Spatial and temporal patterns in trace element deposition to lakes in the Athabasca oil sands region (Alberta, Canada)

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Abstract

The mining and processing of the Athabasca oil sands (Alberta, Canada) has been occurring for decades; however, a lack of consistent regional monitoring has obscured the long-term environmental impact. Here, we present sediment core results to reconstruct spatial and temporal patterns in trace element deposition to lakes in the Athabasca oil sands region. Early mining operations (during the 1970s and 1980s) led to elevated V and Pb inputs to lakes located <50 km from mining operations. Subsequent improvements to mining and upgrading technologies since the 1980s have reduced V and Pb loading to near background levels at many sites. In contrast, Hg deposition increased by a factor of ∼3 to all 20 lakes over the 20th century, reflecting global-scale patterns in atmospheric Hg emissions. Base cation deposition (from fugitive dust emissions) has not measurably impacted regional lake sediments. Instead, results from a principal components analysis suggest that the presence of carbonate bedrock underlying lakes located close to development appears to exert a first-order control over lake sediment base cation concentrations and overall lake sediment geochemical composition. Trace element concentrations generally did not exceed Canadian sediment quality guidelines, and no spatial or temporal trends were observed in the frequency of guideline exceedence. Our results demonstrate that early mining efforts had an even greater impact on trace element cycling than has been appreciated previously, placing recent monitoring efforts in a critical long-term context.

Introduction

The oil sands of northern Alberta and Saskatchewan are estimated to contain 170 billion barrels of oil (Attanasi and Meyer 2010). About 20% of oil sands reserves are thought to be recoverable by surface mining and ~80% by in situ extraction methods. Oil sands production has increased steadily in recent years, with production rising from ~1 × 10^6 barrels of oil per day (b d^-1) in 1980, to 2.42 × 10^8 b d^-1 in 2016. This rapid increase in production has raised concern about potential atmospheric emission, transport, and deposition of inorganic contaminants to ecosystems.

Environmental archives, including lichen (Addison and Puckett 1980, Percy 2012), moss (Shotyk et al 2014, Shotyk et al 2016b), snow (Bari et al 2014, Kelly et al 2010, Kirk et al 2014), soils (Watmough et al 2014), and surficial lake sediments (Neville et al 2013), have been used previously across the oil sands region to reconstruct spatial patterns in trace element deposition. These archives integrate signals over a variety of times scales, spanning a single season (e.g. snow), to a number of seasons (e.g. moss, lichen), or even years and decades (e.g. lake sediments). Lake sediment cores are particularly well suited in the absence of consistent long-term monitoring, which is
Figure 1. Map of the study lakes. Sites are classified as near-field (<20 km; black), mid-field (20–50 km; blue), or far-field (>50 km; red) according to their distance from the midpoint of oil sands open pit mining operations as designated by Kelly et al. (2010) as site AR6 (yellow star). The red circle denotes 50 km from AR6.

the case in the Athabasca oil sands region (AOSR). Lake sediment cores have been used, for example, to understand temporal patterns in atmospheric polycyclic aromatic hydrocarbon (PAH) deposition (Jautzy et al. 2013, Kurcek et al. 2013), climate-driven changes to within-lake (i.e. autochthonous) primary production (Summers et al. 2016), the potential acidification of far-field lakes (Hazewinkel et al. 2008), and the long-range atmospheric transmission of trace metals to lakes located both in the Peace–Athabasca Delta (Wilkund et al. 2012) and in northwestern Saskatchewan (Laird et al. 2013). Here we use the geochemical record preserved within 20 lake sediment cores to examine the environmental legacy of bitumen extraction and processing in the AOSR of northeastern Alberta. The lakes are located both near to and far from mining activities, and thus are uniquely positioned to offer both spatial and temporal insight in the atmospheric deposition of trace elements across the region.

