JOSM monitoring plan aims to establish long-term monitoring sites to more effectively evaluate trends in anthropogenic influence across the region. It is recommended that the focus of future sediment sampling should be on suspended sediment at key locations along the Athabasca River, given that such data can be compared to the pre-industrial floodplain baselines to detect and quantify contaminant enrichment and evaluate trends. This is the finer-grained sediment that will end up being deposited in the floodplain lakes and other slow-moving depositional areas and will bind more of the metals that enter the river, and is therefore more representative than the coarser-grained river-bottom sediment. In addition to focusing on suspended sediment along the Athabasca mainstem, it is recommended that spring be chosen as a key sampling time as well. Currently, suspended sediment data are only available from the winter, fall, and summer. This is not as useful in assessing river contaminant loadings, as expected river loadings are lower. Spring sampling of river sediment could be a way to

potentially detect influxes of contaminated snowpack to the Athabasca River, and assess the concentrations of contaminants in river sediment. The spring and early summer is also the peak time of exposure risk for aquatic organisms during sensitive life stages, and therefore a key period to assess potential risks to vulnerable river species (Colavecchia *et al*., 2007). Due to hazardous conditions along the river when it is ice jamming, which would make sampling the river dangerous to people and equipment, flood sediment deposited on levees and the adjacent floodplain of the river shortly after floodwaters recede might be the best course of action. The flood deposit sample analyzed in this study, from the 2017 spring flood, demonstrated this application. In this sample, collected at an upstream site ~30 km from AR6, the ratios of the metals of interest were consistent with the baseline linear regression. Analysis of flood deposit samples more proximal to, and downstream of, industrial activity would be a key next step.

The normalized V and Ni baselines established in this study provide a starting point to evaluate river monitoring data collected in the past, present, and future, for evidence of pollution. Expanding on this method, baselines could be developed for other metals of interest, as well as PAHs. Paleolimnology studies at additional floodplain lakes in the AOSR are also recommended, to provide additional pre-industrial river information to the baseline. In this study, a binary approach to generally defining sediment flooding intervals was applied, using simple methods of loss-on-ignition and organic carbon and nitrogen elemental analyses. Future studies could employ Bayesian mixing models (e.g., MixSIAR, an open-source R package for mixing systems) to more accurately determine the relative source proportion contributions of autochthonous and allochthonous sediment at a finer scale (for example, Stock *et al*., 2018). The use of suspended sediment as a river end member, as opposed to river-bottom sediment, should be explored as this is likely more representative of the type of sediment that ultimately ends up in

the floodplain lakes. Paleolimnological investigations could also continue in the floodplains along some of the major tributaries of the Athabasca River, including the Steepbank, Muskeg, Mackay, Ells, and Firebag rivers. Sites downstream of tributaries remain valuable in assessing contaminant concentrations delivered by the tributaries, but as this study determined, they may not be comparable to the floodplain lakes pre-industrial baselines which reflect the Athabasca River mainstem. From examination of the tributaries on Google Earth, there appear to be a few options for floodplain lakes to core, particularly several kilometers upstream, and away from the AOSR, which could provide an adequate control. Sediment monitoring along the tributaries could then be applied to baselines that better reflect the natural geology of the tributaries.

The missing knowledge of pre-industrial Athabasca River contaminant concentrations has been a key area of concern surrounding the interpretation of river monitoring data in the AOSR for decades. Today, the combined influences of multiple environmental stressors (e.g., climate change, declining river discharge) with industrial expansion, provide more incentive than ever to understand natural variation in this river system. According to Reuther (2009), effective monitoring involves choosing meaningful and achievable objectives, and designing a proper strategy and method. As the JOSM program continues to grow its monitoring scope, evolve with modern monitoring practices, and adapt to new scientific findings from monitoring activities, the governments of Alberta and Canada should continue to evaluate and interpret monitoring data in a long-term context whenever possible. Surface sediments from the floodplain lakes used in this study can continue to be collected and assessed for trends in aerial deposition and as markers of changing river dynamics. As well, following any efforts to better store and control petcoke in the AOSR, it would be interesting to monitor potential changes in sediment and water chemistry in proximal aquatic ecosystems (e.g., Down 1). If we continue to monitor the same locations

consistently, seasonal and yearly trends in contaminants can be evaluated, especially if the oil sands industry implements beneficial changes and wants to know if these changes are having a positive impact.

River systems are complex and dynamic, and no one monitoring site or event is going to be representative of the whole river, with all its seasonal changes. Monitoring of the Athabasca River in the AOSR must be strategic in its efforts to establish representative monitoring sites and frame modern monitoring data in a long-term perspective. Oil sands industrial activities are projected to keep expanding (CAPP, 2018c), and knowledge of natural, baseline conditions in AOSR aquatic ecosystems is of utmost importance for the evaluation of pollution. In demonstrating the application of regional-specific Athabasca River sediment-metal baselines, the state of knowledge of pre-industrial conditions for the Athabasca River has been advanced, setting a new model for the future of river monitoring in the AOSR.

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## Appendix A – Study site information

**Table A1. Lake coring coordinates (latitude and longitude) for floodplain lakes Up 17, Up 10, Down 1, Down 26, and Down 58, and headwater lakes cored with the JOSM program NE13, NE20, and RAMP 418/Kearle.**

| Site ID | Latitude | Longitude |
|---|---|---|
| Up 17 | 56.85278 | -111.4333 |
| Up 10 | 56.96111 | -111.4372 |
| Down 1 | 57.02500 | -111.4847 |
| Down 26 | 57.21806 | -111.6044 |
| Down 58 | 57.52417 | -111.5231 |
| NE13 (JOSM) | 57.07117 | -111.4752 |
| NE20 (JOSM) | 57.12517 | -111.5575 |
| RAMP 418/ Kearle (JOSM) | 57.29180 | -111.2383 |

**Table A2. RAMP & JOSM river sediment sampling locations (latitude and longitude) for river-bottom and suspended sediment.**

| Site ID | Monitoring Agency | Sediment type | Latitude | Longitude |
|---|---|---|---|---|
| ATR-DD-W | RAMP | River-bottom | 57.45273 | -111.616 |
| ATR-MR-W | RAMP | River-bottom | 57.13019 | -111.608 |
| ATR-DD-E | RAMP | River-bottom | 57.4516 | -111.605 |
| ATR-MR-E | RAMP | River-bottom | 57.1319 | -111.603 |
| ATR-ER | RAMP | River-bottom | 58.35332 | -111.542 |
| ATR-SR-W | RAMP | River-bottom | 57.01536 | -111.481 |
| ATR-SR-E | RAMP | River-bottom | 57.01927 | -111.479 |
| ATR-DC-W | RAMP | River-bottom | 56.82655 | -111.408 |
| ATR-DC-E | RAMP | River-bottom | 56.82644 | -111.408 |
| ATR-UFM | RAMP | River-bottom | 56.71833 | -111.403 |
| ATR-FR-W | RAMP | River-bottom | 57.74684 | -111.369 |
| ATR-FC-E | RAMP | River-bottom | 57.40829 | -111.641 |
| ATR-DC-CC | RAMP | River-bottom | 56.82656 | -111.409 |
| ATR-FC-CC-D | RAMP | River-bottom | 57.40902 | -111.645 |
| ATR-FC-E-D | RAMP | River-bottom | 57.40959 | -111.64 |
| ATR-MR-W-D | RAMP | River-bottom | 57.1323 | -111.609 |
| ATR-MR-E-D | RAMP | River-bottom | 57.13303 | -111.605 |
| M0 | JOSM | Suspended sediment | 54.72363 | -113.29 |
| M2 | JOSM | Suspended sediment | 56.7186 | -111.409 |
| M3 | JOSM | Suspended sediment | 56.83859 | -111.415 |
| M4 | JOSM | Suspended sediment | 57.12697 | -111.602 |
| M9 | JOSM | Suspended sediment | 58.17258 | -111.366 |
| M0 | JOSM | River-bottom | 54.72691 | -113.302 |
| M1 | JOSM | River-bottom | 56.68025 | -111.508 |
| M2 | JOSM | River-bottom | 56.75048 | -111.397 |
| M3 | JOSM | River-bottom | 56.83536 | -111.417 |
| M4 | JOSM | River-bottom | 57.09341 | -111.565 |
| M6 | JOSM | River-bottom | 57.19812 | -111.618 |
| M7C | JOSM | River-bottom | 57.50351 | -111.546 |
| M8 | JOSM | River-bottom | 57.67897 | -111.406 |
| M9 | JOSM | River-bottom | 58.05738 | -111.371 |

**Table A3. RAMP/JOSM sample site name location descriptors (sources: Hatfield Consultants, 2009; Wrona & diCenzo, 2011).**

| Site ID | Location description | Monitoring Agency |
|---|---|---|
| ATR-DD-W | Downstream of development (DD), West bank (W) | RAMP |
| ATR-MR-W | Upstream of Muskeg River (MR), West bank (W) | RAMP |
| ATR-DD-E | Downstream of development (DD), East bank (E) | RAMP |
| ATR-MR-E | Upstream of Muskeg River (MR), East bank (E) | RAMP |
| ATR-ER | Upstream of Embarras River (ER) | RAMP |
| ATR-SR-W | Upstream of Steepbank River (SR), West bank (W) | RAMP |
| ATR-SR-E | Upstream of Steepbank River (SR), East bank (E) | RAMP |
| ATR-DC-W | Upstream of Donald Creek (DC), West bank (W) | RAMP |
| ATR-DC-E | Upstream of Donald Creek (DC), East bank (E) | RAMP |
| ATR-UFM | Upstream of Fort McMurray (UFM) | RAMP |
| ATR-FR-W | Upstream of Firebag River (FR), West bank (W) | RAMP |
| ATR-FC-E | Upstream of Fort Creek (FC), East bank (E) | RAMP |
| ATR-DC-CC | Upstream of Donald Creek (DC), composite sample (CC) | RAMP |
| ATR-FC-CC-D | Downstream of Fort Creek (FC), composite sample (CC) | RAMP |
| ATR-FC-E-D | Downstream of Fort Creek (FC), East bank (E) | RAMP |
| ATR-MR-W-D | Downstream of Muskeg River (MR), West bank (W) | RAMP |
| ATR-MR-E-D | Downstream of Muskeg River (MR), East bank (E) | RAMP |
| M0 | U/S of Ft. McMurray: Athabasca River at Athabasca | JOSM |
| M1 | U/S of Ft. McMurray: Athabasca River at Mountain Rapids | JOSM |
| M2 | U/S of Ft. McMurray (formerly: ATR-UFM) | JOSM |
| M3 | D/S Ft. McMurray, U/S oil sands (formerly: ATR-DC) | JOSM |
| M4 | D/S of Steepbank R, U/S of Muskeg R (formerly: ATR-MR) | JOSM |
| M5 | D/S of Muskeg R, U/S of MacKay R | JOSM |
| M6 | D/S of MacKay R, U/S of Ells R | JOSM |
| M7C | D/S of Ells R, U/S of Tar R | JOSM |
| M8 | D/S of Calumet R, U/S of Firebag R (formerly: ATR-FR) | JOSM |
| M9 | D/S of Firebag and near Embarras Airport | JOSM |

**Table A4. YSI probe (YSI ProDSS) data for limnological measurements taken at floodplain lakes at the time of coring for Up 17, Down 1, Down 26, Down 58 (October 2016) and Up 10 (July 2017 – denoted by a *). N/A = indicates measurement was below detection limit of the probe.**

| Lake ID | Depth (m) | Temperature (ºC) | pH | Dissolved oxygen (%) | Turbidity (FNU) | Specific conductivity (µS/cm) |
|---|---|---|---|---|---|---|
| Up 17 | 1.4 | 8.3 | 7.87 | 66.5 | 1.0 | 762.0 |
| Up 10* | 4.7 | 25.2 | 8.43 | 121.7 | N/A | 740.0 |
| Down 1 | 0.6 | 6.9 | 7.93 | 77.9 | 4.3 | 757.2 |
| Down 26 | N/A | 7.0 | 8.21 | 63.7 | 16.3 | 864.0 |
| Down 58 | 1.3 | 6.4 | 8.20 | 68.1 | 4.0 | 403.5 |

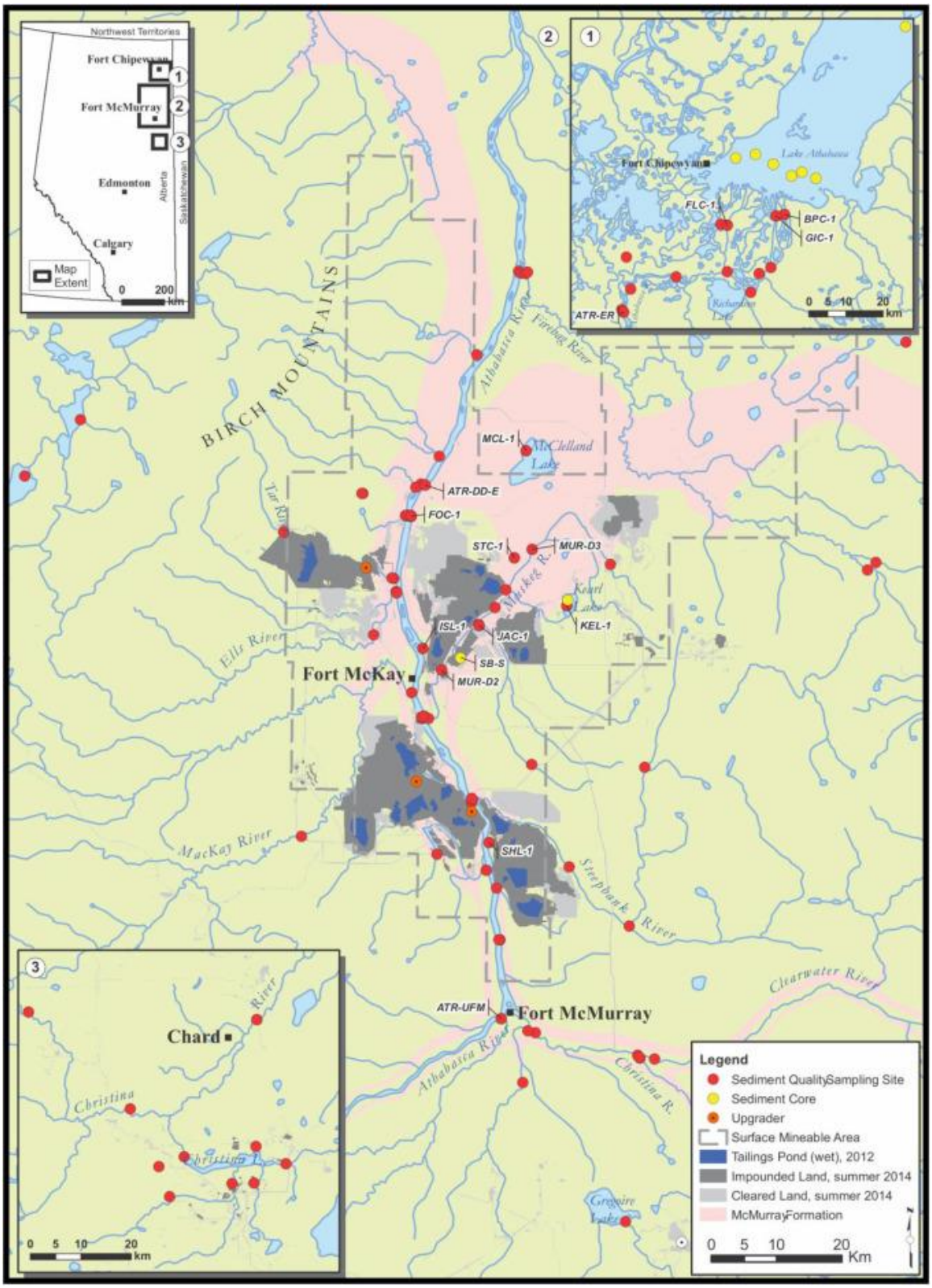


**Figure A1. Map of the RAMP monitoring area (1997-2014) with sediment sampling locations indicated (red dots) (Hatfield Consultants, 2015).**

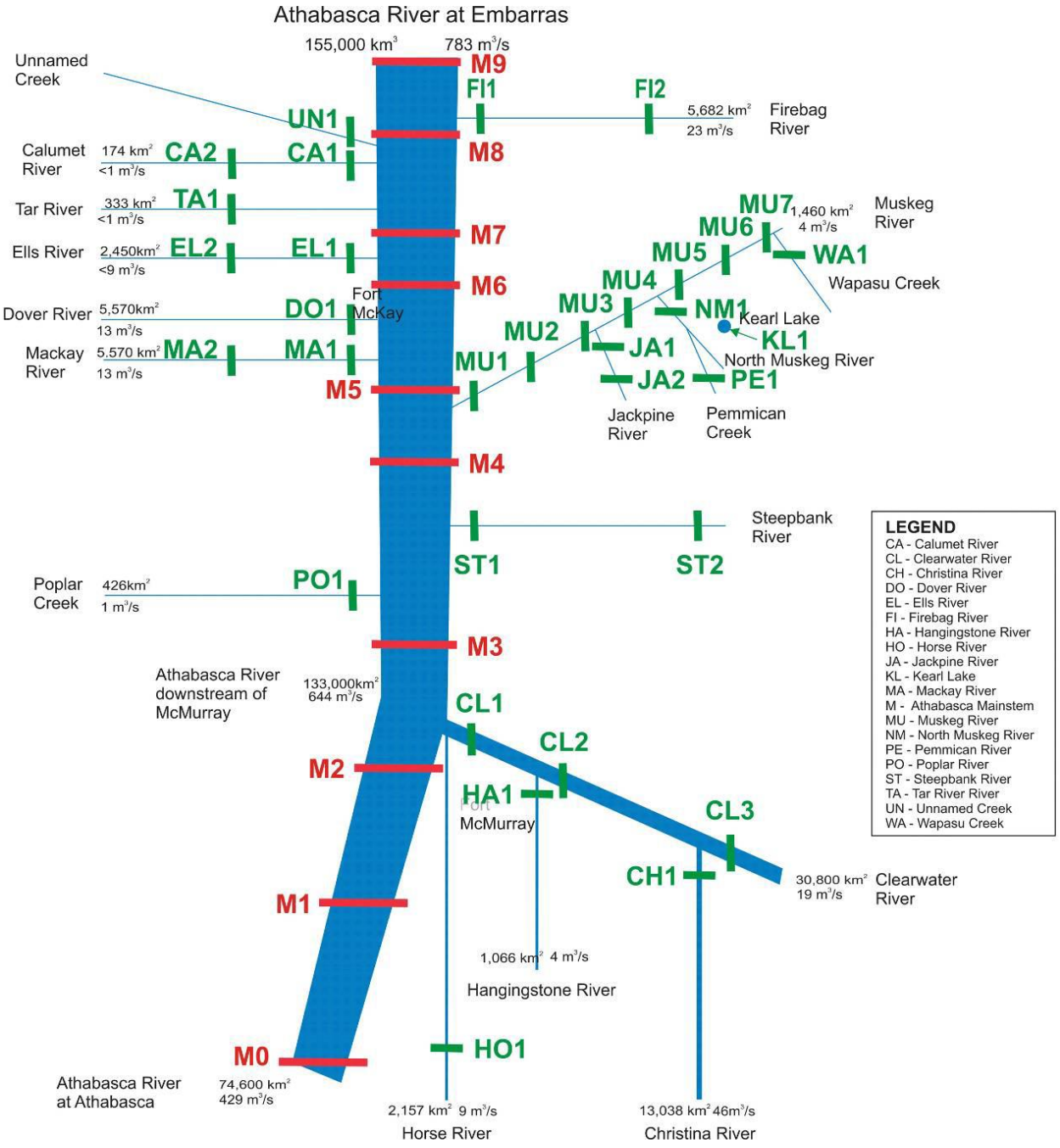


**Figure A2. Schematic of the sampling site locations along the Athabasca River and key tributaries proposed for JOSM in the Phase 1 Water Quality Monitoring Plan for the Lower Athabasca (Wrona & DiCenzo, 2011).**

## Appendix B – Compiled loss-on-ignition & organic carbon and nitrogen elemental and isotope composition data and graphs

