Mercury and methylmercury in snowpacks, snowmelt, and tailings ponds of the Athabasca Oil Sands Region, Alberta, Canada

by

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Abstract

The Alberta Oil Sands Region (AOSR) is the third largest proven oil reserve in the world and one of Canada's major economic drivers. Industrialized extraction of this resource has resulted in the release of contaminants from various sources, such as stack emissions, volatilization and leakage of chemicals from tailings ponds, increased erosion due to land disturbance, and blowing dust from landscape disturbance, road activity, and open-pit mines. Among the contaminants released to the environment from industrial activities are organic pollutants, such as polycyclic aromatic hydrocarbons and naphthenic acids, sulphur dioxide and nitrogenous oxide species, secondary organic aerosols and the 13 elements (Ag, Ar, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sb, Tl, Zn) considered priority pollutants elements under the U.S. Environmental Protection Agency. Mercury (Hg) is also a contaminant of concern in the AOSR, especially methylmercury (MeHg), which is a potent vertebrate neurotoxin that biomagnifies through food webs to concentrations that may be of concern to consumers including humans. Total Hg (THg: all forms of Hg in a sample) concentrations downstream of the AOSR and THg and MeHg loadings in snowpacks have also been found to be elevated; however, sources of this Hg are not known. In this thesis, I: 1) quantify THg and MeHg concentrations in four AOSR tailings ponds varying in composition, age, surface area, and volume; and 2) determine if MeHg is actively produced in AOSR snowpacks and melted snow, or associated with the particles deposited there. I show that surface and sub-surface water concentrations of THg (unfiltered 0.30 ± 0.14 ng/L; filtered 0.26 ± 0.12 ng/L) and MeHg (unfiltered 0.15 ± 0.20 ng/L; filtered 0.08 ± 0.11 ng/L) were low in the four tailings ponds, with the highest concentrations observed in the oldest pond. In mature fine tailings that settle out in the ponds, concentrations of THg (58.6 ± 50.2 ng/g) and MeHg (0.23 ± 0.16 ng/g) were also low, with the highest concentrations also observed in the oldest pond. Overall, these ponds are not likely a major source of THg or MeHg to downstream freshwater ecosystems into which they slowly leak, though further assessment of the source of the MeHg in the oldest pond should be pursued. To determine if MeHg is produced within snowpacks and/or melted snow of the AOSR, I used Hg stable isotope incubation experiments at four sites located varying distances from the major industrial developments. Results from these experiments demonstrated that the potential rate of MeHg production was low in snowpacks (k_m = 0.001–0.004 d^{-1}) and non-detectable in melted snow, except at one site (k_m = 0.0007 d^{-1}), and that *in situ* production is therefore unlikely an important source of MeHg to AOSR snowpacks. Concentrations of MeHg on particles (pMeHg) in snowpacks increased linearly with distance from the upgraders (R^2 = 0.71, $p < 0.0001$); however, snowpack total particle and pMeHg loadings decreased exponentially over this same distance (R^2 = 0.49, p = 0.0002; R^2 = 0.56, $p < 0.0001$). Thus, at near-field sites, total MeHg loadings in snowpacks were high due to high particle loadings, even though particles originating from industrial activities are not MeHg rich compared to those originating from natural sources at distant sites. More research is required to identify snowpack particle sources.

Preface

My thesis is divided into four chapters beginning with an introductory chapter, followed by two research chapters written in manuscript format, and finally a concluding chapter. Chapter 1 introduces why I pursued my specific research program, my research sites and the overall goals of the research. Chapter 2 of this thesis is titled "Concentrations of total mercury, methylmercury, trace elements and general chemistry parameters in tailings ponds process-affected water and settling fine tailings in the Alberta Oil Sands Region, Canada". This chapter is coauthored by C.E. Willis, J.L. Kirk, V.L. St. Louis, K.A. St. Pierre, and Dodge, C. and will be submitted to the journal Environmental Science and Technology. Samples were collected by Clearstone Engineering Ltd. and analyzed primarily by C. Dodge and K.A. St. Pierre. I was responsible for data analysis as well as the manuscript composition. J.L. Kirk, V.L. St. Louis, and K.A. St. Pierre contributed to manuscript edits. J.L. Kirk and V.L. St. Louis were the co-supervisory authors and were involved with concept formation and manuscript composition. Chapter 3 is titled "Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: A study of *in situ* methylation and particulates" and is coauthored by C.E. Willis, V.L. St. Louis, J.L. Kirk, I. Lehnherr, P.A. Ariya, R.B. Rangel-Alvarado. This manuscript is currently submitted to Environmental Science and Technology. I was responsible for the data collection and analysis as well as the manuscript composition. J.L. Kirk assisted with the data collection and V.L. St. Louis, J.L. Kirk, I. Lehnherr, P.A. Ariya, and R.B. Rangel-Alvarado contributed to manuscript edits. V.L. St. Louis and J.L. Kirk were the supervisory coauthors and were involved with concept formation and manuscript composition. Chapter 4 concludes the thesis with research highlights and suggestions for future research directions.

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As with all young scientists the list to whom we must give gratitude is endless, thus to each person who has supported me throughout this endeavor, in any manner, I dedicate this thesis to you.