Methods

Study sites—sediment coring

The sediment coring lakes span a range of biogeographic environments (figure 1; table S1 available at stacks.iop.org/ERL/12/124001/mmedia). The lakes are small (mean lake area = 0.8 km²), shallow (mean lake depth = 2.1 m) and they occupy small watersheds (mean watershed area = 10.8 km²) not directly impacted by anthropogenic activities. Two exceptions include Greagre Lake and Pushup Lake. Gregoire Lake is much larger (25 km²) and deeper (Zmax = 7.2 m) than the other study lakes and occupies a large and developed watershed 232 km² in area, while the Pushup Lake watershed has been developed intensively for in situ bitumen recovery (figure S1). The study lakes are located between 10 and 100 km distant from AR6, which is the center of open pit mining activities as designated by Kelly et al. (2010). Here we group the lakes into three broad categories: near-, mid-, and far-field sites, located <20 km, 20–50 km, and >50 km from AR6, respectively. This grouping is based upon observations that current rates of atmospheric trace element deposition increase in a near-exponential fashion as one approaches the center of oil sands development (i.e. AR6) (Kelly et al. 2010, Kirk et al. 2014, Landis et al. 2012).

Sediment core recovery and dating

Three sediment cores were recovered from the depocenter of each lake basin using a Uwitec corer and following standard paleolimnological equipment and techniques (Glew et al. 2001). Sediment cores were extruded on site at 0.5 cm intervals from 0–20 cm depth and at 1 cm intervals below 20 cm depth. One
core from each lake was dated using $^{210}$Pb and $^{137}$Cs activities measured at Flett Laboratories (Winnipeg, MB, Canada), while a second core was used to generate the trace element data. Sediment ages were calculated using the constant rate of supply (CRS) model (Appleby 2001). These are the same sediment cores used by Kurek et al. (2013) and Summers et al. (2016); additional details about the $^{210}$Pb dating of these cores is provided in these two papers.

**Sediment geochemistry**

Comparing sediment trace element concentrations to CCME sediment quality guidelines (CCME 2001) was an important objective of our efforts. Selected intervals from each sediment core were analyzed for the concentration of 47 elements at the National Laboratory for Environmental Testing (Burlington, Ontario, Canada) using the aqua-regia extraction method 2-2404. In brief, $\sim500$ mg of freeze-dried and homogenized sediment is digested overnight in 1.5 ml of HNO$_3$ and 4.5 ml of HCl in a Teflon digestion vessel. This method deliberately targets those elements weakly bound to organic and inorganic particles and not those elements directly incorporated into mineral lattices (Gobeil et al. 2013, Graney et al. 1995). The goal was to extract most of the labile (i.e. anthropogenic) fraction but only part of the elements associated with silicate phases. Studies conducted using lake sediment, lichen, and other environmental media from other regions impacted by anthropogenic trace element deposition (e.g. the Great Lakes region of North America) have demonstrated consistently that anthropogenic pollution is hosted within this labile phase (Gallon et al. 2005, Gobeil et al. 1995, Gobeil et al. 2013, Graney et al. 1995). One shortcoming of this approach is the poor recovery of lithogenic trace elements (e.g. Al, Ti, etc.). This poor recovery eliminates comparing our lithogenic concentrations to other studies that have employed more aggressive, total digestion extraction methodologies; however, it reflects our desire to compare with the most relevant CCME guidelines available.

Sediment Hg concentrations were analyzed at the Canada Center for Inland Waters Low-Level Analytical Laboratory using thermal decomposition, pre-concentration and atomic absorbance spectrophotometry (Milestone DMA-80 direct Hg analyzer). Standard Reference Materials analyzed included: TORT-2 (lobster hepatopancreas, National Research Council (NRC)); MESS-3 (marine sediment, NRC); SRM-2976 (mussel, National Institute of Standards and Technology (NIST)); and SRM1556b (oyster, NIST) (table S2).