**Table B1. Up 17: LOI data (water content (% $H_2O$), organic matter (% OM), mineral matter (%MM), and calcium carbonate (%$CaCO_3$)) and carbon & nitrogen data (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) by CRS year (constant rate of supply).**

| Depth (cm) | CRS year | % $H_2O$ | % OM | % MM | % $CaCO_3$ | % C | % N | C/N | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2016 | 94.1211 | 18.2724 | 69.4352 | 27.9372 | 10.3323 | 1.0127 | 10.2023 | -28.303 | -0.4429 |
| 2 | 2016 | 89.3226 | 19.3548 | 74.552 | 13.8482 | 10.3323 | 1.0127 | 10.2023 | -28.303 | -0.4429 |
| 3 | 2015 | 80.036 | 16.6499 | 77.6329 | 12.9935 | 7.4578 | 0.7048 | 10.5808 | -28.4305 | -0.155 |
| 4 | 2014 | 73.8406 | 13.4799 | 81.0256 | 12.4875 | 6.4024 | 0.5719 | 11.1948 | -28.3448 | 0.3645 |
| 5 | 2013 | 71.5757 | 12.987 | 80.7245 | 14.2919 | 5.9972 | 0.5606 | 10.6971 | -28.6529 | 0.1821 |
| 6 | 2012 | 71.5962 | 11.5385 | 79.2735 | 20.8819 | 6.2068 | 0.6138 | 10.1126 | -28.7638 | -0.0896 |
| 7 | 2010 | 73.0339 | 11.1508 | 79.0565 | 22.2562 | 5.654 | 0.5574 | 10.144 | -29.0282 | 0.3711 |
| 8 | 2009 | 74.7919 | 15.745 | 75.4992 | 19.8995 | 6.1135 | 0.5955 | 10.2655 | -29.167 | 0.2557 |
| 9 | 2007 | 79.0495 | 17.037 | 73.7037 | 21.0438 | 8.6135 | 0.7984 | 10.7879 | -29.6995 | 0.2738 |
| 10 | 2005 | 80.7494 | 20.4943 | 70.1339 | 21.2995 | 11.8618 | 1.0756 | 11.0283 | -29.9332 | 0.0539 |
| 11 | 2003 | 81.064 | 24.7578 | 66.6308 | 19.5714 | 12.3973 | 1.1091 | 11.178 | -29.8941 | -0.00221 |
| 12 | 2001 | 79.5308 | 23.5912 | 68.3859 | 18.2339 | 13.4727 | 1.1759 | 11.4578 | -29.2432 | -0.21 |
| 13 | 1999 | 78.1375 | 23.5832 | 67.8245 | 19.528 | 10.7329 | 1.0122 | 10.6035 | -28.5558 | -0.3018 |
| 14 | 1997 | 77.3805 | 23.6234 | 67.4956 | 20.1841 | 10.7779 | 1.0149 | 10.6193 | -28.3998 | -0.2002 |
| 15 | 1994 | 71.9807 | 18.8937 | 71.3362 | 22.2048 | 9.5854 | 0.9061 | 10.5782 | -28.555 | 0.1072 |
| 16 | 1992 | 69.068 | 17.263 | 72.6303 | 22.9698 | 10.4618 | 0.9632 | 10.8619 | -28.1446 | -0.1867 |
| 17 | 1990 | 61.8094 | 12.6834 | 79.2453 | 18.3438 | 8.1259 | 0.7519 | 10.8072 | -29.3539 | 0.0105 |
| 18 | 1987 | 53.5656 | 10.4871 | 85.0812 | 10.0722 | 5.5654 | 0.5166 | 10.7733 | -28.5005 | 0.0169 |
| 19 | 1986 | 54.3229 | 12.1435 | 83.7943 | 9.2323 | 5.3102 | 0.4082 | 13.0076 | -27.7294 | 0.7783 |
| 20 | 1984 | 54.4896 | 10.8885 | 84.9303 | 9.5027 | 4.3541 | 0.3384 | 12.8677 | -27.5071 | 0.6457 |
| 21 | 1981 | 49.9032 | 11.0166 | 85.5431 | 7.8188 | 4.8464 | 0.3634 | 13.3354 | -27.5348 | 1.0958 |
| 22 | 1979 | 51.659 | 11.4525 | 84.6369 | 8.8878 | 4.8341 | 0.376 | 12.8568 | -27.5898 | 0.7788 |
| 23 | 1977 | 53.2727 | 10.7067 | 84.1727 | 11.6377 | 4.4505 | 0.3611 | 12.3245 | -27.6967 | 0.8224 |
| 24 | 1975 | 59.1027 | 11.7532 | 80.5583 | 17.474 | 5.9766 | 0.5053 | 11.828 | -28.074 | 0.2331 |
| 25 | 1972 | 56.8244 | 11.4504 | 78.8505 | 22.0435 | 4.8565 | 0.4196 | 11.5745 | -28.0792 | 0.3445 |
| 26 | 1970 | 53.5832 | 9.8211 | 81.3983 | 19.9561 | 5.1565 | 0.4243 | 12.152 | -27.9433 | 0.1498 |
| 27 | 1966 | 50.3479 | 9.3032 | 83.7291 | 15.8357 | 4.4799 | 0.3749 | 11.9483 | -27.8767 | 0.6778 |
| 28 | 1963 | 49.8118 | 9.7908 | 83.4189 | 15.4327 | 4.033 | 0.3259 | 12.3768 | -28.0199 | 1.2858 |
| 29 | 1960 | 50.1777 | 10.0238 | 83.7163 | 14.2271 | 3.9968 | 0.3305 | 12.0916 | -28.0063 | 0.4961 |
| 30 | 1957 | 52.6584 | 10.9725 | 83.4337 | 12.7132 | 4.231 | 0.3322 | 12.7358 | -28.0209 | 1.4351 |
| 31 | 1955 | 58.5022 | 15.6744 | 78.8372 | 12.4736 | 4.4704 | 0.3401 | 13.1432 | -27.9903 | 0.9647 |
| 32 | 1951 | 49.6467 | 10.2646 | 84.2823 | 12.3934 | 4.0702 | 0.3237 | 12.5756 | -27.9171 | 1.6205 |
| 33 | 1948 | 50.0193 | 9.726 | 85.0251 | 11.9294 | 4.6564 | 0.349 | 13.3421 | -28.2443 | 1.6437 |
| 34 | 1946 | 49.8275 | 13.5652 | 81.3527 | 11.5504 | 3.4341 | 0.2608 | 13.1659 | -27.6419 | 1.4785 |
| 35 | 1944 | 41.933 | 8.7392 | 86.9913 | 9.7034 | 2.9862 | 0.212 | 14.0858 | -27.5366 | 1.8329 |
| 36 | 1939 | 37.5662 | 7.8206 | 88.057 | 9.3692 | 2.678 | 0.1921 | 13.9388 | -27.1329 | 2.6147 |
| 37 | 1928 | 39.1279 | 7.5472 | 87.7199 | 10.7568 | 3.1175 | 0.2362 | 13.2002 | -27.4509 | 2.2597 |
| 38 | 1923 | 40.7443 | 8.0703 | 86.6254 | 12.0551 | 2.6929 | 0.2114 | 12.7355 | -27.1775 | 1.7803 |
| 39 | 1918 | 42.0929 | 8.5637 | 86.0755 | 12.1835 | 3.8345 | 0.2857 | 13.4211 | -27.5768 | 1.3569 |
| 40 | 1914 | 41.6266 | 9.5058 | 85.4839 | 11.387 | 3.9581 | 0.3084 | 12.835 | -27.3873 | 1.5103 |
| 41 | 1910 | 40.8774 | 9.5447 | 85.43 | 11.4211 | 4.1728 | 0.324 | 12.8777 | -27.3875 | 1.3806 |
| 42 | 1905 | 40.2008 | 9.8805 | 85.5021 | 10.494 | 3.8419 | 0.2972 | 12.9276 | -27.4478 | 1.3341 |
| 43 | 1901 | 37.7161 | 8.575 | 86.5606 | 11.0554 | 3.7196 | 0.2787 | 13.3445 | -27.5638 | 1.4817 |

**Table B2. Up 10: LOI data (water content (% $H_2O$), organic matter (% OM), mineral matter (%MM), and calcium carbonate (%$CaCO_3$)) and carbon & nitrogen data (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) by CRS year (constant rate of supply).**

| Depth (cm) | CRS year | % $H_2O$ | % OM | % MM | % $CaCO_3$ | % C | % N | C/N | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2016 | 93.5286 | 28.1346 | 67.8899 | 9.0353 | 14.3238 | 1.3552 | 10.5698 | -33.1413 | -1.1686 |
| 2 | 2013 | 86.7061 | 18.3976 | 76.8546 | 10.7904 | 9.7216 | 0.8592 | 11.3147 | -32.6601 | -0.9595 |
| 3 | 2010 | 91.0667 | 26.226 | 68.0171 | 13.0839 | 14.2418 | 1.3267 | 10.7346 | -32.6879 | -0.8129 |
| 4 | 2005 | 90.4149 | 21.0421 | 73.9479 | 11.3864 | 11.1827 | 1.0863 | 10.2943 | -31.1288 | -1.0873 |
| 5 | 1996 | 89.7886 | 23.0469 | 72.0703 | 11.0973 | 11.2754 | 1.0664 | 10.5734 | -31.384 | -0.5744 |
| 6 | 1990 | 85.0219 | 17.4434 | 77.6298 | 11.1972 | 8.3979 | 0.7503 | 11.1927 | -31.1063 | -0.2934 |
| 7 | 1983 | 81.0407 | 13.9853 | 81.4932 | 10.2763 | 5.8471 | 0.5266 | 11.1036 | -30.0392 | -0.4886 |
| 8 | 1974 | 77.2208 | 11.215 | 84.537 | 9.6547 | 5.792 | 0.443 | 13.073 | -30.1662 | -0.1703 |
| 9 | 1963 | 74.3907 | 11.9335 | 81.9486 | 13.9041 | 4.1373 | 0.3721 | 11.1201 | -29.2748 | 0.2755 |
| 10 | 1950 | 70.9029 | 11.0731 | 84.689 | 9.6315 | 4.7011 | 0.3988 | 11.788 | -28.4878 | 0.6204 |
| 11 | 1940 | 64.5059 | 8.6275 | 86.6667 | 10.6952 | 2.753 | 0.2405 | 11.4478 | -29.2016 | 0.3033 |
| 12 | 1928 | 69.2369 | 10.9819 | 84.3669 | 10.5708 | 7.225 | 0.5785 | 12.4894 | -29.1765 | 0.2694 |
| 13 | 1911 | 53.8837 | 8.1253 | 88.0237 | 8.7524 | 2.2971 | 0.1788 | 12.8473 | -29.0642 | -0.0957 |
| 14 | 1885 | 49.7631 | 8.055 | 88.055 | 8.8409 | 3.6602 | 0.1848 | 19.8073 | -28.2842 | 0.8843 |
| 15 | 1867 | 59.7225 | 7.3819 | 88.9272 | 8.3885 | 2.9332 | 0.1519 | 19.3039 | -27.6987 | 0.9401 |
| 16 | 1850 | 64.4849 | 8.5189 | 87.6949 | 8.605 | 2.6219 | 0.1838 | 14.2642 | -27.8348 | 0.4998 |
| 17 | 1832 | 62.0608 | 7.8493 | 87.9644 | 9.5143 | 2.2991 | 0.1833 | 12.5457 | -27.9862 | 0.6693 |
| 18 | 1818 | 73.9629 | 16.2261 | 79.2952 | 10.1789 | 2.4673 | 0.1799 | 13.7166 | -30.0461 | 0.8022 |
| 19 | 1805 | 66.1478 | 9.4878 | 86.3795 | 9.3925 | 4.1418 | 0.3045 | 13.6 | -31.787 | 0.3877 |
| 20 | 1779 | 53.2829 | 5.9625 | 90.4174 | 8.2275 | 2.5019 | 0.1479 | 16.9159 | -27.7153 | 0.8527 |
| 21 | 1760 | 61.3018 | 8.002 | 88.0224 | 9.0353 | 2.8234 | 0.2102 | 13.4305 | -28.3146 | 0.4252 |
| 22 | 1739 | 59.1697 | 7.6026 | 87.6866 | 10.7064 | 2.7445 | 0.2194 | 12.507 | -28.0447 | 0.3849 |
| 23 | 1721 | 65.6536 | 8.4442 | 86.7553 | 10.9101 | 2.8925 | 0.2371 | 12.2013 | -28.1503 | 0.1318 |
| 24 | 1705 | 66.9826 | 8.433 | 87.1411 | 10.0587 | 3.0868 | 0.2647 | 11.6606 | -29.8803 | 0.4086 |
| 25 | 1687 | 62.1732 | 7.7317 | 87.5064 | 10.8225 | 2.329 | 0.1939 | 12.0114 | -27.4873 | 0.6836 |
| 26 | 1669 | 61.7405 | 7.8381 | 86.8852 | 11.9924 | 2.5803 | 0.212 | 12.174 | -27.1749 | 0.4135 |
| 27 | 1651 | 63.2111 | 8.9978 | 86.7996 | 9.5513 | 2.8406 | 0.237 | 11.9834 | -27.1505 | 0.637 |
| 28 | 1632 | 60.1614 | 7.6181 | 86.837 | 12.6019 | 2.3985 | 0.1907 | 12.5786 | -26.863 | 1.0141 |
| 29 | 1610 | 54.5847 | 6.8742 | 87.1595 | 13.5597 | 1.9546 | 0.1478 | 13.2244 | -29.2688 | 1.4358 |
| 30 | 1592 | 59.6065 | 7.9274 | 87.8701 | 9.5511 | 2.2697 | 0.176 | 12.8927 | -27.1436 | 0.7173 |
| 31 | 1575 | 63.8744 | 8.5288 | 87.7932 | 8.3592 | 2.8548 | 0.2339 | 12.203 | -27.519 | 0.8431 |
| 32 | 1557 | 60.7828 | 7.5099 | 88.6364 | 8.7585 | 3.2579 | 0.2469 | 13.1928 | -27.5141 | 0.8138 |
| 33 | 1534 | 53.7111 | 7.3372 | 89.1179 | 8.0567 | 2.7299 | 0.1742 | 15.6688 | -27.3257 | 0.8041 |
| 34 | 1508 | 51.8746 | 8.2028 | 87.8401 | 8.9935 | 3.6134 | 0.253 | 14.2831 | -28.2025 | 0.1868 |
| 35 | 1492 | 63.8983 | 10.1266 | 85.3605 | 10.2567 | 4.3997 | 0.3246 | 13.5556 | -28.653 | 0.4216 |
| 36 | 1479 | 71.6864 | 11.6518 | 84.4414 | 8.8791 | 4.9741 | 0.4414 | 11.268 | -29.337 | -0.0252 |
| 37 | 1468 | 73.8219 | 11.7468 | 83.9817 | 9.7081 | 4.8785 | 0.4251 | 11.4761 | -28.5162 | 0.2915 |
| 38 | 1452 | 70.1737 | 10.2581 | 85.2416 | 10.228 | 3.4441 | 0.2954 | 11.6606 | -27.9261 | 0.4454 |
| 39 | 1432 | 58.5568 | 7.3739 | 88.059 | 10.3797 | 2.4651 | 0.1936 | 12.7308 | -27.2154 | 0.9448 |
| 40 | 1410 | 57.9434 | 7.5269 | 88.172 | 9.7752 | 2.2785 | 0.1832 | 12.4371 | -26.8741 | 1.7251 |
| 41 | 1390 | 59.4046 | 7.6736 | 87.8096 | 10.2654 | 1.9642 | 0.1592 | 12.337 | -26.4038 | 2.0099 |
| 42 | 1368 | 55.571 | 7.1652 | 87.5952 | 11.9082 | 2.2346 | 0.1652 | 13.5248 | -26.8466 | 1.3926 |
| 43 | 1348 | 51.0993 | 6.8647 | 87.3143 | 13.2294 | 2.0085 | 0.1485 | 13.5256 | -26.507 | 1.4316 |
| 44 | 1329 | 59.0402 | 8.4103 | 87.3116 | 9.7229 | 2.5102 | 0.1906 | 13.173 | -29.172 | 0.8973 |
| 45 | 1311 | 61.7924 | 8.832 | 87.8378 | 7.5684 | 3.2827 | 0.2668 | 12.3038 | -28.0423 | 0.5583 |
| 46 | 1294 | 59.9009 | 8.3045 | 87.8893 | 8.6505 | 2.8888 | 0.2293 | 12.5992 | -27.9372 | 0.7961 |
| 47 | 1275 | 60.462 | 8.5249 | 87.5 | 9.0343 | 2.7599 | 0.2094 | 13.1817 | -27.4641 | 0.7063 |
| 48 | 1257 | 61.6332 | 9.0864 | 86.4691 | 10.101 | 3.085 | 0.2519 | 12.2479 | -27.8385 | 0.1414 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 49 | 1241 | 61.8157 | 9.7959 | 85.8163 | 9.9722 | 3.3576 | 0.266 | 12.6235 | -27.7828 | 0.659 |
| 50 | 1221 | 65.1949 | 10.4 | 86.2286 | 7.6623 | 4.1296 | 0.3087 | 13.3758 | -28.2386 | 0.6884 |
| 51 | 1204 | 64.9551 | 10.1307 | 85.8932 | 9.0364 | 3.5188 | 0.2768 | 12.7115 | -28.3241 | 0.4334 |
| 52 | 1186 | 61.2672 | 9.7549 | 86.1931 | 9.2092 | 2.9721 | 0.2349 | 12.6538 | -30.0885 | 0.5887 |
| 53 | 1165 | 53.9722 | 7.3675 | 89.1142 | 7.9959 | 2.5059 | 0.1734 | 14.4531 | -27.2789 | 1.0843 |
| 54 | 1141 | 52.0191 | 6.5417 | 89.6689 | 8.6122 | 2.2589 | 0.1542 | 14.6511 | -28.5449 | 0.7425 |
| 55 | 1117 | 53.4169 | 7.1459 | 88.9029 | 8.9801 | 2.3608 | 0.1565 | 15.0806 | -27.0472 | 0.9786 |
| 56 | 1093 | 53.7251 | 8.136 | 88.1188 | 8.5117 | 2.4239 | 0.1561 | 15.5297 | -28.1993 | 1.1148 |
| 57 | 1072 | 54.2184 | 7.6187 | 88.4324 | 8.9749 | 2.3193 | 0.1523 | 15.2278 | -27.0107 | 0.6787 |
| 58 | 1047 | 52.3151 | 7.7357 | 87.5907 | 10.6219 | 2.3026 | 0.1736 | 13.2625 | -26.7606 | 1.8609 |
| 59 | 1022 | 47.796 | 6.9322 | 87.9056 | 11.7324 | 2.2675 | 0.1677 | 13.5203 | -26.8744 | 1.4088 |
| 60 | 1001 | 53.6135 | 8.8061 | 87.0449 | 9.4296 | 2.6874 | 0.176 | 15.2663 | -27.2915 | 1.2547 |
| 61 | 978 | 59.241 | 10.6208 | 85.742 | 8.2665 | 4.1619 | 0.2803 | 14.8485 | -28.6151 | -0.5483 |
| 62 | 967 | 60.8945 | 10.7794 | 85.1215 | 9.3163 | 4.0766 | 0.3109 | 13.1122 | -28.9925 | 0.1252 |