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Chapter 3 of this thesis would not have been possible without the expertise of Dr. Igor Lehnherr, who was absolutely instrumental in the study design and statistical analysis. Thank you for all the hours you spent explaining every detail of your thought processes

and plans, I could not have accomplished all that I did without you. Of course, I would also like to thank my supervisory committee, Dr. Jon Martin and Dr. Keith Tierney, for reviewing my thesis and providing thoughtful suggestions. Other essential contributors include all of those at the Biogeochemical Analytical Service Laboratory (U of A), including Mingsheng Ma, the manager, Crystal Dodge, who spent countless hours developing innovative techniques to analyze extra particle-rich samples, my good friend, Patrick Milner, who had to centrifuge malodourous mature fine tailings endlessly, and all other who assisted in sample analysis.

For emotional and motivational support, my family and friends were always available; I love you all. My mother, Carol, has always brightened my day and saved me during the ever so common grad school breakdown moments; she is my foundation. My father, Stephen, has consistently pushed me to believe in myself and has been an excellent source of inspiration; always and forever. My stepfather, Scott, who taught me to be more focused, the art of sarcasm, and how to laugh at myself. My sister, Courtney, and her family have been my driving force to finish, the light at the end of the tunnel. Sarah Robinson, although in Ottawa, has been my closest friend, a counselor, a therapist, a strength builder, a comedian, a motivational speaker, and more. My remarkable friend Cara Bulger made every day both amusing and interesting with her quick wit, adventurous spirit, and daily jokes. Sarah Shakil, one of the kindest people I have ever met, has been tremendously selfless and a genuine friend, my experience would not have been the same without her. My good friend and officemate, Kyra St. Pierre, who not only helped me to find definitions of new undergrad slang but has also happily guided me through my entire degree all while invoking academic as well as highly entertaining conversation (Kyra, you have been my rock!). Chris Woolaway has continually delivered mental breaks through stimulating intellectual conversation about everything other than my research, as well as a daily meme to keep me laughing. Lane Liddle gave me dirt road freedom, a family Christmas when I wasn’t able to go home and continuously reinvigorated my passion for science and psychology. Thank you to everyone, we did it!

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Abbreviations

%MeHg	% of all forms of mercury in the sample that is methylmercury
Ag	Silver
Al	Aluminum
AOSR	Alberta Oil Sands Region
Ar	Argon
As	Arsenic
B	Boron
BASL	Biogeochemical Analytical Service Lab
Be	Beryllium
Ca	Calcium
CAEAL	Canadian Association for Environmental Testing
CAPP	Canadian Association of Petroleum Producers
$CaSO_4$	Calcium sulfate
CCIM	Canadian Centre for Isotopic Microanalysis
CCIW	Canadian Centre for Inland Waters
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium
Chl a	Chlorophyll a
Cl	Chlorine
CNRL	Canadian Natural Resources Limited
Cr	Chromium
CRC-ICP-MS	Collision reactions cell inductively coupled plasma spectroscopy
CRM	Certified Reference Material
Cu	Copper
DMA	Direct Mercury Analyzer
DOC	Dissolved organic carbon
ELA	Experimental Lakes Area
EMCCD	Electron Multiplying Charge Coupled Device
F	Fluorine
Fe	Iron
FFT	Fluid Fine Tailings
HCl	Hydrochloric acid
HDPE	High density polyethylene bottle
Hg	Mercury
Hg:Al	Mercury to aluminum ratio
Hg(0)	Gaseous elemental mercury
Hg(II)	Inorganic mercury
HNO_3	Nitric acid
ICP-MS	Intercoupled mass spectrometer
ID	Inner diameter

INSF	Insufficient sample to run as a liquid
ISQG	Interim sediment quality guidelines
JOSM	Joint Oil Sands Monitoring Program
K	Potassium
K_d	Demethylation rate
K_m	Methylation rate
La	Lanthanum
M:D	Methylation to demethylation ratio
MDL	Minimum detection limit
MeHg	Methylmercury
MFT	Mature Fine Tailings
Mg	Magnesium
MLSB	Mildred Lake Settling Basin
Mo	Molybdenum
Na	Sodium
NaOH	Sodium hydroxide
ND	Non-detect (i.e. below detection limit)
NH_3	Ammonia
Ni	Nickel
NLET	National Laboratory for Environmental Testing
NO_2	Nitrite
NO_3	Nitrate
NTA	Nanoparticle Tracking Analysis
OD	Outer diameter
OSPW	Oil sands process-affected water
OSTP	Oil sands tailings ponds
PAC	Polycyclic aromatic carbons
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PC	Particulate carbon
PEL	Probable effects level
Petcoke	Petroleum coke
pMeHg	Particulate methylmercury
POC	Particulate organic carbon
PON	Particulate organic nitrogen
PPE	Priority pollutant elements under
PSV	Primary Separation Vessel
RAMP	Regional Aquatics Monitoring Program
RHg	Reactive mercury
SAGD	Steam Assisted Gravity Drainage
Sb	Antimony
Se	Selenium
$SnCl_2$	Tin chloride