**Trace element ratios**

The geochemical record preserved in lake water and sediment reflects both erosional inputs from the surrounding watershed and atmospheric deposition. To account for natural (erosional) inputs of lithogenic material, we normalized trace element concentrations to Al. We also calculated elemental enrichment factors (EF) using: $EF = (\text{trace element}/\text{Al})_{\text{pre-1900}}/(\text{trace element}/\text{Al})_{\text{pre-1900}}$ (Boës et al. 2011). We normalized to pre-1900 AD sediments from each individual sediment core, rather than, for example, average values for the upper continental crust, because our extraction method deliberately targeted labile, rather than total, element concentrations. Normalization is a common practice when working with both lacustrine (Boës et al. 2011) and fluvial (Wiklund et al. 2014) systems, as well as other types of environmental archives (Shotyk et al. 2002, Uglietti et al. 2015), and previous studies conducted in the oil sands region have used Li (Wiklund et al. 2014) and Th (Shotyk et al. 2016a, Shotyk et al. 2014, Shotyk et al. 2016b) for the same purpose.

Normalizing trace element concentrations in this manner accounts both for changes in mineral input and controls for grain-size effects; however, caution must be exercised with interpreting these ratios (Blais and Donahue 2013). This is because oil sands operations are sources of both trace elements commonly attributed to anthropogenic activities (e.g. Pb, Hg, V, etc) and lithogenic elements (including Al) (Landis et al. 2012, Lynam et al. 2013, Wang et al. 2015). Thus, normalization to lithogenic elements may risk obscuring the full impact of oil sands operations (Blais and Donahue 2015). We therefore also calculated elemental accumulation rates (fluxes), which are the product of elemental concentration data and CRS-derived sedimentation rates, and flux ratios by dividing the trace element accumulation rate for each period by average preindustrial (i.e. pre-1850) accumulation rate.

**Statistical analyses**

To examine spatial and temporal patterns within our lake sediment geochemical dataset, elemental data for each lake were included in a principal component analysis (PCA). PCA reduces the dimensionality of a data set in which there are a large number of interrelated variables, while retaining as much as possible of the variation present within the data set. Elemental data were centered and standardized prior to inclusion in the PCA.

**Results**

**Core chronologies**

Detailed discussion of individual lake sediment core chronologies is provided in Summers et al. (2016). In brief, most sediment cores extend back 100 years or greater with two exceptions: Kearl and Gregoire Lakes. Sediment cores from these sites are limited to the past $\sim$50 and $\sim$45 years, respectively (figure S2(a)). Recent sedimentation rates in our cores exhibit high degree of spatial variability, ranging from $<100$ g m$^{-2}$ y$^{-1}$ to $\sim1000$ g m$^{-2}$ y$^{-1}$, and many are characterized by
changes in sedimentation rate through time (figure S2(b)).

**Guideline exceedences**

Exposure to contaminated sediment represents a potential hazard to aquatic organisms, and seven of the elements we quantified (As, Cd, Cr, Cu, Pb, Hg, and Zn) have CCME sediment quality guidelines. No exceedences of CCME guidelines for Cr, Cu, or Pb were observed; however, interim sediment quality guidelines (ISQG) were exceeded for As (5.9 μg g⁻¹; three lakes), Cd (0.6 μg g⁻¹; eight lakes), Hg (170 ng g⁻¹; three lakes), and Zn (123 μg g⁻¹; nine lakes) (table S4). Sediment CCME probable effect levels (PEL) guidelines were exceeded for As (45 μg g⁻¹; two lakes) and Zn (87 μg g⁻¹; one lake). The greatest number of exceedences occurred in three of our far-field sites: Lake L60, Gregoire Lake, and Pushup Lake. There was no apparent change in the frequency of guideline exceedences through time in any of the sediment cores.