**Table B3. Down 1: LOI data (water content (% $H_2O$), organic matter (% OM), mineral matter (%MM), and calcium carbonate (%$CaCO_3$)) and carbon & nitrogen data (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) by CRS year (constant rate of supply).**

| Depth (cm) | CRS year | % $H_2O$ | % OM | % MM | % $CaCO_3$ | % C | % N | C/N | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2015 | 93.7166 | 34.7003 | 61.1987 | 9.3203 | 20.4205 | 1.6387 | 12.4617 | -28.4995 | -0.9126 |
| 2 | 2014 | 92.4586 | 34.4388 | 61.4796 | 9.2764 | 20.3297 | 1.6084 | 12.6397 | -28.6843 | -1.0473 |
| 3 | 2014 | 89.7639 | 35.2713 | 61.6279 | 7.0472 | 19.0754 | 1.4703 | 12.9738 | -28.5475 | -1.3132 |
| 4 | 2012 | 90.1232 | 36.6337 | 58.6139 | 10.8011 | 21.8254 | 1.6312 | 13.3804 | -28.557 | -0.7776 |
| 5 | 2011 | 92.2685 | 43.2911 | 53.6709 | 6.9045 | 22.995 | 1.8661 | 12.3228 | -28.3471 | -0.8644 |
| 6 | 2009 | 90.4157 | 38.3534 | 58.4337 | 7.3019 | 22.1861 | 1.6569 | 13.3904 | -28.4227 | -1.0074 |
| 7 | 2008 | 88.2826 | 40.0335 | 57.4539 | 5.7104 | 22.6356 | 1.7242 | 13.128 | -28.3764 | -0.8234 |
| 8 | 2006 | 88.2159 | 36.9028 | 60.1318 | 6.7396 | 18.4385 | 1.2936 | 14.2537 | -28.6013 | -1.0416 |
| 9 | 2003 | 90.1656 | 35.9343 | 61.191 | 6.5335 | 21.0479 | 1.533 | 13.7302 | -28.4331 | -0.9458 |
| 10 | 2001 | 88.1135 | 36.1526 | 61.8574 | 4.5228 | 20.4404 | 1.4644 | 13.9584 | -28.4579 | -0.7688 |
| 11 | 1998 | 87.1161 | 33.7461 | 63.1579 | 7.0363 | 19.065 | 1.3896 | 13.7198 | -28.3279 | -0.8779 |
| 12 | 1996 | 87.3824 | 34.6273 | 62.5776 | 6.3523 | 19.4267 | 1.4207 | 13.6744 | -28.4887 | -0.9617 |
| 13 | 1992 | 85.387 | 34.5191 | 62.9776 | 5.6893 | 18.4963 | 1.3675 | 13.5254 | -28.2871 | -1.056 |
| 14 | 1988 | 85.3483 | 34.9669 | 62.649 | 5.4184 | 20.5382 | 1.6526 | 12.428 | -28.5929 | -0.8423 |
| 15 | 1985 | 80.0672 | 24.8016 | 72.3214 | 6.5386 | 12.1767 | 0.8753 | 13.9122 | -28.4131 | -0.7985 |
| 16 | 1983 | 70.7444 | 16.831 | 79.6844 | 7.9194 | 8.1982 | 0.5774 | 14.1996 | -28.2621 | -0.2563 |
| 17 | 1983 | 61.9648 | 12.9406 | 83.4298 | 8.2492 | 6.0259 | 0.4145 | 14.5382 | -28.0645 | -0.1164 |
| 18 | 1981 | 62.4597 | 12.4933 | 83.9142 | 8.1648 | 5.4798 | 0.3766 | 14.5521 | -27.8177 | -0.1365 |
| 19 | 1980 | 66.8802 | 15.1817 | 81.0668 | 8.5261 | 7.1767 | 0.4839 | 14.8303 | -28.0479 | -0.2556 |
| 20 | 1976 | 64.1352 | 14.8004 | 81.6519 | 8.0629 | 6.402 | 0.4377 | 14.628 | -28.1162 | -0.4714 |
| 21 | 1973 | 63.7495 | 15.5043 | 80.6867 | 8.6568 | 6.2151 | 0.4296 | 14.468 | -28.2163 | 0.0752 |
| 22 | 1969 | 58.9115 | 12.6152 | 83.3091 | 9.2629 | 6.547 | 0.4446 | 14.7246 | -27.8025 | 0.0808 |
| 23 | 1961 | 70.8509 | 21.5648 | 74.622 | 8.6665 | 9.468 | 0.6518 | 14.527 | -28.0788 | -0.3409 |
| 24 | 1955 | 74.1942 | 27.5991 | 69.1099 | 7.4794 | 14.1159 | 0.9722 | 14.5197 | -28.4424 | -0.0911 |
| 25 | 1951 | 64.7047 | 17.8866 | 78.1508 | 9.0059 | 10.1384 | 0.6967 | 14.5529 | -28.519 | -0.535 |
| 26 | 1945 | 66.1465 | 19.208 | 77.1277 | 8.328 | 9.5736 | 0.679 | 14.1001 | -28.6946 | -0.5686 |
| 27 | 1937 | 69.5306 | 22.5196 | 74.7389 | 6.2307 | 9.0072 | 0.6435 | 13.9963 | -28.5592 | -0.5044 |
| 28 | 1932 | 48.8641 | 11.3705 | 85.128 | 7.958 | 6.0885 | 0.4167 | 14.6103 | -28.6074 | 0.0577 |
| 29 | 1931 | 45.6206 | 9.1008 | 87.3601 | 8.0436 | 3.4256 | 0.2205 | 15.5327 | -28.0062 | 0.374 |
| 30 | 1929 | 52.0366 | 12.5965 | 84.356 | 6.9262 | 6.1861 | 0.4054 | 15.2587 | -27.7486 | -0.2159 |
| 31 | 1923 | 59.481 | 16.7488 | 79.803 | 7.837 | 7.3948 | 0.491 | 15.0597 | -27.7884 | 0.2747 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 32 | 1920 | 57.7598 | 18.3473 | 78.1979 | 7.8516 | 6.6881 | 0.4698 | 14.2374 | -27.6633 | -0.0484 |
| 33 | 1918 | 63.8528 | 19.8118 | 76.5357 | 8.3011 | 6.9081 | 0.456 | 15.1493 | -27.7143 | 0.1388 |
| 34 | 1916 | 57.3694 | 14.2468 | 82.2595 | 7.9401 | 6.8615 | 0.4529 | 15.1489 | -27.3867 | -0.1937 |
| 35 | 1913 | 81.7054 | 32.5212 | 65.2542 | 5.0559 | 12.0491 | 0.8176 | 14.7368 | -26.6586 | -1.4894 |
| 36 | 1905 | 71.2657 | 29.617 | 67.9891 | 5.4409 | 12.1232 | 0.7836 | 15.472 | -27.5946 | -0.247 |
| 37 | 1891 | 70.2857 | 28.7798 | 69.0981 | 4.8228 | 13.2171 | 0.8189 | 16.1409 | -27.6675 | -0.3392 |
| 38 | 1887 | 68.9595 | 27.0287 | 70.4744 | 5.6747 | 13.8263 | 0.8395 | 16.4697 | -28.7506 | -0.3237 |
| 39 | 1879 | 69.8368 | 25.5277 | 71.8338 | 5.9966 | 12.3519 | 0.7819 | 15.798 | -28.4841 | -0.224 |
| 40 | 1876 | 69.0593 | 27.3704 | 70.2276 | 5.4591 | 8.6389 | 0.4857 | 17.785 | -27.8892 | -0.3036 |
| 41 | 1872 | 71.5798 | 35.8835 | 62.3561 | 4.0007 | 13.5965 | 0.7819 | 17.3888 | -27.5346 | -0.502 |
| 42 | 1869 | 68.2343 | 27.7601 | 69.8787 | 5.3664 | 10.9936 | 0.6929 | 15.8658 | -28.2773 | -0.3808 |
| 43 | 1865 | 65.8613 | 24.4534 | 73.13 | 5.4922 | 11.6592 | 0.736 | 15.8417 | -27.9533 | -0.2151 |
| 44 | 1862 | 71.829 | 35.427 | 62.597 | 4.4909 | 13.1538 | 0.7467 | 17.6155 | -27.9426 | -0.0847 |
| 45 | 1859 | 70.6846 | 26.4468 | 71.5343 | 4.5883 | 12.5895 | 0.6784 | 18.5576 | -28.8508 | -0.0928 |
| 46 | 1855 | 70.8743 | 31.6766 | 66.1365 | 4.9702 | 12.64 | 0.7288 | 17.3447 | -28.4425 | 0.3797 |
| 47 | 1851 | 64.0703 | 26.2924 | 71.3174 | 9.03 | 12.7971 | 0.7392 | 17.3127 | -28.9897 | 0.1072 |
| 48 | 1848 | 66.8381 | 27.3866 | 69.8687 | 6.2378 | 12.8499 | 0.7388 | 17.3923 | -28.8149 | -0.2269 |
| 49 | 1844 | 71.1055 | 30.5017 | 67.291 | 5.0167 | 14.9883 | 0.9801 | 15.2931 | -28.3172 | -0.4071 |
| 50 | 1840 | 82.1907 | 42.146 | 54.9779 | 6.5366 | 23.1909 | 1.7388 | 13.3372 | -28.3307 | -0.8461 |
| 51 | 1836 | 69.2783 | 24.854 | 72.5503 | 5.8994 | 11.9012 | 0.8519 | 13.9707 | -27.7903 | -0.2914 |
| 52 | 1831 | 63.5366 | 19.5699 | 77.6882 | 6.2317 | 9.1884 | 0.6079 | 15.1157 | -27.9963 | -0.2053 |
| 53 | 1824 | 53.049 | 16.6384 | 81.0272 | 5.3056 | 8.162 | 0.4866 | 16.7727 | -27.664 | 0.171 |
| 54 | 1816 | 59.6293 | 20.509 | 77.2455 | 5.1034 | 8.3672 | 0.4997 | 16.7459 | -27.5036 | -0.1892 |

**Table B4: Down 26: LOI data (water content (% $H_2O$), organic matter (% OM), mineral matter (%MM), and calcium carbonate (%$CaCO_3$)) and carbon & nitrogen data (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) by CRS year (constant rate of supply).**

| Depth (cm) | CRS year | % $H_2O$ | % OM | % MM | % $CaCO_3$ | % C | % N | C/N | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2018 | 96.4441 | 41.6667 | 48.8889 | 21.4646 | 18.8608 | 2.2379 | 8.4278 | -29.3692 | 0.3681 |
| 2 | 2017 | 93.3307 | 34.6269 | 54.6269 | 24.4233 | 23.9066 | 2.7237 | 8.7772 | -30.1919 | 0.0666 |
| 3 | 2016 | 91.1597 | 27.1715 | 62.8062 | 22.7779 | 15.7192 | 1.672 | 9.4011 | -30.8543 | 0.1055 |
| 4 | 2014 | 79.4795 | 18.2962 | 76.3795 | 12.1007 | 8.405 | 0.7333 | 11.4625 | -29.6922 | 0.3792 |
| 5 | 2012 | 74.6893 | 16.9135 | 77.2408 | 13.2856 | 6.7584 | 0.5845 | 11.5633 | -29.5443 | 0.4211 |
| 6 | 2010 | 70.9722 | 17.3616 | 77.1018 | 12.5831 | 6.9404 | 0.5665 | 12.2508 | -29.1008 | 0.2444 |
| 7 | 2007 | 70.8523 | 16.1465 | 78.5617 | 12.0266 | 5.9815 | 0.4936 | 12.1187 | -28.7882 | 0.5294 |
| 8 | 2004 | 61.3721 | 13.5369 | 81.2723 | 11.7974 | 4.8947 | 0.3926 | 12.4679 | -28.3461 | 0.5397 |
| 9 | 2001 | 56.4545 | 11.5665 | 82.9235 | 12.5228 | 5.2986 | 0.4099 | 12.9275 | -28.1995 | 0.707 |
| 10 | 1998 | 63.8774 | 12.3437 | 82.9799 | 10.6283 | 4.61 | 0.3628 | 12.7079 | -28.0836 | 0.7018 |
| 11 | 1994 | 55.8865 | 11.101 | 83.4617 | 12.3574 | 4.0061 | 0.3061 | 13.0873 | -28.0109 | 0.6854 |
| 12 | 1990 | 60.404 | 12.0852 | 82.5656 | 12.1572 | 4.6666 | 0.3659 | 12.7537 | -28.3464 | 0.5525 |
| 13 | 1986 | 54.3042 | 11.0108 | 83.828 | 11.7302 | 5.0603 | 0.3884 | 13.0277 | -28.6378 | 0.4804 |
| 14 | 1982 | 44.1602 | 9.6591 | 85.902 | 10.0885 | 3.9132 | 0.2779 | 14.0798 | -28.1538 | 0.6738 |
| 15 | 1976 | 43.2782 | 9.4803 | 85.9902 | 10.2943 | 3.0114 | 0.2046 | 14.7171 | -27.7021 | 1.0276 |
| 16 | 1969 | 46.128 | 8.6909 | 86.2853 | 11.4178 | 2.727 | 0.1968 | 13.8569 | -27.6799 | 1.1301 |
| 17 | 1963 | 37.6057 | 6.8368 | 87.9647 | 11.8147 | 2.9701 | 0.2167 | 13.7041 | -27.7718 | 1.2325 |
| 18 | 1956 | 38.6462 | 7.4407 | 87.7806 | 10.8607 | 2.791 | 0.2005 | 13.9195 | -27.7325 | 0.8952 |
| 19 | 1949 | 35.7213 | 7.0116 | 87.1402 | 13.2912 | 2.4511 | 0.1714 | 14.3037 | -27.369 | 1.4056 |
| 20 | 1943 | 42.9481 | 10.251 | 84.3096 | 12.3621 | 2.739 | 0.1793 | 15.2735 | -27.6372 | 0.2022 |
| 21 | 1937 | 38.7895 | 7.7689 | 87.4799 | 10.7982 | 2.6265 | 0.1693 | 15.5117 | -27.7065 | 1.0331 |
| 22 | 1931 | 43.2347 | 8.2696 | 84.4336 | 16.5835 | 3.4964 | 0.2512 | 13.9168 | -28.5997 | 0.7675 |
| 23 | 1926 | 45.4979 | 9.4457 | 82.0204 | 19.3953 | 4.8227 | 0.3926 | 12.2851 | -29.2296 | 0.1607 |
| 24 | 1922 | 49.1894 | 10.7782 | 77.9767 | 25.5571 | 5.1355 | 0.4253 | 12.0745 | -29.5239 | 0.1294 |
| 25 | 1917 | 50.2367 | 11.2961 | 76.8133 | 27.0241 | 5.7333 | 0.4836 | 11.8553 | -29.582 | -0.1009 |
| 26 | 1913 | 51.3234 | 12.4693 | 76.1774 | 25.8028 | 7.6777 | 0.6382 | 12.0299 | -29.931 | -0.3813 |
| 27 | 1909 | 52.5464 | 13.2576 | 75.2525 | 26.1134 | 7.7604 | 0.6728 | 11.5339 | -30.1746 | -0.4725 |
| 28 | 1904 | 52.1163 | 15.2416 | 75.3408 | 21.4036 | 6.9082 | 0.5583 | 12.374 | -29.6903 | 0.1551 |
| 29 | 1899 | 46.1342 | 11.4754 | 80.4372 | 18.3805 | 4.4978 | 0.3305 | 13.6085 | -29.1192 | 0.6051 |
| 30 | 1892 | 38.2232 | 7.2698 | 86.5079 | 14.1414 | 3.3145 | 0.229 | 14.4725 | -28.1354 | 0.8876 |
| 31 | 1885 | 37.3527 | 7.3981 | 86.8652 | 13.0379 | 2.9562 | 0.1968 | 15.0234 | -27.56 | 1.2752 |
| 32 | 1878 | 35.6857 | 6.9319 | 87.5971 | 12.4339 | 3.0897 | 0.2044 | 15.1155 | -27.4987 | 0.9964 |
| 33 | 1871 | 37.1863 | 7.7697 | 86.7883 | 12.3681 | 3.0952 | 0.2114 | 14.6395 | -27.6764 | 0.8452 |
| 34 | 1865 | 38.24 | 7.1406 | 87.3914 | 12.4273 | 3.0201 | 0.2087 | 14.4729 | -27.8201 | 0.8585 |
| 35 | 1858 | 36.3438 | 8.2763 | 86.5588 | 11.7384 | 3.0878 | 0.2143 | 14.4095 | -27.7764 | 0.6572 |
| 36 | 1852 | 37.2958 | 6.7169 | 88.1984 | 11.5562 | 3.5212 | 0.2409 | 14.6197 | -28.0391 | 0.7339 |
| 37 | 1846 | 38.9554 | 7.43 | 87.1985 | 12.208 | 2.8078 | 0.1896 | 14.8129 | -27.7234 | 0.7257 |
| 38 | 1841 | 41.2714 | 9.5351 | 85.0696 | 12.2621 | 3.7097 | 0.2532 | 14.6491 | -28.039 | 0.5345 |
| 39 | 1834 | 42.466 | 9.6542 | 84.9024 | 12.3712 | 3.3017 | 0.2274 | 14.5187 | -27.9871 | 0.8741 |
| 40 | 1828 | 41.3056 | 8.9653 | 85.5747 | 12.4092 | 3.7456 | 0.2541 | 14.7405 | -28.0939 | 0.8596 |
| 41 | 1823 | 42.8203 | 11.4117 | 84.2178 | 9.9328 | 4.3414 | 0.2909 | 14.9222 | -27.8362 | 0.622 |
| 42 | 1817 | 41.6387 | 11.2314 | 84.6414 | 9.38 | 4.4703 | 0.3019 | 14.8082 | -27.9017 | 0.9557 |

**Table B5. Down 58: LOI data (water content (% $H_2O$), organic matter (% OM), mineral matter (%MM), and calcium carbonate (%$CaCO_3$)) and carbon & nitrogen data (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) by depth.**

| Depth (cm) | % $H_2O$ | % OM | % MM | % $CaCO_3$ | % C | % N | C/N | $\delta^{13}C$ | $\delta^{15}N$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 83.2254 | 9.0806 | 86.6061 | 9.8029 | 3.4918 | 0.2834 | 12.3227 | -28.2786 | 1.0426 |
| 2 | 64.0286 | 7.7461 | 87.7891 | 10.1472 | 2.9126 | 0.2134 | 13.6503 | -28.2589 | 1.8576 |
| 3 | 57.864 | 8.0481 | 88.0204 | 8.9353 | 2.8636 | 0.2083 | 13.7497 | -28.041 | 1.5656 |
| 4 | 57.5055 | 6.444 | 88.8053 | 10.7971 | 2.4989 | 0.19 | 13.1532 | -27.9074 | 2.0695 |
| 5 | 47.7355 | 5.9816 | 89.8773 | 9.4116 | 1.9248 | 0.1461 | 13.1784 | -27.4499 | 1.7201 |
| 6 | 59.4504 | 7.1 | 87.7363 | 11.7356 | 2.6256 | 0.2052 | 12.7957 | -28.0086 | 1.5256 |
| 7 | 61.6549 | 7.6884 | 85.3409 | 15.8427 | 3.5885 | 0.3312 | 10.8348 | -28.9738 | 0.6883 |
| 8 | 65.5669 | 9.1754 | 83.043 | 17.6856 | 3.9752 | 0.3642 | 10.9152 | -29.0106 | 0.2946 |
| 9 | 63.9029 | 8.4992 | 84.9919 | 14.7929 | 3.2091 | 0.2905 | 11.0474 | -28.0954 | 0.7807 |
| 10 | 61.1232 | 7.2228 | 84.7915 | 18.1494 | 3.3465 | 0.2965 | 11.288 | -28.35 | 1.0603 |
| 11 | 53.6131 | 7.341 | 87.3666 | 12.0281 | 2.6443 | 0.2077 | 12.7292 | -27.6897 | 1.5642 |
| 12 | 61.0156 | 8.2665 | 83.5671 | 18.5598 | 3.2149 | 0.2843 | 11.3088 | -28.4232 | 0.8673 |
| 13 | 60.5386 | 7.9624 | 83.6795 | 18.9956 | 3.4408 | 0.3069 | 11.2119 | -28.6664 | 1.1123 |
| 14 | 58.7022 | 8.1743 | 84.6794 | 16.2417 | 3.112 | 0.2773 | 11.2242 | -28.4845 | 1.1347 |
| 15 | 57.8474 | 7.3899 | 85.5992 | 15.9339 | 2.4934 | 0.195 | 12.7875 | -28.0919 | 1.3514 |
| 16 | 42.4727 | 5.5283 | 90.3827 | 9.2931 | 2.1627 | 0.1572 | 13.7605 | -27.472 | 1.9831 |
| 17 | 36.1601 | 5.1114 | 90.9064 | 9.0504 | 2.0071 | 0.1174 | 17.0891 | -27.2321 | 2.2951 |
| 18 | 44.2052 | 5.8947 | 90.1053 | 9.0909 | 2.0946 | 0.1385 | 15.1185 | -27.0279 | 2.4422 |
| 19 | 40.2977 | 5.5609 | 90.3484 | 9.2972 | 2.166 | 0.1487 | 14.5708 | -26.9548 | 2.4166 |
| 20 | 46.1312 | 6.5818 | 89.1273 | 9.7521 | 2.3411 | 0.1763 | 13.2789 | -27.3523 | 1.8315 |
| 21 | 52.4239 | 7.0957 | 85.9736 | 15.7516 | 3.0831 | 0.2666 | 11.5655 | -28.2434 | 1.1884 |
| 22 | 55.5682 | 7.8723 | 84.8936 | 16.441 | 3.1697 | 0.248 | 12.7806 | -27.9739 | 1.1318 |
| 23 | 49.9117 | 6.6223 | 87.069 | 14.3381 | 2.5635 | 0.1798 | 14.2572 | -27.5393 | 1.6218 |
| 24 | 40.2336 | 6.248 | 89.4905 | 9.6851 | 2.1761 | 0.144 | 15.1113 | -26.805 | 1.6795 |
| 25 | 37.0198 | 5.6559 | 90.6426 | 8.4125 | 2.5057 | 0.1541 | 16.2556 | -26.9578 | 1.7321 |
| 26 | 43.2008 | 5.7053 | 89.5695 | 10.7392 | 2.4315 | 0.1768 | 13.7506 | -27.2468 | 1.7068 |
| 27 | 44.9363 | 6.5101 | 88.794 | 10.6724 | 2.3048 | 0.1745 | 13.2068 | -27.5767 | 1.4323 |
| 28 | 43.7685 | 6.7088 | 87.8469 | 12.3735 | 2.5228 | 0.1932 | 13.0587 | -27.675 | 1.2987 |
| 29 | 52.8116 | 7.6986 | 86.9369 | 12.1919 | 3.2912 | 0.2761 | 11.9206 | -28.2356 | 1.2141 |
| 30 | 47.6646 | 6.7301 | 88.2224 | 11.4717 | 2.3602 | 0.176 | 13.4093 | -27.3785 | 1.3787 |
| 31 | 44.1523 | 5.4111 | 89.6697 | 11.18 | 1.84 | 0.1276 | 14.4229 | -28.7427 | 1.9112 |
| 32 | 37.6691 | 4.7543 | 90.3318 | 11.1678 | 1.6175 | 0.0951 | 17.0135 | -26.5677 | 1.6209 |
| 33 | 48.156 | 6.0708 | 87.2626 | 15.1515 | 1.9846 | 0.1285 | 15.4476 | -26.6954 | 1.8482 |
| 34 | 58.4315 | 8.039 | 77.6487 | 32.5279 | 4.4392 | 0.4323 | 10.2686 | -27.9186 | 0.1985 |
| 35 | 51.4582 | 6.1694 | 82.2177 | 26.393 | 2.5329 | 0.2064 | 12.2706 | -27.2798 | 1.5232 |
| 36 | 49.0295 | 6.4737 | 87.8903 | 12.809 | 2.2268 | 0.1661 | 13.4077 | -26.9431 | 1.6325 |
| 37 | 42.5121 | 5.7479 | 88.6387 | 12.7578 | 1.9971 | 0.1371 | 14.5718 | -26.3838 | 1.9708 |
| 38 | 43.4774 | 5.6637 | 88.4248 | 13.4352 | 1.99 | 0.1309 | 15.1981 | -26.3853 | 1.8458 |
| 39 | 46.8732 | 6.8869 | 87.3858 | 13.0167 | 2.8649 | 0.1804 | 15.8834 | -27.5267 | 1.0413 |
| 40 | 46.2339 | 6.547 | 87.5748 | 13.3596 | 2.5722 | 0.1731 | 14.8614 | -27.256 | 1.7123 |
| 41 | 45.7327 | 6.8954 | 87.8736 | 11.8886 | 2.4468 | 0.188 | 13.0145 | -27.2785 | 1.0915 |
| 42 | 46.3516 | 6.871 | 86.8569 | 14.2546 | 3.145 | 0.2854 | 11.0193 | -27.4836 | 0.3294 |
| 43 | 36.8797 | 5.3533 | 90.3334 | 9.8028 | 2.2471 | 0.1548 | 14.5117 | -27.1983 | 1.0982 |
| 44 | 35.0591 | 5.3747 | 91.1018 | 8.0078 | 1.9989 | 0.1266 | 15.7902 | -26.6261 | 1.429 |
| 45 | 34.6863 | 5.3524 | 91.1091 | 8.0421 | 1.7828 | 0.1106 | 16.1128 | -26.4547 | 1.6542 |

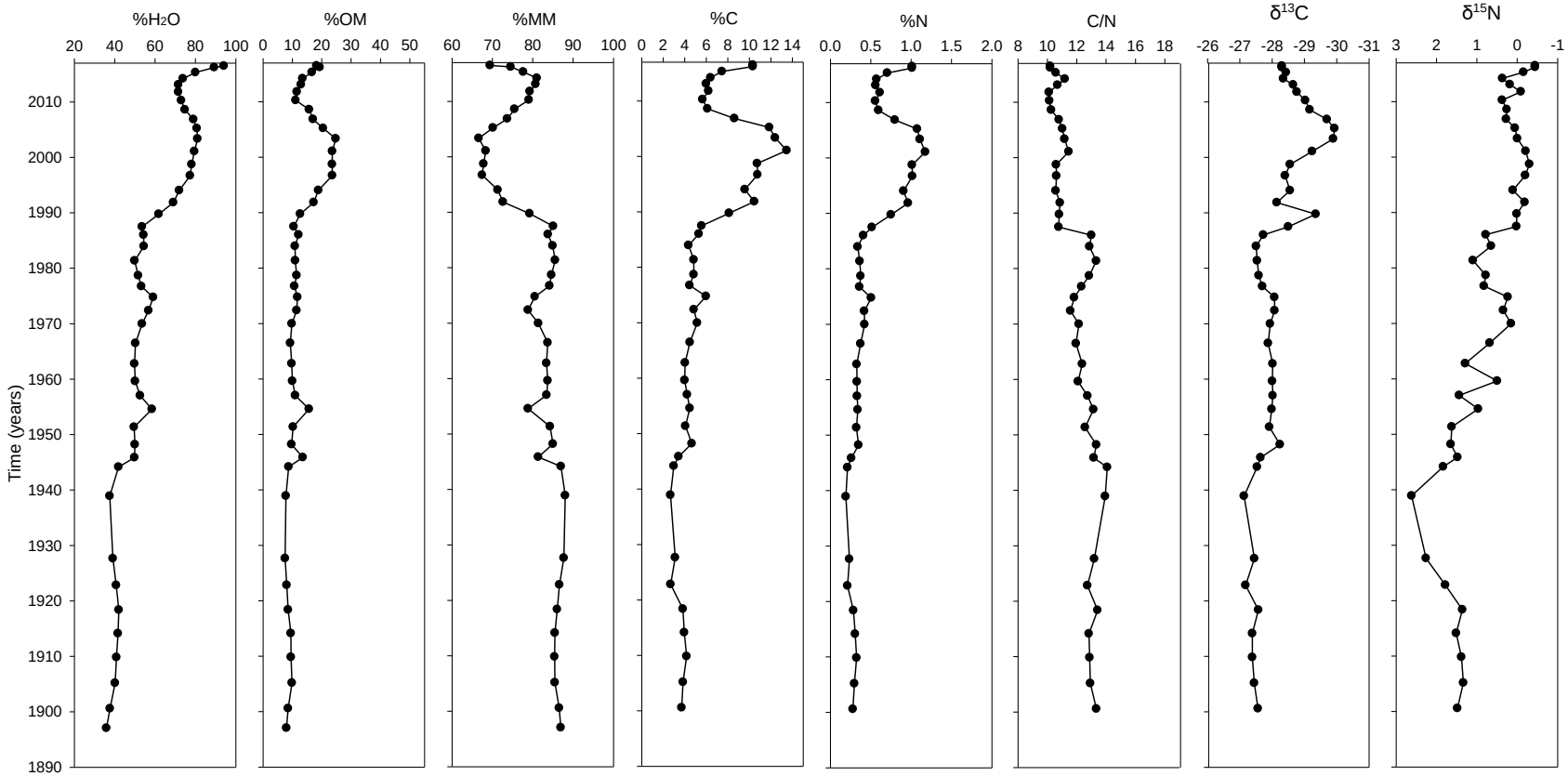


**Figure B1. Stratigraphies for loss-on-ignition (% $H_2O$, OM & MM) and organic carbon and nitrogen elemental and isotopic composition (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) at lake Up 17**

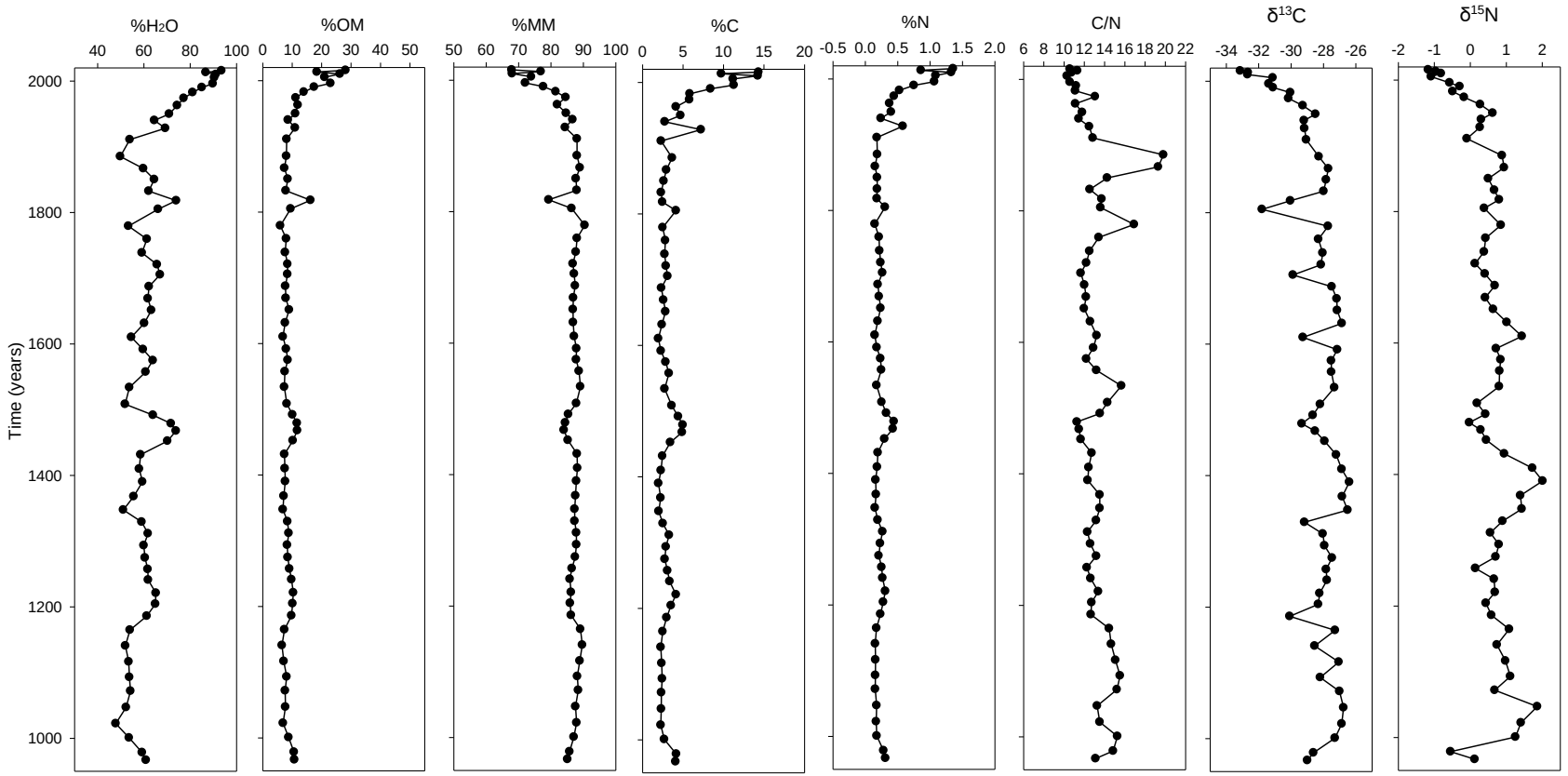


**Figure B2. Stratigraphies for loss-on-ignition (% $H_2O$, OM & MM) and organic carbon and nitrogen elemental and isotopic composition (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) at lake Up 10.**

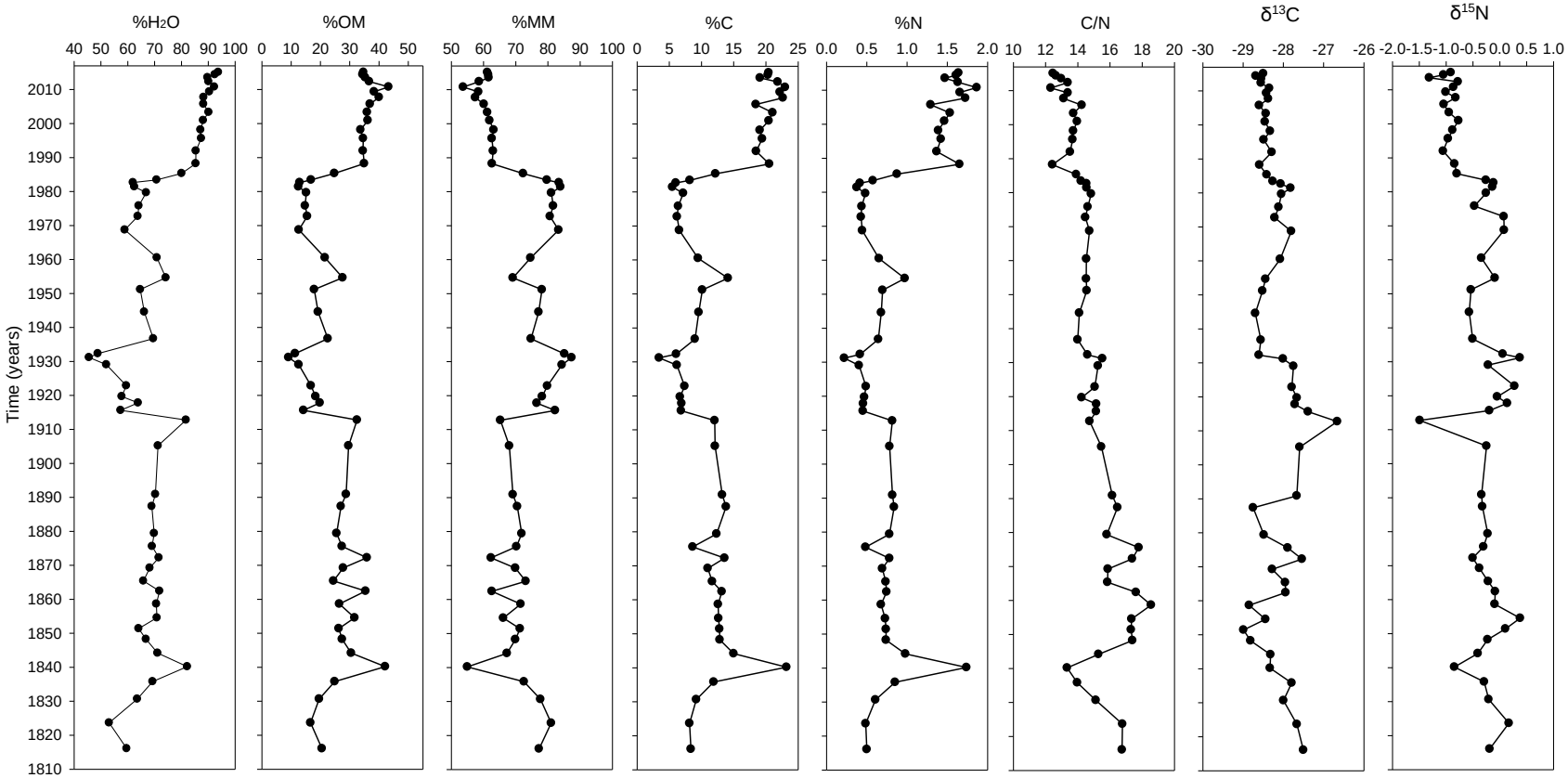


**Figure B3. Stratigraphies for loss-on-ignition (% $H_2O$, OM & MM) and organic carbon and nitrogen elemental and isotopic composition (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) at lake Down 1.**

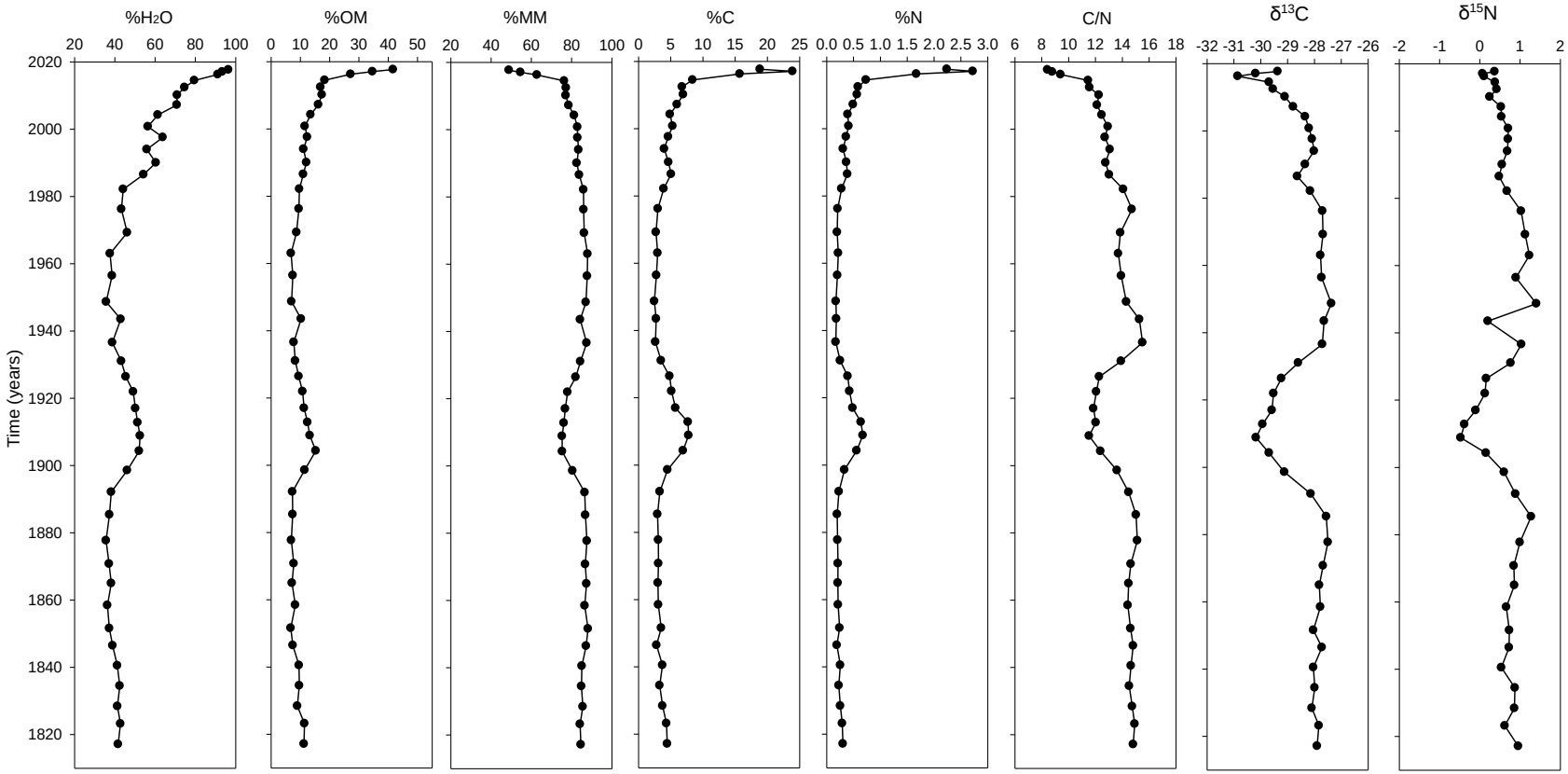


**Figure B4. Stratigraphies for loss-on-ignition (% $H_2O$, OM & MM) and organic carbon and nitrogen elemental and isotopic composition (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) at lake Down 26.**

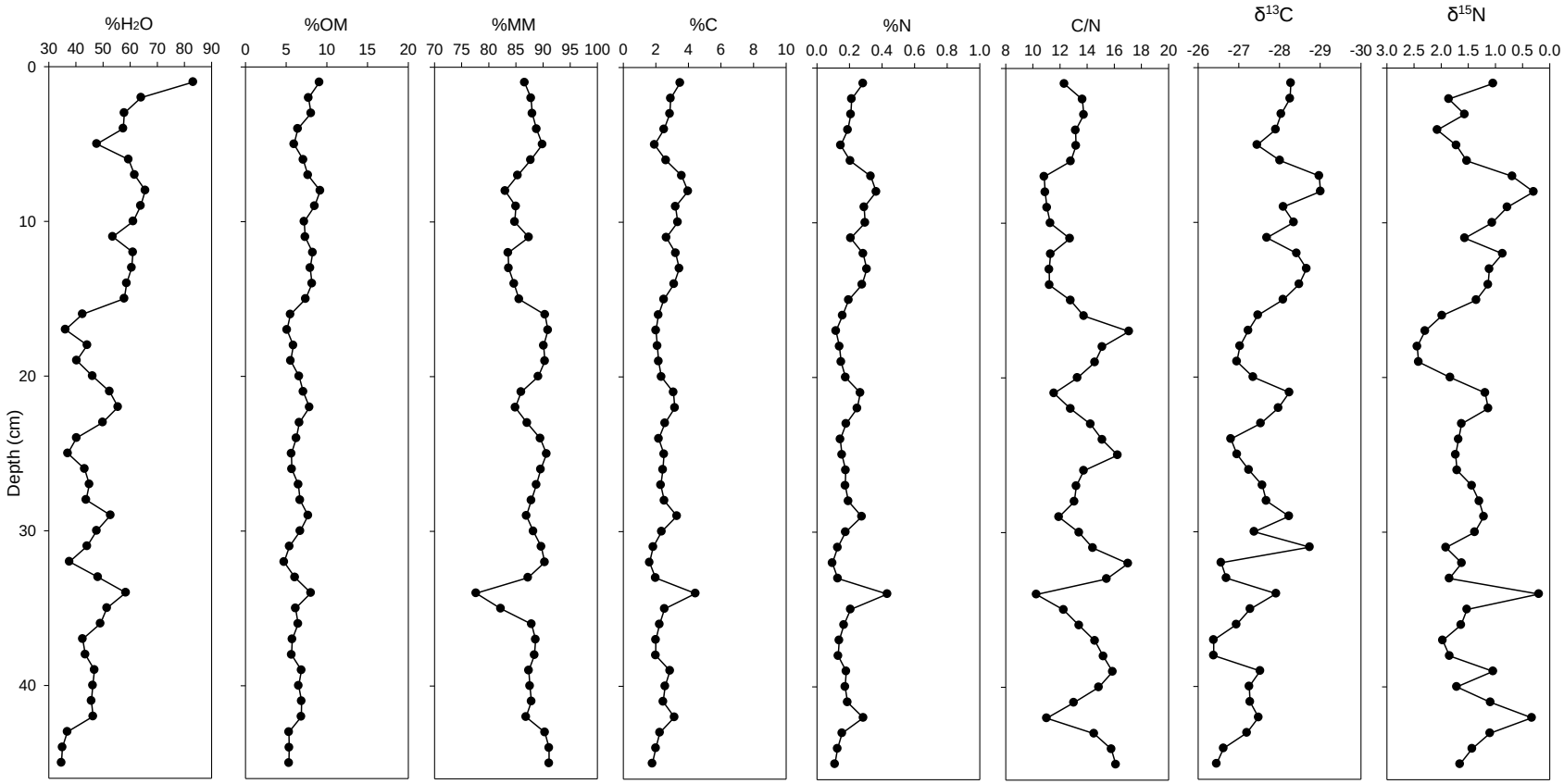


**Figure B5. Stratigraphies for loss-on-ignition (% $H_2O$, OM & MM) and organic carbon and nitrogen elemental and isotopic composition (%C, %N, C/N, $\delta^{13}C$, and $\delta^{15}N$) at lake Down 58.**