**Trace element geochemistry**

Due to the large number of elements considered, we first summarize the results from five elements: V, Pb, Hg, Ca, and Al. These elements uniquely characterize natural or anthropogenic sources in the region and they are spatially and temporally representative of geochemical patterns among all lakes (discussed further below). For example, V is enriched in bitumen from the AOSR (Hodgson 1954, Jacobs and Filby 1983). Thus, as with many previous studies (Alexander and Chamber 2016, Murray 1981, Shelfenko 1978, Shotyk et al 2014), we rely on V as our primary geochemical tracer for oil sands extraction and processing. We include Pb and Hg because they are both released by a variety of anthropogenic activities and because previous studies have shown that Pb and Hg concentrations in snow (Kelly et al 2010, Kirk et al 2014), lichen (Landis et al 2012), and living moss (Shotyk et al 2014) decrease with distance from the open pit mines. Ca is a key component of the carbonate terrain that underlies some of our study sites and the bitumen-bearing McMurray Formation, and, as with Pb and Hg, regional industrial activities are an important regional source of base cation emissions (Lynam et al 2015, Watham et al 2014). Finally, we rely on Al to normalize for changes in mineral (i.e. lithogenic) inputs and to facilitate comparisons with other studies of lake sediment cores and peat cores that similarly used normalization to lithogenic elements (Shotyk et al 2016a, Wiklund et al 2014).

To summarize spatial and temporal patterns among all 20 study lakes, we calculated 10 year mean trace element concentrations for our study sites. Study sites were then classified as being near-field (<20 km from AR6), mid-field (20–50 km from AR6), or far-field (>50 km from AR6). These spatial groupings are based upon published studies that have demonstrated a near-exponential decline in modern-day atmospheric contaminant deposition with distance from AR6, with the highest deposition occurring within 20 km of AR6 (Landis et al 2012, Manzano et al 2016).

Our sediment cores are characterized by a high degree of spatial and temporal variability in trace element concentrations and fluxes (figure 2). For example, during the 18th and 19th century, both V concentrations and fluxes were 2–3x higher and more variable in far-field sites than in near- or mid-field sites; however, after ∼1960, V concentrations and fluxes in NE13 and NE20 increased rapidly. Peak values occurred during the 1980s, when V concentrations increased to 35 μg g⁻¹ in NE13 and to 16 μg g⁻¹ in NE20, while V fluxes increased to 10000 μg m⁻² y⁻¹ in NE13 and 5000 μg m⁻² y⁻¹ in NE20. Near-field V concentrations and fluxes then decreased steadily, reaching near background levels in the most recent sediment intervals.

Both mid- and far-field sites exhibit variable V concentrations and fluxes through time, particularly in concentrations and in preindustrial (i.e. pre-1900 AD) sediments (figure 2). Indeed, decadal mean V concentrations in far-field sites during the late-1700s and early-1800s were ∼30 μg g⁻¹, which is similar to peak values observed in NE20 during the 1980s. Accounting for sedimentation rate removes some of this variability in mid-field sites, but far-field V fluxes remain higher in the preindustrial past than in modern sediments.

Similar spatial and temporal patterns to the ones described above are also evident for Pb (figure 2), though with two important differences: (i) Pb concentrations and fluxes remain highest in far-field sites throughout the past ~250 years; and (ii) Pb concentrations and fluxes increase contemporaneously and to a similar magnitude in both near- and mid-field sites. For example, decadal mean Pb concentrations in both near- and far-field sites remain below 5 μg g⁻¹ over the period of record, and, as with V, far-field Pb concentrations and fluxes were higher in preindustrial sediments than in modern times. Hg concentrations and fluxes increase steadily over the past ~150 years in all lakes, with far-field sites exhibiting the highest Hg concentrations and fluxes. The range of Hg concentrations observed in our sediment cores (20–120 μg g⁻¹) are quantitatively similar to those reported by Neville et al (2013) during their survey of surficial sediments from 63 lakes in the AOSR. Finally, Ca concentrations and fluxes are ~20x higher in near-field sites than in either mid- or far-field sites, while Al concentrations and fluxes remain higher in far-field sites than in all others. Neither Ca nor Al profiles exhibit a strong temporal trend, with the exception of the variable Al concentrations in pre-1850 sediment.