**Table B6. RAMP (1997-2004) and JOSM (2012-2014) river-bottom and suspended sediment organic carbon data retrieved from online RAMP and JOSM databases.**

| Agency | Site ID | Date | Sediment type | % organic carbon |
|---|---|---|---|---|
| RAMP | ATR-MR-E | 2004-09-20 | river-bottom | 1.70 |
| RAMP | ATR-MR-W | 2004-09-20 | river-bottom | 2.10 |
| RAMP | ATR-DD-E | 2004-09-19 | river-bottom | 1.40 |
| RAMP | ATR-DD-W | 2004-09-19 | river-bottom | 0.20 |
| RAMP | ATR-SR-W | 2004-09-18 | river-bottom | 0.90 |
| RAMP | ATR-FR-W | 2004-09-18 | river-bottom | 0.50 |
| RAMP | ATR-SR-E | 2004-09-18 | river-bottom | 1.60 |
| RAMP | ATR-FR-E | 2004-09-18 | river-bottom | 0.60 |
| RAMP | ATR-DC-W | 2004-09-17 | river-bottom | 0.20 |
| RAMP | ATR-UFM | 2004-09-17 | river-bottom | 0.60 |
| RAMP | ATR-DC-E | 2004-09-17 | river-bottom | 1.30 |
| RAMP | ATR-MR-W | 2003-09-17 | river-bottom | 1.50 |
| RAMP | ATR-MR-E | 2003-09-17 | river-bottom | 1.40 |
| RAMP | ATR-FC-E | 2003-09-13 | river-bottom | 1.60 |
| RAMP | ATR-FR-W | 2003-09-12 | river-bottom | 0.40 |
| RAMP | ATR-DD-E | 2003-09-12 | river-bottom | 1.10 |
| RAMP | ATR-DD-W | 2003-09-12 | river-bottom | < 0.1 |
| RAMP | ATR-FR-E | 2003-09-12 | river-bottom | < 0.1 |
| RAMP | ATR-FC-W | 2003-09-09 | river-bottom | 0.80 |
| RAMP | ATR-SR-E | 2003-09-07 | river-bottom | < 0.1 |
| RAMP | ATR-SR-W | 2003-09-07 | river-bottom | 0.50 |
| RAMP | ATR-UFM | 2003-09-06 | river-bottom | 1.20 |
| RAMP | ATR-DC-W | 2003-09-06 | river-bottom | 0.60 |
| RAMP | ATR-DC-E | 2003-09-06 | river-bottom | 4.50 |
| RAMP | ATR-FR-W | 2002-09-13 | river-bottom | 1.40 |
| RAMP | ATR-FR-E | 2002-09-13 | river-bottom | 1.00 |
| RAMP | ATR-DC-E | 2002-09-07 | river-bottom | 2.80 |
| RAMP | ATR-DC-W | 2002-09-07 | river-bottom | < 0.01 |
| RAMP | ATR-UFM | 2002-09-07 | river-bottom | 1.60 |
| RAMP | ATR-MR-W | 2002-09-06 | river-bottom | 1.80 |
| RAMP | ATR-MR-E | 2002-09-06 | river-bottom | 1.00 |
| RAMP | ATR-SR-E | 2002-09-06 | river-bottom | 2.10 |
| RAMP | ATR-SR-W | 2002-09-06 | river-bottom | 1.10 |
| RAMP | ATR-DD-W | 2002-09-05 | river-bottom | 0.90 |
| RAMP | ATR-FC-E | 2002-09-05 | river-bottom | 1.60 |
| RAMP | ATR-DD-E | 2002-09-05 | river-bottom | 4.70 |
| RAMP | ATR-FC-W | 2002-09-05 | river-bottom | 1.00 |
| RAMP | ATR-DC-W | 2001-11-02 | river-bottom | < 0.01 |
| RAMP | ATR-DC-E | 2001-11-02 | river-bottom | < 0.01 |
| RAMP | ATR-SR-W | 2001-11-01 | river-bottom | 0.60 |
| RAMP | ATR-MR-E | 2001-11-01 | river-bottom | < 0.01 |
| RAMP | ATR-SR-E | 2001-11-01 | river-bottom | 0.20 |
| RAMP | ATR-MR-W | 2001-11-01 | river-bottom | < 0.01 |
| RAMP | ATR-FC-E | 2001-10-14 | river-bottom | 0.80 |
| RAMP | ATR-FC-W | 2001-10-14 | river-bottom | 0.62 |
| RAMP | ATR-MR-W | 2000-10-04 | river-bottom | 0.70 |
| RAMP | ATR-MR-E | 2000-10-04 | river-bottom | 0.80 |
| RAMP | ATR-FC-W | 2000-10-03 | river-bottom | 2.70 |
| RAMP | ATR-FC-E | 2000-10-03 | river-bottom | 4.00 |

| | | | | |
|---|---|---|---|---|
| RAMP | ATR-DC-W | 2000-10-02 | river-bottom | 0.10 |
| RAMP | ATR-SR-W | 2000-10-02 | river-bottom | 2.10 |
| RAMP | ATR-SR-E | 2000-10-02 | river-bottom | 0.50 |
| RAMP | ATR-DC-E | 2000-10-02 | river-bottom | 2.50 |
| RAMP | ATR-ER | 2000-09-15 | river-bottom | 1.10 |
| RAMP | ATR-FC-E-D | 1998-09-17 | river-bottom | 0.65 |
| RAMP | ATR-FC-W-D | 1998-09-17 | river-bottom | 2.02 |
| RAMP | ATR-MR-E-D | 1998-09-16 | river-bottom | 1.57 |
| RAMP | ATR-DC-W | 1998-09-16 | river-bottom | 0.43 |
| RAMP | ATR-MR-W-D | 1998-09-16 | river-bottom | 0.67 |
| RAMP | ATR-DC-E | 1998-09-16 | river-bottom | 0.92 |
| RAMP | ATR-FC-CC-D | 1997-10-10 | river-bottom | 1.67 |
| RAMP | ATR-DC-CC | 1997-10-06 | river-bottom | 0.67 |
| JOSM | M3 SAND | 2012-09-18 | river-bottom | 1.15 |
| JOSM | M3 GRAVEL | 2012-09-18 | river-bottom | 0.40 |
| JOSM | M3B GRAVEL | 2012-09-24 | river-bottom | 0.57 |
| JOSM | M3B SAND | 2012-09-24 | river-bottom | 0.01 |
| JOSM | M4 GRAVEL | 2012-09-20 | river-bottom | 0.18 |
| JOSM | M4 SAND | 2012-09-20 | river-bottom | 0.46 |
| JOSM | M6 SAND | 2012-09-21 | river-bottom | 0.03 |
| JOSM | M6 GRAVEL | 2012-09-21 | river-bottom | 0.55 |
| JOSM | M7 GRAVEL | 2012-09-22 | river-bottom | 1.78 |
| JOSM | M7 SAND | 2012-09-22 | river-bottom | 0.27 |
| JOSM | M7C SAND | 2012-09-22 | river-bottom | 0.19 |
| JOSM | M7C GRAVEL | 2012-09-23 | river-bottom | 4.09 |
| JOSM | M8 GRAVEL | 2012-09-25 | river-bottom | 0.88 |
| JOSM | M8 SAND | 2012-09-25 | river-bottom | 2.91 |
| JOSM | M3 GRAVEL | 2013-09-18 | river-bottom | 0.51 |
| JOSM | M3 SAND | 2013-09-18 | river-bottom | 0.07 |
| JOSM | M3B GRAVEL | 2013-09-17 | river-bottom | 0.63 |
| JOSM | M3B SAND | 2013-09-17 | river-bottom | 1.55 |
| JOSM | M4 SAND | 2013-09-19 | river-bottom | 1.81 |
| JOSM | M4 GRAVEL | 2013-09-19 | river-bottom | 1.50 |
| JOSM | M6 GRAVEL | 2013-09-22 | river-bottom | 1.29 |
| JOSM | M6 SAND | 2013-09-22 | river-bottom | 1.18 |
| JOSM | M7 GRAVEL | 2013-09-21 | river-bottom | 0.41 |
| JOSM | M7 SAND | 2013-09-21 | river-bottom | 2.01 |
| JOSM | M7C GRAVEL | 2013-09-23 | river-bottom | 1.71 |
| JOSM | M7C SAND | 2013-09-23 | river-bottom | 1.67 |
| JOSM | M8 GRAVEL | 2013-09-21 | river-bottom | 1.21 |
| JOSM | M8 SAND | 2013-09-21 | river-bottom | 1.06 |
| JOSM | M3 GRAVEL | 2014-09-21 | river-bottom | 0.40 |
| JOSM | M3 GRAVEL | 2014-09-21 | river-bottom | 0.60 |
| JOSM | M9 GRAVEL | 2014-09-21 | river-bottom | 2.46 |
| JOSM | M3 GRAVEL | 2014-09-21 | river-bottom | 0.20 |
| JOSM | M3B GRAVEL | 2014-09-21 | river-bottom | 1.92 |
| JOSM | M3B SAND | 2014-09-21 | river-bottom | 0.11 |
| JOSM | M4 GRAVEL | 2014-09-14 | river-bottom | 0.89 |
| JOSM | M4 GRAVEL | 2014-09-26 | river-bottom | 0.86 |
| JOSM | M4 SAND | 2014-09-26 | river-bottom | 2.06 |
| JOSM | M6 GRAVEL | 2014-09-24 | river-bottom | 1.70 |
| JOSM | M6 SAND | 2014-09-24 | river-bottom | 2.25 |
| JOSM | M7 GRAVEL | 2014-09-23 | river-bottom | 0.30 |

| | | | | |
|---|---|---|---|---|
| JOSM | M7 SAND | 2014-09-23 | river-bottom | 0.98 |
| JOSM | M7C GRAVEL | 2014-09-22 | river-bottom | 1.14 |
| JOSM | M7C SAND | 2014-09-22 | river-bottom | 3.33 |
| JOSM | M8 GRAVEL | 2014-09-20 | river-bottom | 1.03 |
| JOSM | M8 SAND | 2014-09-20 | river-bottom | 1.72 |
| JOSM | M0 | 06-2012 | suspended sed. | 1.32 |
| JOSM | M0 | 09-2012 | suspended sed. | 5.77 |
| JOSM | M2 | 06-2012 | suspended sed. | 1.92 |
| JOSM | M2 | 09-2012 | suspended sed. | 5.54 |
| JOSM | M3 | 06-2012 | suspended sed. | 1.75 |
| JOSM | M3 | 09-2012 | suspended sed. | 5.53 |
| JOSM | M9 | 06-2012 | suspended sed. | 1.77 |
| JOSM | M9 | 10-2012 | suspended sed. | 3.78 |
| JOSM | M0 | 06-2013 | suspended sed. | 1.56 |
| JOSM | M0 | 09-2013 | suspended sed. | 4.70 |
| JOSM | M0 | 02-2014 | suspended sed. | 5.43 |
| JOSM | M2 | 06-2013 | suspended sed. | 1.38 |
| JOSM | M2 | 09-2013 | suspended sed. | 7.78 |
| JOSM | M2 | 02-2014 | suspended sed. | 4.90 |
| JOSM | M3 | 06-2013 | suspended sed. | 1.60 |
| JOSM | M3 | 09-2013 | suspended sed. | 7.57 |
| JOSM | M4 | 02-2014 | suspended sed. | 5.58 |
| JOSM | M9 | 06-2013 | suspended sed. | 2.04 |
| JOSM | M0 | 06-2014 | suspended sed. | 2.45 |
| JOSM | M0 | 09-2014 | suspended sed. | 3.96 |
| JOSM | M2 | 09-2014 | suspended sed. | 1.97 |
| JOSM | M3 | 06-2014 | suspended sed. | 1.81 |
| JOSM | M3 | 09-2014 | suspended sed. | 2.27 |
| JOSM | M9 | 06-2014 | suspended sed. | 1.87 |
| JOSM | M9 | 09-2014 | suspended sed. | 3.23 |

**Table B7. Organic carbon (%) for exposed river sediments, and a flood deposit, collected during this study (2016, 2017).**

| Site | Date | % org. C |
|---|---|---|
| AR* near Down 26 | 10-2016 | 1.54 |
| AR* near Up 17 | 10-2016 | 0.97 |
| AR* Downstream of Clearwater R. | 07-2017 | 0.40 |
| Fort McMurray flood deposit sed. | 07-2017 | 1.07 |

*AR = Athabasca River

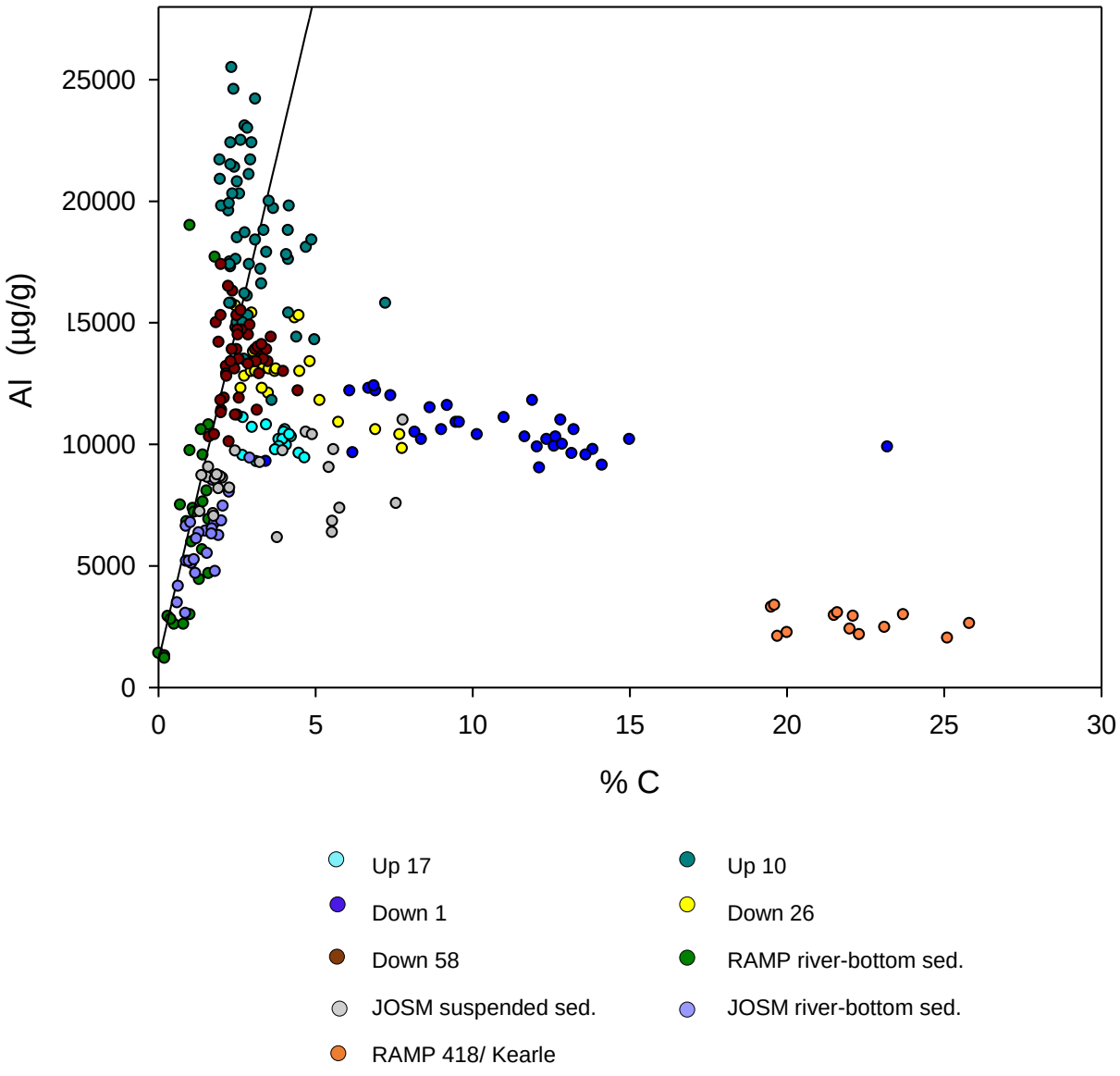


**Figure B6. Pre-1967 concentrations of aluminum plotted with organic carbon content from floodplain lakes Up 17 (light blue), Up 10 (green), Down 1 (dark blue), Down 26 (yellow), post-1967 sediment from Down 58 (brown), headwater lake RAMP 418/ Kearle, and RAMP/JOSM river samples (RAMP river-bottom sediment (black), JOSM river-bottom sediment (white), and JOSM suspended sediment (grey)). The linear regression presented uses RAMP & JOSM river-bottom samples to establish the "river end member" for the lithogenic metal of interest (Al) compared to organic carbon (autochthonous, lake-generated organic matter end member).**

## Appendix C – Compiled metals data

**Table C1. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g by depth and CRS-derived year at lake Up 17. Normalized values of Ni and V are presented as ratios to Al.**

| Depth (cm) | CRS year | Al (µg/g) | Ni (µg/g) | V (µg/g) | Ni/Al | V/Al |
|---|---|---|---|---|---|---|
| 1 | 2016 | 5490 | 18.7 | 18.1 | 0.0034 | 0.0033 |
| 2 | 2016 | 8390 | 21.9 | 26.5 | 0.0026 | 0.0032 |
| 3 | 2015 | 8620 | 22 | 26.9 | 0.0026 | 0.0031 |
| 4 | 2014 | 10800 | 25 | 32.6 | 0.0023 | 0.0030 |
| 5 | 2013 | 11600 | 26.8 | 33.4 | 0.0023 | 0.0029 |
| 6 | 2012 | 11600 | 26.3 | 32.6 | 0.0023 | 0.0028 |
| 7 | 2010 | 11600 | 28.3 | 33.8 | 0.0024 | 0.0029 |
| 8 | 2009 | 11700 | 30.1 | 35 | 0.0026 | 0.0030 |
| 9 | 2007 | 10500 | 31.3 | 32.7 | 0.0030 | 0.0031 |
| 10 | 2005 | 10200 | 29.9 | 30.7 | 0.0029 | 0.0030 |
| 11 | 2003 | 8430 | 28.3 | 28 | 0.0034 | 0.0033 |
| 12 | 2001 | 7950 | 26.3 | 26.2 | 0.0033 | 0.0033 |
| 13 | 1999 | 8430 | 25.9 | 27.9 | 0.0031 | 0.0033 |
| 14 | 1997 | 8400 | 26.5 | 28.1 | 0.0032 | 0.0033 |
| 15 | 1994 | 9590 | 26.8 | 30.8 | 0.0028 | 0.0032 |
| 16 | 1992 | 10400 | 28.7 | 31.5 | 0.0028 | 0.0030 |
| 17 | 1990 | 9140 | 26.3 | 30.5 | 0.0029 | 0.0033 |
| 18 | 1987 | 8590 | 25.9 | 29.8 | 0.0030 | 0.0035 |
| 19 | 1986 | 8150 | 25.1 | 29.7 | 0.0031 | 0.0036 |
| 20 | 1984 | 8490 | 25.4 | 31.2 | 0.0030 | 0.0037 |
| 21 | 1981 | 7420 | 22.8 | 27.4 | 0.0031 | 0.0037 |
| 22 | 1979 | 8780 | 27.6 | 31.4 | 0.0031 | 0.0036 |
| 23 | 1977 | 10700 | 26.2 | 34.2 | 0.0024 | 0.0032 |
| 24 | 1975 | 10300 | 27.3 | 37.7 | 0.0027 | 0.0037 |
| 25 | 1972 | 9640 | 25.9 | 34.6 | 0.0027 | 0.0036 |
| 26 | 1970 | 10600 | 27.2 | 37.2 | 0.0026 | 0.0035 |
| 27 | 1966 | 10300 | 28.2 | 35.6 | 0.0027 | 0.0035 |
| 28 | 1963 | 10600 | 30.5 | 35.4 | 0.0029 | 0.0033 |
| 29 | 1960 | 10500 | 27.9 | 33.6 | 0.0027 | 0.0032 |
| 30 | 1957 | 10300 | 26.6 | 33.1 | 0.0026 | 0.0032 |
| 31 | 1955 | 9630 | 28.7 | 31.4 | 0.0030 | 0.0033 |
| 32 | 1951 | 9960 | 26.6 | 31.8 | 0.0027 | 0.0032 |
| 33 | 1948 | 9440 | 26.9 | 30.4 | 0.0028 | 0.0032 |
| 34 | 1946 | 10800 | 30.2 | 33.3 | 0.0028 | 0.0031 |
| 35 | 1944 | 10700 | 26.9 | 32.4 | 0.0025 | 0.0030 |
| 36 | 1939 | 9540 | 25.8 | 30 | 0.0027 | 0.0031 |
| 37 | 1928 | 9290 | 25.3 | 29.7 | 0.0027 | 0.0032 |
| 38 | 1923 | 11100 | 27.1 | 32.3 | 0.0024 | 0.0029 |
| 39 | 1918 | 10200 | 26.5 | 31.6 | 0.0026 | 0.0031 |
| 40 | 1914 | 10200 | 26.5 | 33 | 0.0026 | 0.0032 |
| 41 | 1910 | 10400 | 25.7 | 32.3 | 0.0025 | 0.0031 |
| 42 | 1905 | 9910 | 25.7 | 32.4 | 0.0026 | 0.0033 |
| 43 | 1901 | 9770 | 26.1 | 31.3 | 0.0027 | 0.0032 |

**Table C2. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g by depth and CRS-derived year at lake Up 10. Normalized values of Ni and V are presented as ratios to Al.**

| Depth (cm) | CRS year | Al (µg/g) | Ni (µg/g) | V (µg/g) | Ni/Al | V/Al |
|---|---|---|---|---|---|---|
| 1 | 2016 | 7460 | 21.8 | 32.4 | 0.0029 | 0.0043 |
| 2 | 2013 | 16100 | 29 | 52.7 | 0.0018 | 0.0033 |
| 3 | 2010 | 10900 | 24.4 | 43.1 | 0.0022 | 0.0040 |
| 4 | 2005 | 13900 | 28.5 | 48.6 | 0.0021 | 0.0035 |
| 5 | 1996 | 13600 | 28.3 | 56.6 | 0.0021 | 0.0042 |
| 6 | 1990 | 18700 | 39.4 | 74.1 | 0.0021 | 0.0040 |
| 7 | 1983 | 18800 | 39 | 74.4 | 0.0021 | 0.0040 |
| 8 | 1974 | 22000 | 42.1 | 86.8 | 0.0019 | 0.0039 |
| 9 | 1963 | 17600 | 31.1 | 65.1 | 0.0018 | 0.0037 |
| 10 | 1950 | 18100 | 31.8 | 59.3 | 0.0018 | 0.0033 |
| 11 | 1940 | 23100 | 39.6 | 66.1 | 0.0017 | 0.0029 |
| 12 | 1928 | 15800 | 29.7 | 49.8 | 0.0019 | 0.0032 |
| 13 | 1911 | 17300 | 32.1 | 48.9 | 0.0019 | 0.0028 |
| 14 | 1885 | 19700 | 34.1 | 54.7 | 0.0017 | 0.0028 |
| 15 | 1867 | 21700 | 36 | 59.3 | 0.0017 | 0.0027 |
| 16 | 1850 | 22500 | 34.7 | 58.7 | 0.0015 | 0.0026 |
| 17 | 1832 | 22400 | 36.3 | 56.4 | 0.0016 | 0.0025 |
| 18 | 1818 | 14800 | 31.3 | 49.8 | 0.0021 | 0.0034 |
| 19 | 1805 | 15400 | 33.9 | 46.3 | 0.0022 | 0.0030 |
| 20 | 1779 | 15000 | 30.5 | 40.2 | 0.0020 | 0.0027 |
| 21 | 1760 | 16100 | 30.9 | 46.8 | 0.0019 | 0.0029 |
| 22 | 1739 | 16200 | 30.5 | 43.7 | 0.0019 | 0.0027 |
| 23 | 1721 | 17400 | 33.2 | 49.3 | 0.0019 | 0.0028 |
| 24 | 1705 | 24200 | 45.2 | 66 | 0.0019 | 0.0027 |
| 25 | 1687 | 25500 | 47.1 | 67.1 | 0.0018 | 0.0026 |
| 26 | 1669 | 20300 | 38.6 | 52.6 | 0.0019 | 0.0026 |
| 27 | 1651 | 23000 | 44.8 | 64.4 | 0.0019 | 0.0028 |
| 28 | 1632 | 24600 | 47.9 | 66.8 | 0.0019 | 0.0027 |
| 29 | 1610 | 21700 | 41 | 54.6 | 0.0019 | 0.0025 |
| 30 | 1592 | 17500 | 34.7 | 46.9 | 0.0020 | 0.0027 |
| 31 | 1575 | 15300 | 31.6 | 42.8 | 0.0021 | 0.0028 |
| 32 | 1557 | 17200 | 34 | 49 | 0.0020 | 0.0028 |
| 33 | 1534 | 13500 | 29 | 39.9 | 0.0021 | 0.0030 |
| 34 | 1508 | 11800 | 27.3 | 36.4 | 0.0023 | 0.0031 |
| 35 | 1492 | 14400 | 30.5 | 43.3 | 0.0021 | 0.0030 |
| 36 | 1479 | 14300 | 31.2 | 41.3 | 0.0022 | 0.0029 |
| 37 | 1468 | 18400 | 40.2 | 52.4 | 0.0022 | 0.0028 |
| 38 | 1452 | 17900 | 37.5 | 48.3 | 0.0021 | 0.0027 |
| 39 | 1432 | 17600 | 35.6 | 48.1 | 0.0020 | 0.0027 |
| 40 | 1410 | 17400 | 37.5 | 48 | 0.0022 | 0.0028 |
| 41 | 1390 | 20900 | 42.4 | 55.2 | 0.0020 | 0.0026 |
| 42 | 1368 | 19600 | 39.8 | 50.9 | 0.0020 | 0.0026 |
| 43 | 1348 | 19800 | 39.6 | 49.4 | 0.0020 | 0.0025 |
| 44 | 1329 | 18500 | 39 | 50.2 | 0.0021 | 0.0027 |
| 45 | 1311 | 16600 | 32.4 | 48 | 0.0020 | 0.0029 |
| 46 | 1294 | 21100 | 41.5 | 56.7 | 0.0020 | 0.0027 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 47 | 1275 | 18700 | 36 | 50.6 | 0.0019 | 0.0027 |
| 48 | 1257 | 18400 | 33.8 | 50.3 | 0.0018 | 0.0027 |
| 49 | 1241 | 18800 | 35.9 | 51.9 | 0.0019 | 0.0028 |
| 50 | 1221 | 18800 | 34.7 | 53.1 | 0.0018 | 0.0028 |
| 51 | 1204 | 20000 | 34.9 | 55.5 | 0.0017 | 0.0028 |
| 52 | 1186 | 22400 | 38.8 | 61.3 | 0.0017 | 0.0027 |
| 53 | 1165 | 20800 | 36.7 | 57.2 | 0.0018 | 0.0028 |
| 54 | 1141 | 19900 | 35.3 | 53.2 | 0.0018 | 0.0027 |
| 55 | 1117 | 20300 | 35.4 | 56 | 0.0017 | 0.0028 |
| 56 | 1093 | 21400 | 38.7 | 59.3 | 0.0018 | 0.0028 |
| 57 | 1072 | 15800 | 30.8 | 43.1 | 0.0019 | 0.0027 |
| 58 | 1047 | 21500 | 41.3 | 57.3 | 0.0019 | 0.0027 |
| 59 | 1022 | 15800 | 32.4 | 42.8 | 0.0021 | 0.0027 |
| 60 | 1001 | 15000 | 27.4 | 36.9 | 0.0018 | 0.0025 |
| 61 | 978 | 19800 | 35.5 | 51.5 | 0.0018 | 0.0026 |
| 62 | 967 | 17800 | 34 | 49.4 | 0.0019 | 0.0028 |

**Table C3. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g by depth and CRS-derived year at lake Down 1. Normalized values of Ni and V are presented as ratios to Al.**

| Depth (cm) | CRS year | Al (µg/g) | Ni (µg/g) | V (µg/g) | Ni/Al | V/Al |
|---|---|---|---|---|---|---|
| 1 | 2015 | 6170 | 23.5 | 38.9 | 0.0038 | 0.0063 |
| 2 | 2014 | 6740 | 22.8 | 41.5 | 0.0034 | 0.0062 |
| 3 | 2014 | 5960 | 22.9 | 40.1 | 0.0038 | 0.0067 |
| 4 | 2012 | 5830 | 23.1 | 42 | 0.0040 | 0.0072 |
| 5 | 2011 | 6560 | 23.8 | 44.4 | 0.0036 | 0.0068 |
| 6 | 2009 | 6740 | 25 | 45.6 | 0.0037 | 0.0068 |
| 7 | 2008 | 6870 | 25.5 | 43.2 | 0.0037 | 0.0063 |
| 8 | 2006 | 7600 | 25.7 | 48.6 | 0.0034 | 0.0064 |
| 9 | 2003 | 6340 | 24.6 | 44.4 | 0.0039 | 0.0070 |
| 10 | 2001 | 7200 | 26.1 | 47.2 | 0.0036 | 0.0066 |
| 11 | 1998 | 7860 | 25.7 | 48.1 | 0.0033 | 0.0061 |
| 12 | 1996 | 8850 | 27.5 | 52.7 | 0.0031 | 0.0060 |
| 13 | 1992 | 8350 | 27.2 | 50.2 | 0.0033 | 0.0060 |
| 14 | 1988 | 8960 | 28.1 | 52.9 | 0.0031 | 0.0059 |
| 15 | 1985 | 8610 | 26.7 | 46.3 | 0.0031 | 0.0054 |
| 16 | 1983 | 10300 | 26.6 | 41.2 | 0.0026 | 0.0040 |
| 17 | 1983 | 10600 | 25 | 37.4 | 0.0024 | 0.0035 |
| 18 | 1981 | 10200 | 25.3 | 35.7 | 0.0025 | 0.0035 |
| 19 | 1980 | 11100 | 26 | 37.6 | 0.0023 | 0.0034 |
| 20 | 1976 | 10900 | 26.3 | 37.5 | 0.0024 | 0.0034 |
| 21 | 1973 | 11200 | 26.4 | 36.6 | 0.0024 | 0.0033 |
| 22 | 1969 | 11200 | 27.4 | 36.6 | 0.0024 | 0.0033 |
| 23 | 1961 | 10900 | 26.1 | 34.9 | 0.0024 | 0.0032 |
| 24 | 1955 | 9140 | 24.2 | 31.7 | 0.0026 | 0.0035 |
| 25 | 1951 | 10400 | 26 | 34.2 | 0.0025 | 0.0033 |
| 26 | 1945 | 10900 | 26.5 | 36.3 | 0.0024 | 0.0033 |
| 27 | 1937 | 10600 | 25.2 | 33.2 | 0.0024 | 0.0031 |
| 28 | 1932 | 12200 | 25.8 | 38.1 | 0.0021 | 0.0031 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 29 | 1931 | 9300 | 21.8 | 31.4 | 0.0023 | 0.0034 |
| 30 | 1929 | 9650 | 22.3 | 30.2 | 0.0023 | 0.0031 |
| 31 | 1923 | 12000 | 26.1 | 36.3 | 0.0022 | 0.0030 |
| 32 | 1920 | 12300 | 25.9 | 38.4 | 0.0021 | 0.0031 |
| 33 | 1918 | 12200 | 26.2 | 38 | 0.0021 | 0.0031 |
| 34 | 1916 | 12400 | 26.4 | 37.8 | 0.0021 | 0.0030 |
| 35 | 1913 | 9890 | 23.3 | 32.8 | 0.0024 | 0.0033 |
| 36 | 1905 | 12200 | 29.2 | 41.4 | 0.0024 | 0.0034 |
| 37 | 1891 | 10600 | 29.7 | 38.1 | 0.0028 | 0.0036 |
| 38 | 1887 | 9790 | 28.2 | 37 | 0.0029 | 0.0038 |
| 39 | 1879 | 10200 | 27.4 | 38 | 0.0027 | 0.0037 |
| 40 | 1876 | 11500 | 27.3 | 40.2 | 0.0024 | 0.0035 |
| 41 | 1872 | 9560 | 25.4 | 36.3 | 0.0027 | 0.0038 |
| 42 | 1869 | 11100 | 28.6 | 37.8 | 0.0026 | 0.0034 |
| 43 | 1865 | 10300 | 25.5 | 36.5 | 0.0025 | 0.0035 |
| 44 | 1862 | 9620 | 27.3 | 36.3 | 0.0028 | 0.0038 |
| 45 | 1859 | 9920 | 26 | 37.2 | 0.0026 | 0.0038 |
| 46 | 1855 | 10300 | 25.9 | 37.6 | 0.0025 | 0.0037 |
| 47 | 1851 | 11000 | 26.3 | 37.4 | 0.0024 | 0.0034 |
| 48 | 1848 | 10000 | 25.6 | 35.5 | 0.0026 | 0.0036 |
| 49 | 1844 | 10200 | 26.8 | 34.7 | 0.0026 | 0.0034 |
| 50 | 1840 | 9890 | 25.5 | 32 | 0.0026 | 0.0032 |
| 51 | 1836 | 11800 | 27 | 38.4 | 0.0023 | 0.0033 |
| 52 | 1831 | 11600 | 27.1 | 38.3 | 0.0023 | 0.0033 |
| 53 | 1824 | 10500 | 24.1 | 34.3 | 0.0023 | 0.0033 |
| 54 | 1816 | 10200 | 24.2 | 33.9 | 0.0024 | 0.0033 |

**Table C4. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g by depth and CRS-derived year at lake Down 26. Normalized values of Ni and V are presented as ratios to Al.**

| Depth (cm) | CRS year | Al (µg/g) | Ni (µg/g) | V (µg/g) | Ni/Al | V/Al |
|---|---|---|---|---|---|---|
| 1 | 2018 | 4310 | 12.5 | 14.7 | 0.0029 | 0.0034 |
| 2 | 2017 | 2470 | 8.82 | 10 | 0.0036 | 0.0040 |
| 3 | 2016 | 4770 | 13.5 | 16 | 0.0028 | 0.0034 |
| 4 | 2014 | 11300 | 22.7 | 32.5 | 0.0020 | 0.0029 |
| 5 | 2012 | 12700 | 24.1 | 35.2 | 0.0019 | 0.0028 |
| 6 | 2010 | 12600 | 25 | 36.1 | 0.0020 | 0.0029 |
| 7 | 2007 | 12500 | 24.6 | 34.9 | 0.0020 | 0.0028 |
| 8 | 2004 | 13000 | 25.8 | 37.4 | 0.0020 | 0.0029 |
| 9 | 2001 | 12400 | 25.9 | 35.3 | 0.0021 | 0.0028 |
| 10 | 1998 | 12400 | 26.2 | 35.3 | 0.0021 | 0.0028 |
| 11 | 1994 | 13200 | 26.8 | 36.5 | 0.0020 | 0.0028 |
| 12 | 1990 | 13700 | 28 | 37.9 | 0.0020 | 0.0028 |
| 13 | 1986 | 14100 | 28.7 | 40.7 | 0.0020 | 0.0029 |
| 14 | 1982 | 15000 | 29.1 | 40.7 | 0.0019 | 0.0027 |
| 15 | 1976 | 15000 | 30 | 40.8 | 0.0020 | 0.0027 |
| 16 | 1969 | 13400 | 28.5 | 37.5 | 0.0021 | 0.0028 |
| 17 | 1963 | 15400 | 31.3 | 40.5 | 0.0020 | 0.0026 |
| 18 | 1956 | 14800 | 28 | 38.2 | 0.0019 | 0.0026 |
| 19 | 1949 | 15700 | 30 | 41.2 | 0.0019 | 0.0026 |
| 20 | 1943 | 12800 | 29.4 | 37.7 | 0.0023 | 0.0029 |
| 21 | 1937 | 12300 | 25.5 | 35.3 | 0.0021 | 0.0029 |
| 22 | 1931 | 12100 | 25.3 | 34.8 | 0.0021 | 0.0029 |
| 23 | 1926 | 13400 | 25.3 | 37.5 | 0.0019 | 0.0028 |
| 24 | 1922 | 11800 | 22.9 | 33.8 | 0.0019 | 0.0029 |
| 25 | 1917 | 10900 | 22.8 | 31.5 | 0.0021 | 0.0029 |
| 26 | 1913 | 10400 | 21.2 | 29.7 | 0.0020 | 0.0029 |
| 27 | 1909 | 9830 | 20.2 | 28.3 | 0.0021 | 0.0029 |
| 28 | 1904 | 10600 | 22.5 | 32.7 | 0.0021 | 0.0031 |
| 29 | 1899 | 13000 | 24.3 | 37 | 0.0019 | 0.0028 |
| 30 | 1892 | 13100 | 24.3 | 35.9 | 0.0019 | 0.0027 |
| 31 | 1885 | 13000 | 26.1 | 36.8 | 0.0020 | 0.0028 |
| 32 | 1878 | 13000 | 26.5 | 37.8 | 0.0020 | 0.0029 |
| 33 | 1871 | 13700 | 26 | 39.1 | 0.0019 | 0.0029 |
| 34 | 1865 | 13800 | 26.7 | 39 | 0.0019 | 0.0028 |
| 35 | 1858 | 13400 | 25.3 | 38.8 | 0.0019 | 0.0029 |
| 36 | 1852 | 13100 | 26.2 | 38.9 | 0.0020 | 0.0030 |
| 37 | 1846 | 13400 | 26.4 | 39.8 | 0.0020 | 0.0030 |
| 38 | 1841 | 13000 | 27.1 | 38.8 | 0.0021 | 0.0030 |
| 39 | 1834 | 12300 | 28.3 | 37.6 | 0.0023 | 0.0031 |
| 40 | 1828 | 13100 | 27.4 | 39.2 | 0.0021 | 0.0030 |
| 41 | 1823 | 15200 | 30.3 | 44.4 | 0.0020 | 0.0029 |
| 42 | 1817 | 15300 | 31.4 | 46.4 | 0.0021 | 0.0030 |

**Table C5. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g by depth at lake Down 58. Normalized values of Ni and V are presented as ratios to Al.**

| Depth (cm) | Al (µg/g) | Ni (µg/g) | V (µg/g) | Ni/Al | V/Al |
|---|---|---|---|---|---|
| 1 | 13400 | 23.9 | 38.4 | 0.0018 | 0.0029 |
| 2 | 14900 | 24.9 | 40.1 | 0.0017 | 0.0027 |
| 3 | 14500 | 24.9 | 40.2 | 0.0017 | 0.0028 |
| 4 | 15300 | 27.4 | 40.8 | 0.0018 | 0.0027 |
| 5 | 14200 | 25.8 | 38 | 0.0018 | 0.0027 |
| 6 | 15500 | 27.7 | 41.6 | 0.0018 | 0.0027 |
| 7 | 14400 | 24.3 | 39.2 | 0.0017 | 0.0027 |
| 8 | 13000 | 24.1 | 36.9 | 0.0019 | 0.0028 |
| 9 | 12900 | 24.3 | 36.5 | 0.0019 | 0.0028 |
| 10 | 13500 | 24.3 | 37 | 0.0018 | 0.0027 |
| 11 | 14700 | 27 | 41.4 | 0.0018 | 0.0028 |
| 12 | 13900 | 24.9 | 38.9 | 0.0018 | 0.0028 |
| 13 | 13900 | 24.4 | 39.2 | 0.0018 | 0.0028 |
| 14 | 13400 | 25.6 | 37.8 | 0.0019 | 0.0028 |
| 15 | 13900 | 26.5 | 38.3 | 0.0019 | 0.0028 |
| 16 | 13200 | 27.1 | 37.3 | 0.0021 | 0.0028 |
| 17 | 11400 | 23.7 | 33.3 | 0.0021 | 0.0029 |
| 18 | 11900 | 24.8 | 35.5 | 0.0021 | 0.0030 |
| 19 | 12900 | 23.8 | 36.2 | 0.0018 | 0.0028 |
| 20 | 13900 | 25 | 40 | 0.0018 | 0.0029 |
| 21 | 13900 | 25.7 | 37.6 | 0.0018 | 0.0027 |
| 22 | 14000 | 25.6 | 40.1 | 0.0018 | 0.0029 |
| 23 | 13500 | 25.3 | 38.4 | 0.0019 | 0.0028 |
| 24 | 12800 | 26.9 | 38.9 | 0.0021 | 0.0030 |
| 25 | 11200 | 24.5 | 35 | 0.0022 | 0.0031 |
| 26 | 13100 | 24.2 | 36.4 | 0.0018 | 0.0028 |
| 27 | 13400 | 24.5 | 37.3 | 0.0018 | 0.0028 |
| 28 | 14700 | 25.1 | 40.7 | 0.0017 | 0.0028 |
| 29 | 14100 | 25.4 | 40.8 | 0.0018 | 0.0029 |
| 30 | 16300 | 28.8 | 43.4 | 0.0018 | 0.0027 |
| 31 | 15000 | 28 | 40.6 | 0.0019 | 0.0027 |
| 32 | 10300 | 22.9 | 30.4 | 0.0022 | 0.0030 |
| 33 | 11800 | 24.1 | 33.9 | 0.0020 | 0.0029 |
| 34 | 12200 | 23.8 | 36.8 | 0.0020 | 0.0030 |
| 35 | 14500 | 26.9 | 39.3 | 0.0019 | 0.0027 |
| 36 | 16500 | 30.1 | 43.6 | 0.0018 | 0.0026 |
| 37 | 17400 | 32.5 | 47.4 | 0.0019 | 0.0027 |
| 38 | 15300 | 29.8 | 40.7 | 0.0019 | 0.0027 |
| 39 | 13300 | 26.9 | 39.6 | 0.0020 | 0.0030 |
| 40 | 11900 | 26.3 | 35.6 | 0.0022 | 0.0030 |
| 41 | 11200 | 24.5 | 33.9 | 0.0022 | 0.0030 |
| 42 | 11400 | 25.5 | 35.2 | 0.0022 | 0.0031 |
| 43 | 10100 | 22.5 | 33.6 | 0.0022 | 0.0033 |
| 44 | 11300 | 22.7 | 34.1 | 0.0020 | 0.0030 |
| 45 | 10400 | 21.1 | 31.6 | 0.0020 | 0.0030 |