Much of the variability in trace element concentrations and fluxes described above is removed after calculating EF and flux ratios (figure 3). For example, far-field V EF and flux ratios both remain stable (~1) for the past 250 years, in contrast to the high variability observed in V concentrations and fluxes in these lake systems. This suggests that V concentrations in these
far-field lake systems is controlled by natural watershed inputs of lithogenic material. In contrast, V EFs and flux ratio profiles vary among near- and mid-field sites. For example, early increases in V flux ratios are noted during 1860s and 1920s in NE13, yet V EFs remain below 2 until the 1950s. This discrepancy suggests the pre-1950 increases in V flux ratios in NE13 are likely due to an increase in lithogenic (i.e. mineral) matter, which increased sedimentation rates. In contrast, both V EFs and flux ratios increase rapidly in near-field sites after 1960. In NE13, V EFs and flux ratios increased to 3x and 24x background, respectively during the 1960s and 1970s, while in NE20, V EFs and flux ratios both increased to ~15x background during the 1980s. Both ratios then in both lakes through time. In modern-day sediment, V EFs remain elevated (~8x background) in NE13 but are near 1 in NE20. In contrast, V flux ratios remain elevated (~8x background) in both lakes. A similarly (but smaller) temporal pattern is noted in V EF and flux ratios in mid-field sites, which rise to ~2x background after ~1950 before peaking ~3x and 4x background, respectively by 2000.

We attribute the rapid increase in V EF and flux ratios within near- and mid-field sites to the onset
of regional oil sands extraction and processing, which were initiated in 1967 by Great Canadian Oil Sands (now Suncor). A second mine (Syncrude) opened in 1978, and, shortly after this time, we observe peak V EF and flux ratios in NE20 (figure 3). While the size and extent of mining operations have continued to expand through time, our data suggest V loading to near-field sites has decreased steadily since the 1980s. This is despite a steady increase in mining operations through time. We suggest two possible explanations for this decrease in V delivery: changes in mining technology, and emission control efforts. Initial mining operations relied upon the use of long conveyor belts to move unprocessed bitumen from the mine to the extraction plant. The gradual replacement these long conveyor belts during the 1980s and 1990s with heavy-haul trucks and shovels may have decreased fugitive dust emissions. Alternatively (or synergistically), the installation of electrostatic precipitators on Suncor’s upgrader stack in November 1979 may have also reduced particulate emissions. Support for this latter explanation comes from Landis et al (2012), who characterized the trace element composition of various potential trace element sources within the AOSR, including stack emissions. They showed that particulate stack emissions averaged ∼5x more V than any other source they measured. While the relative importance of each of these sources has likely changed through time, the deposition of V to near-field lakes (i.e. those within 20 km of AR6) appears to have declined over the past three decades. In contrast, V deposition to sites located >20 km from AR6 steadily increased until the last decade. This is most likely a reflection of the steady expansion of mining activities across the landscape.

The Pb EF and flux ratio profiles exhibit a similar pattern to V (figure 3). For example, Pb flux ratios increase in NE13 during the 1860s and 1900s while Pb EF are stable during this same period. However, unlike V, Pb EFs increase steadily in both near- and mid-field sites after ∼1920, rising steadily to ∼5 by the 1980s. A similarly timed, yet smaller, increase is also evident in far-field sites, in which Pb EFs rise to ∼2x background over the same time period. Thus, both Pb EFs and flux ratios suggest greater Pb deposition to near- and mid-field sites than to far-field sites since the 1920s. This pattern suggests important sources of Pb beyond oil sands mining and processing. This is not surprising, as 20th century Pb pollution was a global phenomenon. Nonetheless, the higher Pb EFs and flux ratios in near- and mid-field sites (relative to far-field sites) strongly suggests enhanced Pb emissions associated with regional anthropogenic activities. These anthropogenic activities were very likely not limited to oil sands mining and processing, but likely incorporate emissions from the city of Fort McMurray itself.

In contrast to V and Pb, Hg EF and flux ratios reveal remarkably similar profiles among nearly all of the lakes, increasing steadily after ∼1850 (figure 3). Both ratios rise to between 2 and 3, and we observe little evidence for a significant increase after the onset of oil sands mining activities in 1967. Instead, our Hg records record a threefold increase over the industrial era, which is consistent with other lake sediment cores recovered from across western North America Drevnick et al (2016) and around the globe (Biester et al 2007, Engstrom et al 2014). Thus, despite higher winter-time loadings of Hg close to the Suncor upgrader and its associated petroleum coke piles (Kirk et al 2014),
we observe no obvious uptick in lake sediment Hg attributable directly to oil sands mining and processing.

Profiles of Ca EF and flux ratios exhibit a different temporal pattern than V, Pb, or Hg (figure 3). Near-field Ca EF fluctuate through time, but remain below 2, while Ca flux ratios are much higher in NE20 than in NE13. There is little evidence for any increase in Ca delivery to mid- or far-field sites, as Ca EFs and flux ratios both remain below 2 throughout the period of record. This is despite evidence from spatial surveys of lichen (Landis et al. 2012), wet atmospheric deposition (Lynam et al. 2015), and regional soils (Fenn et al. 2014, Wang et al. 2015, W atmough et al. 2014) all of which reveal high inputs of base cation deposition at sites located close to modern-day mining operations. The source of these base cations is fugitive dust, which is emitted to the atmosphere from a wide range of sources within the AOSR, including paved and unpaved roads, limestone mining, sands from tailings pond dykes, oil sands upgrading byproducts, and others (Landis et al. 2012). Indeed, atmospheric base cation deposition has been shown to mitigate the risk of soil acidification from NO\textsubscript{x} and SO\textsubscript{2} emissions (Fenn et al. 2014, W atmough et al. 2014). In contrast, our sediment cores suggest fugitive dust emissions have yet to measurably change regional lake sediment Ca concentrations. We hypothesize that this is because the base cation budget for our study lakes is dominated by groundwater and watershed inputs; atmospheric deposition has to exert a measureable impact.

Considered collectively, our results indicate that normalization to a conservative lithogenic element (in our case Al) provides a robust method to distinguish the input of anthropogenic trace elements in regional lake sediments. This supports the recent suggestion of Wiklund et al. (2014) that this approach be used to identify trace element pollution in regional freshwater systems. Our results also demonstrate that EFs have not been stable through time; near-field V EFs peaked at ∼15 in NE13 and to ∼3 in NE20, but they have returned to ∼8 (in NE13) and to ∼1 in NE20 over the past ∼20 years. This is despite a rapid expansion in the number and size of mines over this same period. We suggest this reflects a shift in the predominant source of atmospheric trace element emissions through time. During early mining and upgrading operations, which were limited to Suncor and Syncrude, blowing dust from the use of conveyor belts and stack emissions were likely the two most important sources of anthropogenic V emissions to the atmosphere. But improvements to mining technology and an increase in the aerial extent of open-pit mines appears to have changed the relative importance of different sources within the region. Today, fugitive dust emissions have many different sources, including haul road dust, overburden, processed materials (e.g. coke), tailing sands, and fleet emissions. This is why, for example, previous studies have reported a near linear relationship between the concentration of Pb and various lithogenic elements in various environmental media (Landis et al. 2012, Lynam et al. 2015, Shotyk et al. 2014). Our lake sediment core results place these recent findings in a long-term context, and help to mitigate the lack of consistent environmental monitoring over the past ∼40 years of anthropogenic activities within the AOSR.