**Table C6. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g for river-bottom sediment data from RAMP and JOSM.**

| Agency | Site | Date | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|---|
| RAMP | ATR-FR-W | 2002-09-13 | 5660 | 16.5 | 20 |
| RAMP | ATR-FR-E | 2002-09-13 | 2990 | 9.4 | 10.6 |
| RAMP | ATR-DC-E | 2002-09-07 | 2760 | 17.3 | 10.2 |
| RAMP | ATR-DC-W | 2002-09-07 | 1400 | 5.1 | 4.8 |
| RAMP | ATR-UFM | 2002-09-07 | 6910 | 18.3 | 19.6 |
| RAMP | ATR-MR-W | 2002-09-06 | 17700 | 42.1 | 32.6 |
| RAMP | ATR-MR-E | 2002-09-06 | 9740 | 26.6 | 23.1 |
| RAMP | ATR-SR-E | 2002-09-06 | 9020 | 29.7 | 27.2 |
| RAMP | ATR-SR-W | 2002-09-06 | 7360 | 29.2 | 24.6 |
| RAMP | ATR-DD-W | 2002-09-05 | 6820 | 17.8 | 14.4 |
| RAMP | ATR-FC-E | 2002-09-05 | 10800 | 24.9 | 16.9 |
| RAMP | ATR-DD-E | 2002-09-05 | 4720 | 16.3 | 10.2 |
| RAMP | ATR-FC-W | 2002-09-05 | 19000 | 36.7 | 23.8 |
| RAMP | ATR-DC-W | 2001-11-02 | 2600 | 10 | 8 |
| RAMP | ATR-DC-E | 2001-11-02 | 1300 | 5 | 5 |
| RAMP | ATR-SR-W | 2001-11-01 | 18600 | 48 | 22 |
| RAMP | ATR-MR-E | 2001-11-01 | 1200 | 4 | 4 |
| RAMP | ATR-SR-E | 2001-11-01 | 7500 | 17 | 11 |
| RAMP | ATR-MR-W | 2001-11-01 | 2800 | 9 | 7 |
| RAMP | ATR-FC-E | 2001-10-14 | 7200 | 23 | 14 |
| RAMP | ATR-FC-W | 2001-10-14 | 10600 | 28 | 17 |
| RAMP | ATR-MR-W | 2000-10-04 | 4440 | 19.1 | 12.6 |
| RAMP | ATR-MR-E | 2000-10-04 | 4680 | 28.8 | 19.4 |
| RAMP | ATR-FC-W | 2000-10-03 | 1850 | 8.9 | 7.9 |
| RAMP | ATR-FC-E | 2000-10-03 | 3440 | 15.9 | 12.9 |
| RAMP | ATR-DC-W | 2000-10-02 | 2920 | 12.1 | 10.7 |
| RAMP | ATR-SR-W | 2000-10-02 | 5160 | 30.4 | 20.2 |
| RAMP | ATR-SR-E | 2000-10-02 | 2600 | 11.4 | 8.8 |
| RAMP | ATR-DC-E | 2000-10-02 | 3920 | 17.6 | 23.9 |
| RAMP | ATR-FC-E-D | 1998-09-17 | 7630 | 20 | 14 |
| RAMP | ATR-FC-W-D | 1998-09-17 | 9440 | 22 | 20 |
| RAMP | ATR-MR-E-D | 1998-09-16 | 10900 | 28 | 19 |
| RAMP | ATR-DC-W | 1998-09-16 | 5990 | 18 | 14 |
| RAMP | ATR-MR-W-D | 1998-09-16 | 9560 | 24 | 17 |
| RAMP | ATR-DC-E | 1998-09-16 | 8080 | 22 | 13 |
| RAMP | ATR-FC-CC-D | 1997-10-10 | 8160 | 19 | 21 |
| RAMP | ATR-DC-CC | 1997-10-06 | 10700 | 28 | 16 |
| JOSM | M3 SAND | 2012-09-18 | 2390 | 11.6 | 7.3 |
| JOSM | M3 GRAVEL | 2012-09-18 | 3730 | 13.3 | 10.3 |
| JOSM | M3B GRAVEL | 2012-09-24 | 4450 | 14.6 | 12.7 |
| JOSM | M3B SAND | 2012-09-24 | 934 | 4.1 | 4.5 |
| JOSM | M4 GRAVEL | 2012-09-20 | 2740 | 10.4 | 8.9 |
| JOSM | M4 SAND | 2012-09-20 | 4290 | 15 | 16.9 |
| JOSM | M6 SAND | 2012-09-21 | 688 | 4.7 | 3.4 |
| JOSM | M6 GRAVEL | 2012-09-21 | 3510 | 12.9 | 11.3 |
| JOSM | M7 GRAVEL | 2012-09-22 | 6730 | 20.1 | 19.4 |

| | | | | | |
|---|---|---|---|---|---|
| JOSM | M7 SAND | 2012-09-22 | 3400 | 12 | 10.3 |
| JOSM | M7C SAND | 2012-09-22 | 1800 | 7.9 | 7 |
| JOSM | M7C GRAVEL | 2012-09-23 | 3030 | 10.7 | 23.8 |
| JOSM | M8 GRAVEL | 2012-09-25 | 6630 | 19.2 | 18 |
| JOSM | M8 SAND | 2012-09-25 | 9430 | 27.4 | 24.8 |
| JOSM | M3 GRAVEL | 2013-09-18 | 4110 | 13.6 | 10.2 |
| JOSM | M3 SAND | 2013-09-18 | 2280 | 8.2 | 8 |
| JOSM | M3B GRAVEL | 2013-09-17 | 4160 | 14.4 | 11.9 |
| JOSM | M3B SAND | 2013-09-17 | 5510 | 16.2 | 16.6 |
| JOSM | M4 SAND | 2013-09-19 | 4770 | 14.6 | 14.8 |
| JOSM | M4 GRAVEL | 2013-09-19 | 6430 | 19.9 | 17.6 |
| JOSM | M6 GRAVEL | 2013-09-22 | 6360 | 18.1 | 18.2 |
| JOSM | M6 SAND | 2013-09-22 | 4690 | 12.9 | 13.8 |
| JOSM | M7 GRAVEL | 2013-09-21 | 4000 | 12.5 | 11.9 |
| JOSM | M7 SAND | 2013-09-21 | 6850 | 18.2 | 20.1 |
| JOSM | M7C GRAVEL | 2013-09-23 | 6520 | 19.3 | 18.2 |
| JOSM | M7C SAND | 2013-09-23 | 4260 | 13 | 13.6 |
| JOSM | M8 GRAVEL | 2013-09-21 | 6110 | 16.9 | 17.5 |
| JOSM | M8 SAND | 2013-09-21 | 5100 | 14.6 | 15.5 |
| JOSM | M3 GRAVEL | 2014-09-21 | 2160 | 9.5 | 6.2 |
| JOSM | M3 GRAVEL | 2014-09-21 | 3480 | 12.7 | 9.4 |
| JOSM | M9 GRAVEL | 2014-09-21 | 2820 | 11.3 | 7.6 |
| JOSM | M3 GRAVEL | 2014-09-21 | 5400 | 14.6 | 16 |
| JOSM | M3B GRAVEL | 2014-09-21 | 6250 | 19.5 | 16.5 |
| JOSM | M3B SAND | 2014-09-21 | 1570 | 6.3 | 5.7 |
| JOSM | M4 GRAVEL | 2014-09-14 | 5190 | 16 | 15.1 |
| JOSM | M4 GRAVEL | 2014-09-26 | 3050 | 11 | 9.4 |
| JOSM | M4 SAND | 2014-09-26 | 7460 | 21.1 | 22.6 |
| JOSM | M6 GRAVEL | 2014-09-24 | 6310 | 19.2 | 17.6 |
| JOSM | M6 SAND | 2014-09-24 | 8030 | 21.4 | 21.6 |
| JOSM | M7 GRAVEL | 2014-09-23 | 4330 | 14.3 | 12.9 |
| JOSM | M7 SAND | 2014-09-23 | 5190 | 16.9 | 15.3 |
| JOSM | M7C GRAVEL | 2014-09-22 | 5250 | 16.8 | 16.3 |
| JOSM | M7C SAND | 2014-09-22 | 6520 | 21 | 23.1 |
| JOSM | M8 GRAVEL | 2014-09-20 | 6780 | 19.4 | 18.5 |
| JOSM | M8 SAND | 2014-09-20 | 8520 | 22.7 | 22.9 |

**Table C7. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g for river suspended sediment data from JOSM.**

| Agency | Site | Date | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|---|
| JOSM | M0 | 06-2012 | 7225 | 18.45 | 22.1 |
| JOSM | M0 | 09-2012 | 7370 | 16 | 28.3 |
| JOSM | M2 | 06-2012 | 8175 | 21.5 | 24.6 |
| JOSM | M2 | 09-2012 | 6830 | 16.6 | 27.6 |
| JOSM | M3 | 06-2012 | 7150 | 19.4 | 22.45 |
| JOSM | M3 | 09-2012 | 6370 | 16 | 22.8 |
| JOSM | M9 | 06-2012 | 7035 | 18.85 | 21.25 |
| JOSM | M9 | 10-2012 | 6160 | 15.8 | 21 |
| JOSM | M0 | 06-2013 | 8645 | 19.25 | 22.15 |
| JOSM | M0 | 09-2013 | 10500 | 18.9 | 28.3 |
| JOSM | M0 | 02-2014 | 9045 | 22.15 | 27.85 |
| JOSM | M2 | 06-2013 | 8710 | 18.3 | 22 |
| JOSM | M2 | 09-2013 | 11000 | 26.5 | 33.3 |
| JOSM | M2 | 02-2014 | 10400 | 28.8 | 28.25 |
| JOSM | M3 | 06-2013 | 9060 | 19.35 | 22.3 |
| JOSM | M3 | 09-2013 | 7570 | 20.8 | 27.7 |
| JOSM | M4 | 02-2014 | 9780 | 28.45 | 24.55 |
| JOSM | M9 | 06-2013 | 8610 | 21.65 | 21.05 |
| JOSM | M0 | 06-2014 | 9725 | 22 | 27.8 |
| JOSM | M0 | 09-2014 | 9730 | 22 | 32.5 |
| JOSM | M2 | 09-2014 | 8670 | 22.45 | 24.25 |
| JOSM | M3 | 06-2014 | 8580 | 21.5 | 22.55 |
| JOSM | M3 | 09-2014 | 8200 | 21.2 | 24.725 |
| JOSM | M9 | 06-2014 | 8745 | 22.75 | 22.1 |
| JOSM | M9 | 09-2014 | 9248 | 24.125 | 25.7 |

**Table C8. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) presented in µg/g for exposed river sediments collected during this study.**

| Site | Date | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|
| AR* near Down 26 | 10-2016 | 11100 | 29.9 | 22 |
| AR* near Up 17 | 10-2016 | 13400 | 31.6 | 24.7 |
| AR* Downstream of Clearwater R. | 07-2017 | 3600 | 12.2 | 9.01 |
| Fort McMurray flood deposit sed. | 07-2017 | 5580 | 18.2 | 15.4 |

*AR = Athabasca River

**Table C9. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) in µg/g by depth and CRS-derived year (only pre-1967 values used in baseline creation shown) at JOSM lake NE13. Blank spaces indicate depths where metals were not measured. Data received from Colin Cooke.**

| Lake ID | Depth (cm) | Pre-67 Chronology | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|---|
| NE13 | 11.5 | 1951 | 339 | 8.1 | 4.9 |
| NE13 | 12 | 1946 | | | |
| NE13 | 12.5 | 1942 | 318 | 8.5 | 5.2 |
| NE13 | 13 | 1937 | | | |
| NE13 | 13.5 | 1933 | 299 | 7.1 | 4.5 |
| NE13 | 14 | 1928 | | | |
| NE13 | 14.5 | 1923 | 281 | 4.8 | 4.2 |
| NE13 | 15 | 1918 | | | |
| NE13 | 15.5 | 1913 | 332 | 5.2 | 4.5 |
| NE13 | 16 | 1908 | | | |
| NE13 | 16.5 | 1903 | 255 | 3.4 | 3.2 |
| NE13 | 17 | 1897 | | | |
| NE13 | 17.5 | 1891 | 317 | 7.3 | 5 |
| NE13 | 18 | 1886 | | | |
| NE13 | 18.5 | 1880 | 253 | 6.2 | 4.4 |
| NE13 | 19 | 1874 | | | |
| NE13 | 19.5 | 1867 | 328 | 6.2 | 4.6 |
| NE13 | 20 | 1861 | 311 | 6.8 | 4.9 |
| NE13 | 21 | 1848 | | | |
| NE13 | 22 | 1835 | | | |
| NE13 | 23 | 1821 | | | |
| NE13 | 24 | 1806 | | | |
| NE13 | 25 | 1791 | 295 | 1.6 | 3.2 |
| NE13 | 26 | 1775 | | | |
| NE13 | 27 | 1759 | | | |
| NE13 | 28 | 1743 | | | |
| NE13 | 29 | 1725 | 234 | 0.65 | 2.8 |
| NE13 | 30 | 1708 | | | |
| NE13 | 31 | 1690 | | | |
| NE13 | 32 | 1671 | | | |
| NE13 | 33 | 1652 | | | |
| NE13 | 34 | 1632 | 146 | 0.4 | 2 |

**Table C10. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) in µg/g by depth and CRS-derived year (only pre-1967 values used in baseline creation shown) at JOSM lake NE20. Blank spaces indicate depths where metals were not measured. Data received from Colin Cooke.**

| Lake ID | Depth (cm) | Pre-67 Chronology | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|---|
| NE20 | 15.5 | 1955 | 835 | 6.2 | 6.4 |
| NE20 | 16 | 1953 | | | |
| NE20 | 16.5 | 1951 | 848 | 5.5 | 6.7 |
| NE20 | 17 | 1949 | | | |
| NE20 | 17.5 | 1947 | 743 | 4.3 | 6.1 |
| NE20 | 18 | 1945 | | | |
| NE20 | 18.5 | 1943 | 808 | 4.6 | 7.4 |
| NE20 | 19 | 1941 | | | |
| NE20 | 19.5 | 1939 | | | |
| NE20 | 20 | 1937 | 814 | 4.9 | 8.2 |
| NE20 | 21 | 1933 | | | |
| NE20 | 22 | 1928 | | | |
| NE20 | 23 | 1924 | | | |
| NE20 | 24 | 1919 | | | |
| NE20 | 25 | 1915 | 832 | 4.2 | 7.7 |
| NE20 | 26 | 1910 | | | |
| NE20 | 27 | 1906 | | | |
| NE20 | 28 | 1901 | | | |
| NE20 | 29 | 1897 | 785 | 3.1 | 6.4 |
| NE20 | 30 | 1892 | | | |
| NE20 | 31 | 1887 | | | |
| NE20 | 32 | 1882 | | | |
| NE20 | 33 | 1877 | | | |
| NE20 | 34 | 1872 | 727 | 3 | 6.1 |
| NE20 | 35 | 1867 | | | |
| NE20 | 36 | 1862 | | | |
| NE20 | 37 | 1857 | | | |
| NE20 | 38 | 1852 | | | |
| NE20 | 39 | 1847 | 862 | 2.1 | 5.7 |

**Table C11. Raw values of aluminum (Al), nickel (Ni), and vanadium (V) in µg/g by depth and CRS-derived year (only pre-1967 values used in baseline creation shown) at JOSM lake RAMP 418/ Kearle. Blank spaces indicate depths where metals were not measured. Data received from Colin Cooke.**

| Lake ID | Depth (cm) | Pre-67 Chronology | Al (µg/g) | V (µg/g) | Ni (µg/g) |
|---|---|---|---|---|---|
| RAMP 418/Kearle | 14.5 | 1943 | 2930 | 12.3 | 14.9 |
| RAMP 418/Kearle | 15 | 1939 | | | |
| RAMP 418/Kearle | 15.5 | 1934 | 2960 | 10.1 | 12.9 |
| RAMP 418/Kearle | 16 | 1930 | | | |
| RAMP 418/Kearle | 16.5 | 1926 | | | |
| RAMP 418/Kearle | 17 | 1921 | 3300 | 9.4 | 13 |
| RAMP 418/Kearle | 17.5 | 1916 | | | |
| RAMP 418/Kearle | 18 | 1912 | | | |
| RAMP 418/Kearle | 18.5 | 1907 | 2990 | 8 | 11.6 |
| RAMP 418/Kearle | 19 | 1902 | | | |
| RAMP 418/Kearle | 19.5 | 1897 | 3380 | 8.3 | 11.7 |
| RAMP 418/Kearle | 20 | 1892 | | | |
| RAMP 418/Kearle | 21 | 1882 | 3070 | 8.9 | 10.7 |
| RAMP 418/Kearle | 22 | 1872 | | | |
| RAMP 418/Kearle | 23 | 1861 | | | |
| RAMP 418/Kearle | 24 | 1850 | 2630 | 7.2 | 9.2 |
| RAMP 418/Kearle | 25 | 1839 | | | |
| RAMP 418/Kearle | 26 | 1827 | | | |
| RAMP 418/Kearle | 27 | 1816 | 2260 | 9.6 | 11.2 |
| RAMP 418/Kearle | 28 | 1804 | | | |
| RAMP 418/Kearle | 29 | 1792 | 2100 | 6 | 6.9 |
| RAMP 418/Kearle | 30 | 1780 | | | |
| RAMP 418/Kearle | 31 | 1768 | | | |
| RAMP 418/Kearle | 32 | 1756 | | | |
| RAMP 418/Kearle | 33 | 1743 | 2030 | 6.1 | 7 |
| RAMP 418/Kearle | 34 | 1731 | | | |
| RAMP 418/Kearle | 35 | 1719 | | | |
| RAMP 418/Kearle | 36 | 1706 | 2470 | 7.4 | 7.5 |
| RAMP 418/Kearle | 37 | 1694 | | | |
| RAMP 418/Kearle | 38 | 1681 | | | |
| RAMP 418/Kearle | 39 | 1669 | 2400 | 6.9 | 7.4 |

## Appendix D – Chronology information (for developing age-depth models)

**Table D1. Radioisotope values ($^{210}$Pb, $^{137}$Cs, $^{226}$Ra in dpm/g) and CRS-inferred chronology for lake Up 17. Grey highlighted cells are extrapolated dates using the CRS model. (--) = no measurement taken; (ND) = below the detection limit and should be treated as 0.**

| Sediment core top depth (cm) | CRS chronology | CRS Error ± 2 sigma | $^{210}$Pb dpm/g | $^{210}$Pb error (1 std. dev.) dpm/g | $^{137}$Cs dpm/g | $^{137}$Cs error (1 std. dev.) dpm/g | $^{226}$Ra* dpm/g | $^{226}$Ra error (1 std. dev.) dpm/g |
|---|---|---|---|---|---|---|---|---|
| 0 | 2016.50 | 0.16 | 6.3095 | 1.2327 | 0.3104 | 0.1882 | 1.9107 | 0.4660 |
| 1 | 2016.20 | 0.28 | 4.6195 | 1.0175 | 0.4856 | 0.1298 | 1.7793 | 0.3209 |
| 2 | 2015.32 | 0.42 | 5.6799 | 0.4862 | 0.4929 | 0.0661 | 1.8819 | 0.2407 |
| 4 | 2013.09 | 0.88 | 5.0883 | 0.4819 | 0.4633 | 0.0650 | 2.1882 | 0.2489 |
| 6 | 2010.26 | 1.38 | 5.9878 | 0.5397 | 0.1566 | 0.0750 | 2.3502 | 0.3096 |
| 8 | 2006.84 | 1.92 | 7.7947 | 0.5600 | 0.1549 | 0.0820 | 2.5471 | 0.3340 |
| 10 | 2003.36 | 2.54 | 8.2611 | 0.9809 | 0.0698 | 0.2180 | 2.0301 | 0.3865 |
| 12 | 1998.71 | 3.45 | 7.1947 | 0.5751 | 0.2355 | 0.0797 | 2.0611 | 0.2829 |
| 14 | 1994.04 | 4.48 | 5.6053 | 0.5795 | 0.2589 | 0.0814 | 1.8541 | 0.3072 |
| 16 | 1989.75 | 5.54 | 3.4968 | 0.4448 | 0.2855 | 0.0612 | 1.6950 | 0.2330 |
| 18 | 1986.00 | 6.51 | 2.8901 | 0.3902 | 0.2041 | 0.0549 | 1.8499 | 0.2109 |
| 20 | 1981.37 | 7.77 | 3.0728 | 0.3931 | 0.2108 | 0.0552 | 1.8771 | 0.2018 |
| 22 | 1976.73 | 9.06 | 3.0173 | 0.4040 | 0.2226 | 0.0561 | 2.0868 | 0.2261 |
| 24 | 1972.36 | 10.44 | 3.1736 | 0.4446 | 0.4615 | 0.0625 | 2.1021 | 0.2667 |
| 26 | 1966.46 | 12.51 | 3.2715 | 0.4144 | 1.1431 | 0.0627 | 2.2298 | 0.2423 |
| 28 | 1959.63 | 14.94 | 3.1185 | 0.3668 | 2.3770 | 0.0652 | 2.3866 | 0.2500 |
| 30 | 1954.57 | 17.11 | 2.8196 | 0.3343 | 1.6088 | 0.0529 | 2.2386 | 0.2311 |
| 32 | 1948.21 | 19.71 | 2.8427 | 0.3760 | 1.0892 | 0.0564 | 2.3065 | 0.2403 |
| 34 | 1944.15 | 20.26 | 2.5353 | 0.3529 | 0.3675 | 0.0495 | 2.3324 | 0.2386 |
| 36 | 1927.63 | 27.97 | 2.7292 | 0.3155 | ND | ND | 1.8941 | 0.1930 |
| 38 | 1918.38 | -- | 2.5056 | 0.3362 | ND | ND | 2.3161 | 0.2263 |
| 40 | 1909.83 | -- | 2.0914 | 0.3419 | ND | ND | 2.0502 | 0.2432 |
| 42 | 1900.58 | -- | 2.3796 | 0.3427 | ND | ND | 1.9004 | 0.1922 |