**Spatial patterns in trace element deposition**

The results summarized above for just a few elements reveal large spatial differences in the geochemical composition of regional lake sediments (figure 2). Nonetheless, these results are broadly representative of our entire geochemical dataset, as illustrated by the PCA results (figures 4(a) and (b)). The first axis (PC1; \( \lambda = 67\% \)) is dominated by positive loadings of all elements measured except for Na, Sr, and Ca. The second axis (PC2; \( \lambda = 11\% \)) is dominated by high positive loadings for Ca, Sr, and Mg and negative loadings for Hg, Cd, and Zn. This pattern reflects the much higher trace element concentrations in two of our far-field sites (Gregoire Lake and L60) and the ∼20x higher base cation concentrations in our two near-field study sites (NE13 and NE20). In addition, we see almost complete separation of our study sites based upon their PC sample scores, with little overlap among near-, mid-, and far-field sample scores.

The PCA results summarized above suggest the geochemical differences among our study sites are controlled by each lake’s location on the landscape. The highest concentrations of nearly every element measured are found in sites located >50 km from AR6 (figure 1). Similar spatial variability is also evident in the results of an annual water quality monitoring survey of 50 regional lakes. Lakes located in the Birch Mountains (including L60) are characterized by trace metal concentrations that are elevated relative to lakes located closer to the open pit mines (figure S3). The Birch Mountains host metal-rich black shales that, in some cases, approach economically significant concentrations (Dufresne et al. 2001). Thus, we suggest the high metal concentrations observed within our three Birch Mountain lake sediment cores (Lakes L60, 2014-X, and 2014-Z) to be reflective of their unique bedrock geology, and not due to anthropogenic impact. In contrast, two of our study sites (Gregoire Lake and Pushup Lake) rest within watersheds that have been impacted by anthropogenic activities (figure S1). This likely accounts for the higher trace element concentrations noted in these two lake systems.

The high trace element concentrations in Gregoire Lake and L60 obscure patterns within the PCA. We therefore removed these two lakes and reran the PCA (figures 4(c) and (d)). Ca and Sr still loading negatively along PC1, and we now observe a greater range of species and sample scores. We also observe greater variability among lakes than within any individual lake, with sites located closer to AR6 exhibiting higher concentrations of Ca, Sr, and Mg, and therefore lower PC1 and higher PC2 sample scores. However, this spatial
pattern cannot be due to the deposition of atmospheric oil sands emissions. If this were the case, we would expect a shift from positive to negative PC1 sample scores after the onset of oil sands extraction activities (i.e. after 1967). Instead, we hypothesize that the input of carbonate-rich groundwater drives this spatial pattern. Lakes NE13 and NE20 rest near surficial outcrops of the carbonate-rich Waterways Formation and the bitumen-bearing McMurray Formation. Groundwater within both formations can be highly saline because of the dissolution of halite and anhydrite-containing evaporite units (Cowie et al. 2015). Indeed, high-salinity groundwater discharges directly to the Athabasca River (Gibson et al. 2013). Thus, we suggest that regional geology, and not the open-pit mines, drive the overall elemental composition of lake sediments within the AOSR.

Conclusion

Our results provide a new long-term perspective on trace element emissions to, and deposition from, the atmosphere in the oil sands region of northeastern Alberta. As with previous studies, we find V to be a useful geochemical indicator of oil sands mining activities both today and in the past. Early mining operations resulted in V and Pb being deposited to sites within 50 km of AR6, but improvements to mining and upgrading technologies have reduced V and Pb loading to the regional landscape since the 1980s. In contrast, we find no evidence that oil sands emissions have resulted in trace element deposition beyond 50 km, and Hg deposition appears to reflect global-scale patterns in atmospheric Hg emissions. Base cation deposition, which currently mitigates the acidification of regional forest soils, has yet to measurably impact regional lake sediments. Instead, we suggest that the dissolution of carbonate bedrock exerts a first-order control over lake sediment geochemical composition, mainly through its influence over groundwater composition.

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