*$^{226}$Ra = weighted mean of $^{214}$Bi and $^{214}$Pb

**Table D2. Radioisotope values ($^{210}$Pb, $^{137}$Cs, $^{226}$Ra in dpm/g) and CRS-inferred chronology for lake Up 10. Grey highlighted cells are extrapolated dates using the CRS model. (--) = no measurement taken; (ND) = below the detection limit and should be treated as 0.**

| Sediment core top depth (cm) | CRS chronology | CRS Error ± 2 sigma | $^{210}$Pb dpm/g | $^{210}$Pb error (1 std. dev.) dpm/g | $^{137}$Cs dpm/g | $^{137}$Cs error (1 std. dev.) dpm/g | $^{226}$Ra* dpm/g | $^{226}$Ra error (1 std. dev.) dpm/g |
|---|---|---|---|---|---|---|---|---|
| 0 | 2015.72 | 0.50 | 16.7288 | 1.1745 | 0.2568 | 0.1271 | 5.0332 | 0.6165 |
| 1 | 2013.22 | 1.11 | 10.6011 | 1.0028 | 0.0100 | 0.0329 | 4.6124 | 0.5352 |
| 2 | 2010.01 | 1.64 | 10.1991 | 0.8401 | 0.1425 | 0.0886 | 3.8841 | 0.3885 |
| 3 | 2005.14 | 2.48 | 14.1155 | 1.2735 | 0.0462 | 0.0906 | 4.3345 | 0.5331 |
| 4 | 1995.97 | 4.25 | 10.1307 | 0.7076 | 0.2860 | 0.0793 | 2.7641 | 0.3323 |
| 5 | 1990.22 | 5.58 | 8.3982 | 0.6933 | 0.4377 | 0.0848 | 3.9585 | 0.4054 |
| 6 | 1982.70 | 7.57 | 6.8161 | 0.5845 | 0.5129 | 0.0726 | 3.3980 | 0.3104 |
| 7 | 1973.86 | 10.45 | 5.3673 | 0.4442 | 0.7466 | 0.0592 | 2.6887 | 0.2239 |
| 8 | 1962.86 | 14.82 | 5.0042 | 0.4194 | 1.2270 | 0.0611 | 3.0032 | 0.2559 |
| 9 | 1949.81 | 21.74 | 4.7618 | 0.4023 | 1.8727 | 0.0634 | 3.1440 | 0.2594 |
| 10 | 1940.13 | 25.54 | 3.7551 | 0.3650 | 0.6806 | 0.0496 | 3.1228 | 0.2800 |
| 11 | 1928.11 | 31.27 | 3.8823 | 0.3905 | 0.0982 | 0.0437 | 3.2280 | 0.2559 |
| 12 | 1910.85 | -- | 2.7863 | 0.3523 | 0.0452 | 0.0349 | 2.3845 | 0.2306 |
| 13 | 1885.12 | -- | 2.9934 | 0.3764 | 0.0346 | 0.0352 | 3.1274 | 0.2466 |
| 14 | 1866.87 | -- | 2.8880 | 0.3459 | ND | ND | 2.8529 | 0.2410 |
| 16 | 1832.50 | -- | 3.1451 | 0.4014 | ND | ND | 3.5410 | 0.3001 |
| 18 | 1805.06 | -- | 2.9475 | 0.3835 | ND | ND | 2.4876 | 0.2246 |
| 20 | 1759.60 | -- | 2.9060 | 0.3511 | ND | ND | 2.6468 | 0.2032 |

*$^{226}$Ra = weighted mean of $^{214}$Bi and $^{214}$Pb

**Table D3. Radioisotope values ($^{210}$Pb, $^{137}$Cs, $^{226}$Ra in dpm/g) and CRS-inferred chronology for lake Down 1. Grey highlighted cells are extrapolated dates using the CRS model. (--) = no measurement taken; (ND) = below the detection limit and should be treated as 0.**

| Sediment core top depth (cm) | CRS chronology | CRS Error ± 2 sigma | $^{210}$Pb dpm/g | $^{210}$Pb error (1 std. dev.) dpm/g | $^{137}$Cs dpm/g | $^{137}$Cs error (1 std. dev.) dpm/g | $^{226}$Ra* dpm/g | $^{226}$Ra error (1 std. dev.) dpm/g |
|---|---|---|---|---|---|---|---|---|
| 0 | 2015.093 | 0.16195 | 7.70508 | 0.671049 | 1.04700 | 0.093979 | 1.54702 | 0.35138 |
| 1 | 2014.427 | 0.25890 | 9.23562 | 0.684137 | 1.04953 | 0.094137 | 1.67917 | 0.317527 |
| 2 | 2013.559 | 0.38590 | 8.12270 | 0.503178 | 1.01518 | 0.071548 | 1.70241 | 0.29588 |
| 4 | 2010.776 | 0.92220 | 8.90909 | 0.795308 | 1.13032 | 0.113887 | 2.02139 | 0.43906 |
| 6 | 2007.716 | 1.42050 | 7.41149 | 0.415308 | 1.15030 | 0.061073 | 1.54629 | 0.204988 |
| 8 | 2003.325 | 2.20790 | 7.51882 | 0.46483 | 1.35828 | 0.069499 | 1.84616 | 0.258486 |
| 10 | 1998.15 | 3.27824 | 7.94900 | 0.499078 | 1.55803 | 0.075532 | 1.52207 | 0.240002 |
| 12 | 1991.975 | 4.79936 | 7.13162 | 0.450641 | 1.53417 | 0.068816 | 1.87323 | 0.249207 |
| 14 | 1985.326 | 6.78008 | 5.82380 | 0.416644 | 1.57179 | 0.066854 | 1.91458 | 0.258428 |
| 16 | 1982.641 | 7.67993 | 2.63243 | 0.322248 | 1.18678 | 0.050241 | 1.78041 | 0.208004 |
| 18 | 1979.659 | 8.75053 | 2.99326 | 0.305857 | 1.29265 | 0.047732 | 1.76607 | 0.205164 |
| 20 | 1972.718 | 10.9771 | 3.01570 | 0.315882 | 1.83791 | 0.053739 | 2.34584 | 0.248333 |
| 22 | 1960.527 | 15.7462 | 3.29311 | 0.354234 | 0.86721 | 0.050664 | 2.15298 | 0.263178 |
| 24 | 1951.166 | 20.8478 | 2.72947 | 0.314193 | 0.25000 | 0.039906 | 1.8921 | 0.205468 |
| 26 | 1936.726 | 32.1645 | 2.8273 | 0.312914 | 0.16161 | 0.040836 | 1.92443 | 0.224256 |
| 28 | 1931.178 | 36.2619 | 1.87157 | 0.261929 | ND | 0.035768 | 1.99580 | 0.21185 |
| 30 | 1922.858 | 42.8582 | 2.44717 | 0.323548 | ND | 0.042708 | 2.12096 | 0.230698 |
| 32 | 1917.807 | 43.5988 | 1.94628 | 0.276473 | ND | 0.022526 | 1.86711 | 0.206888 |
| 34 | 1912.752 | 41.8847 | 2.20217 | 0.415102 | 0.22721 | 0.052404 | 2.04820 | 0.23907 |
| 36 | 1890.885 | 14.5848 | 2.43824 | 0.369719 | ND | 0.116494 | 2.09137 | 0.282384 |
| 40 | 1872.258 | -- | 2.10082 | 0.358699 | ND | 0.053478 | 2.09912 | 0.269616 |
| 44 | 1858.659 | -- | 2.20189 | 0.34472 | ND | 0.035708 | 1.8232 | 0.247613 |
| 48 | 1844.189 | -- | 1.69173 | 0.300447 | ND | 0.033711 | 1.94252 | 0.216895 |
| 52 | 1823.669 | -- | 2.00968 | 0.297729 | ND | 0.034163 | -- | -- |

*$^{226}$Ra = weighted mean of $^{214}$Bi and $^{214}$Pb

**Table D4. Radioisotope values ($^{210}$Pb, $^{137}$Cs, $^{226}$Ra in dpm/g) and CRS-inferred chronology for lake Down 26. Grey highlighted cells are extrapolated dates using the CRS model. (--) = no measurement taken; (ND) = below the detection limit and should be treated as 0.**

| Sediment core top depth (cm) | 137Cs chronology | Error 1 std. dev. | $^{210}$Pb dpm/g | $^{210}$Pb error (1 std. dev.) dpm/g | $^{137}$Cs dpm/g | $^{137}$Cs error (1 std. dev.) dpm/g | $^{226}$Ra* dpm/g | $^{226}$Ra error (1 std. dev.) dpm/g |
|---|---|---|---|---|---|---|---|---|
| 0 | 2017.681 | 0.0163 | 9.4482 | 2.040914 | 0.0277 | 0.117141 | 3.1399 | 0.2969 |
| 1 | 2017.054 | 0.0833 | 8.8297 | 1.019024 | 0.2378 | 0.097759 | 1.6877 | 0.2760 |
| 2 | 2016.276 | 0.1666 | 6.2269 | 0.875248 | 0.0825 | 0.075252 | 2.2229 | 0.1385 |
| 4 | 2012.405 | 0.5809 | 4.0735 | 0.563051 | 0.1855 | 0.038866 | 2.5904 | 0.0953 |
| 6 | 2007.195 | 1.1383 | 3.3886 | 0.553148 | 0.2404 | 0.038397 | 2.6982 | 0.0594 |
| 8 | 2000.756 | 1.8273 | 2.6192 | 0.472477 | 0.2495 | 0.031846 | 2.4704 | 0.0268 |
| 10 | 1994.003 | 2.5498 | 2.7231 | 0.572047 | 0.1763 | 0.034548 | 2.8542 | 0.1455 |
| 12 | 1986.499 | 3.3527 | 2.7714 | 0.582597 | 0.2281 | 0.038093 | 2.9012 | 0.1408 |
| 14 | 1976.212 | 4.4535 | 2.1747 | 0.476213 | 0.2741 | 0.028792 | 2.6000 | 0.0693 |
| 16 | 1963 | 5.8671 | 2.4451 | 0.518256 | 0.3263 | 0.033804 | 2.6833 | 0.0890 |
| 18 | 1948.674 | 7.4000 | 2.0767 | 0.572821 | 0.0502 | 0.031676 | 3.0545 | 0.0815 |
| 22 | 1926.404 | 9.7829 | 1.8545 | 0.470878 | 0.0479 | 0.033804 | 2.0533 | 0.1111 |
| 26 | 1908.83 | 11.6633 | 2.0019 | 0.46639 | -0.0324 | 0.042916 | 2.0369 | 0.0313 |
| 30 | 1885.362 | 14.1743 | 1.5281 | 0.508948 | -0.0235 | 0.038382 | 2.5943 | 0.0629 |
| 34 | 1858.457 | 17.0532 | 2.3944 | 0.483765 | -0.0201 | 0.03643 | 2.3945 | 0.0940 |
| 35 | 1851.578 | 17.7892 | -- | -- | -- | -- | -- | -- |
| 36 | 1846.44 | 18.3390 | -- | -- | -- | -- | -- | -- |
| 37 | 1840.507 | 18.9739 | -- | -- | -- | -- | -- | -- |
| 38 | 1834.49 | 19.6177 | -- | -- | -- | -- | -- | -- |
| 39 | 1828.399 | 20.2694 | -- | -- | -- | -- | -- | -- |
| 40 | 1823.201 | 20.8255 | -- | -- | -- | -- | -- | -- |
| 41 | 1817.126 | 21.4756 | -- | -- | -- | -- | -- | -- |

*$^{226}$Ra = weighted mean of $^{214}$Bi and $^{214}$Pb

**Table D5. Radioisotope values ($^{210}$Pb, $^{137}$Cs, $^{226}$Ra in dpm/g) and CRS-inferred chronology for lake Down 58. Grey highlighted cells are extrapolated dates using the CRS model. (--) = no measurement taken; (ND) = below the detection limit and should be treated as 0.**

| Sediment core top depth (cm) | $^{210}$Pb dpm/g | $^{210}$Pb error (1 std. dev.) dpm/g | $^{137}$Cs dpm/g | $^{137}$Cs error (1 std. dev.) dpm/g | $^{226}$Ra* dpm/g | $^{226}$Ra error (1 std. dev.) dpm/g |
|---|---|---|---|---|---|---|
| 26 | 2.8884 | 0.3242 | 0.2254 | 0.0407 | 2.0665 | 0.1785 |
| 30 | 2.4054 | 0.3082 | 0.0727 | 0.0400 | 2.3459 | 0.1802 |
| 34 | 2.6184 | 0.3342 | 0.2443 | 0.0422 | 1.9567 | 0.1807 |
| 36 | 3.2180 | 0.3457 | 0.1404 | 0.0453 | 1.8910 | 0.1785 |
| 38 | 2.7394 | 0.3703 | 0.2198 | 0.0460 | 2.3542 | 0.1990 |
| 40 | 2.9248 | 0.3292 | 0.2133 | 0.0429 | 1.6983 | 0.1697 |
| 42 | 1.9933 | 0.2968 | 0.1612 | 0.0365 | 2.1368 | 0.1761 |
| 44 | 2.3570 | 0.2977 | 0.1396 | 0.0372 | 1.8631 | 0.1639 |

*$^{226}$Ra = weighted mean of $^{214}$Bi and $^{214}$Pb

**Table D6. Focus factors used to calculate adjusted excess flux for lakes Up 17, Up 10, and Down 1, following method by Muir *et al*., 2009 (*Envir. Sci. & Tech.*).**

| **Lake** | **Focus factor (± measured error)** |
|---|---|
| Up 17 | 1.841 (0.125) |
| Up 10 | 0.505 (0.034) |
| Down 1 | 0.875 (0.060) |

## Appendix E – Statistical analyses

**Table E1. AICc values, change in AIC values, and model weights of a model set formulated to test the hypothesis that a linear model for aluminum best predicts vanadium concentration in the floodplain lakes in the AOSR.**

| Model | K | AICc | ΔAICc | Model weights |
|---|---|---|---|---|
| V ~ Al | 3 | 862.45 | 0.00 | 1 |
| V ~ logAl | 3 | 1137.88 | 275.43 | 0 |

**Table E2. AICc values, change in AIC values, and model weights of a model set formulated to test the hypothesis that a linear model for aluminum best predicts nickel concentration in the floodplain lakes in the AOSR.**

| Model | K | AICc | ΔAICc | Model weights |
|---|---|---|---|---|
| Ni ~ Al | 3 | 808.55 | 0.00 | 1 |
| Ni ~ logAl | 3 | 942.21 | 133.66 | 0 |

**Table E3. Breakpoints for temporally determined enrichment factors for V and Ni calculated at Down 1 using R package 'segmented'.**

| | Nickel | | Vanadium | |
|---|---|---|---|---|
| | **Breakpoint 1** | **Breakpoint 2** | **Breakpoint 1** | **Breakpoint 2** |
| Predicted breakpoint | 1980 | 1990 | 1980 | 1990 |
| Model estimated breakpoint ± S.E. | 1982 ± 1.08 | 1986 ± 1.01 | 1982 ± 0.326 | 1986 ± 0.509 |
| p-value | $5.74 \times 10^{-5}$ | | $6.63 \times 10^{-5}$ | |

**Table E4. Slopes for the three-segmented breakpoint analysis on V and Ni EF data at Down 1. Multiple $R^2$ of 0.8172 (Ni) and 0.9727 (V), and adjusted $R^2$ of 0.7982 (Ni) and 0.9698 (V).**

| Slope | Nickel | Vanadium |
|---|---|---|
| Segment 1 ± S.E. | $-3.55 \times 10^{-4} \pm 2.10 \times 10^{-4}$ | $-3.90 \times 10^{-4} \pm 2.22 \times 10^{-4}$ |
| Segment 2 ± S.E. | $9.03 \times 10^{-2} \pm 4.82 \times 10^{-2}$ | $2.04 \times 10^{-1} \pm 3.37 \times 10^{-2}$ |
| Segment 3 ± S.E. | $2.30 \times 10^{-2} \pm 2.06 \times 10^{-3}$ | $2.60 \times 10^{-3} \pm 2.11 \times 10^{-3}$ |

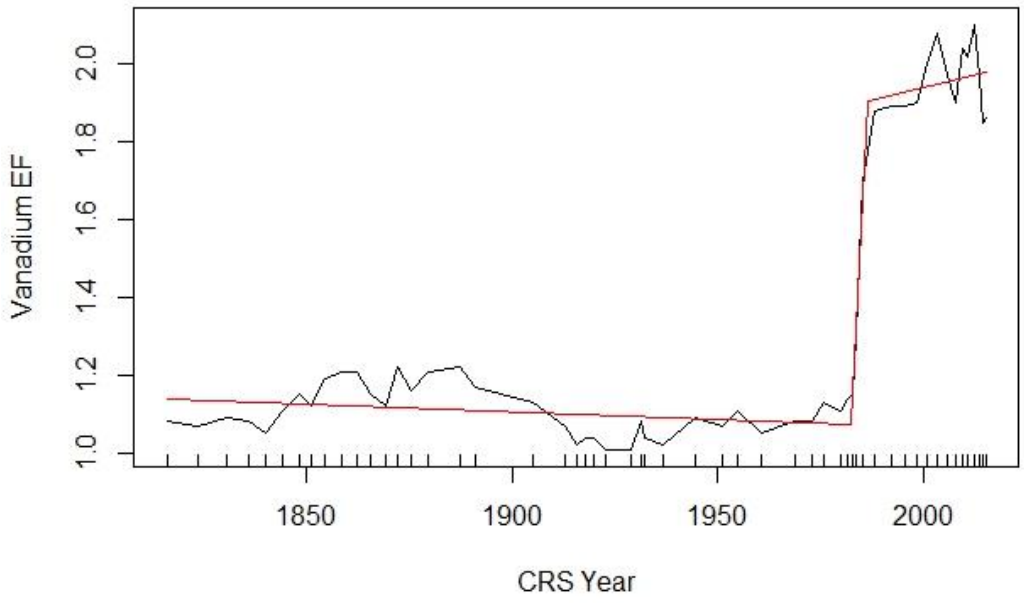


**Figure E1. Three-segmented breakpoint model superimposed on a plot of the change in vanadium enrichment factor (EF) over time at lake Down 1.**

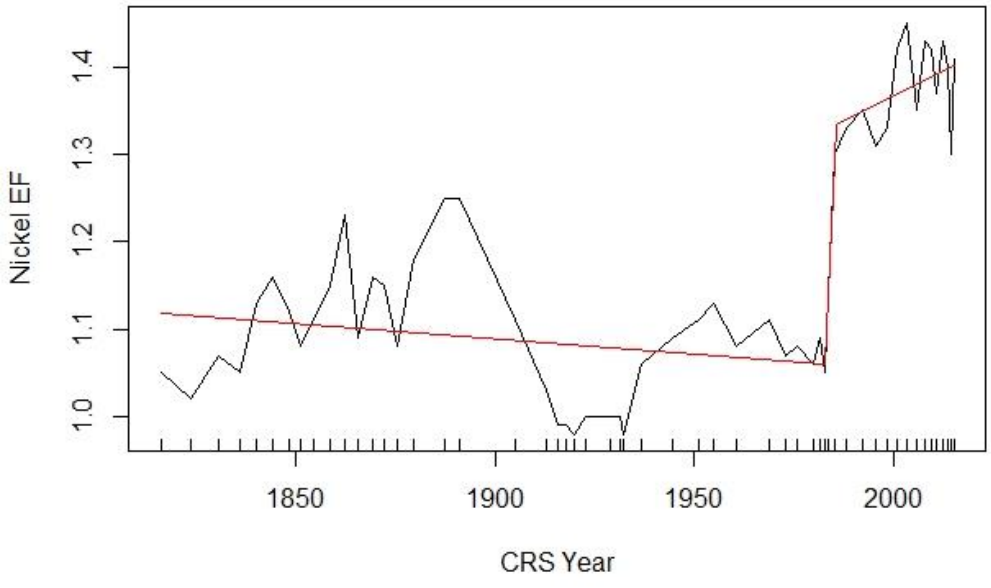


**Figure E2. Three-segmented breakpoint model superimposed on a plot of the change in nickel enrichment factor (EF) over time at lake Down 1.**