SO_4	Sulfate
Sr	Strontium
SRM	Standard reference material
SWIP	Southwest In-pit
SWSS	Southwest Sand Storage
Syncrude	Syncrude Canada Limited
TDN	Total dissolved nitrogen
TEL	Threshold effect level
THg	Total mercury
Tl	Thallium
TMG	Trace metal grade
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
UF	Unfiltered
UNEP	United Nations Environmental Program
USEPA	United States Environmental Protection Agency
V	Vanadium
Zn	Zinc

1 Introduction

1.1 Alberta Oil Sands Region

The Alberta Oil Sands Region (AOSR) of northeastern Alberta, Canada is home to ~170 billion barrels of economically recoverable oil, making it the third largest crude oil reserve in the world and one of Canada's major economic drivers.[1-3] Commercial oil production in the AOSR has been in operation for five decades and, in 2015, had a footprint extending over 142,000 km^2, similar in size to New York State (141,300 km^2).[4] Through a combination of enhanced oil strategies, 2.4 million barrels of oil are produced daily, with projections of 4.0 million barrels being produced daily by 2025.[5, 6] The oil is a highly upgraded and refined form of the bituminous deposits, which are primarily composed of sand, silt, and clay, containing only 4-6% bitumen.[2] As a result of the highly viscous nature of bitumen, the oil cannot be recovered using conventional extraction methods, such as well drilling.[4]

1.1.1 Bitumen extraction

Bitumen is extracted from the landscape either by *in situ* steam assisted gravity drainage (SAGD) or via open-pit mining.[1] Open-pit mining constitutes ~20% of recovery operations in the AOSR and is used when bitumen is found <75 m below the earth's surface.[7, 8] Once the oils sands mixture has been mined using massive (40 m^3) hydraulic shovels, 400 T capacity heavy haulers deliver the ore to large crushers (Figure 1.1). [7, 8] Within the crushers, caustic hot water is added to the ore to begin the bitumen separation process and facilitate hydrotransportation to the extraction plant. The first step at the extraction plant begins in a Primary Separation Vessel (PSV) where the Clark Hot Water Flotation process is applied by adding more hot water and oscillating the crushed ore.[9] The less dense bitumen will, for the most part, rise to the top of the PSV as froth, while the heavier material sinks to the bottom.[1, 10] The heavier material is separated and diverted to oil sands tailings ponds (OSTPs) along with some of the oil sands process-affected water (OSPW), whereas the bitumen froth is skimmed from the top and undergoes further separation as does the middle portion (middlings) of the OSPW. The secondary separation processes for both bitumen froth and middlings vary within and between companies but typically include the addition of diluents, such as naphtha or paraffinic solvents, to enhance water separation and decrease bitumen viscosity to facilitate transportation through pipelines.[8]

At the extraction plant, each step produces waste that gets diverted to OSTPs, which function as holding basins as a result of a zero discharge to the environment policy.[4, 11-13] Currently, OSTPs cover a surface area of ~220 km^2 and contain ~1 billion m^3 of fluid fine tailings (FFT; tailings ≤44 μm and 15-30%).[10]

1.1.2 Bitumen upgrading

Once bitumen is separated from mining materials, the diluent (bitumen and added solvents) is transported to an upgrading facility where it is converted to a more usable, lighter and higher quality form of crude oil. This process is achieved through the removal of unwanted materials, such as chemical additives from the extraction process and trace metals, and through molecular alteration, which involves either the addition of hydrogen atoms or the removal of carbon atoms.[14] At each facility, upgrading processes vary, but all involve: (1) a general feed separation, which involves the removal of salts and asphaltenes, (2) thermal cracking, which is the application of extreme heat and vacuum pressure making the heavy bituminous oil lighter (3) hydrogenation, (4) dehydrogenation, (5) coke formation, and (6) removal of sulfur and nitrogen.[14] These processes result in stack emission of atmospheric contaminants, as well as contaminant fugitive dust from open-air stockpiles of upgrading by-product, such as sulfur and coke.[14]

1.1.3 Environmental Pollutants in the AOSR

As with most large-scale industrial activities, there are concerns about human and ecosystem health within the AOSR.[15-17] Contaminants in the AOSR are released from sources such as stack emissions, [18-21] tailings ponds, [22, 23] increased erosion, [24] blowing dust from landscape disturbance, road activity, and open-pit mines.[24, 25] Among these contaminants are an array of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs),[26-30] naphthenic acids,[31-33] sulphur dioxide and nitrogenous oxide species,[3, 34, 35] secondary organic aerosols,[36] and metals, including mercury (Hg).[37-39] The National Pollutant Release Inventory estimated ~52 kg/year of Hg was released into the atmosphere from bitumen upgrading facilities in 2009; although, Hg release reports are not currently mandatory. This thesis focuses on understanding sources of Hg in the AOSR.

1.2 Mercury

Hg exists naturally in the environment, though is commonly anthropogenically redistributed, mostly through the release of gaseous elemental mercury (GEM) from industrial sources, such as coal fired power plants.[40] Once in the atmosphere, GEM can be oxidized to inorganic Hg(II), which has a much shorter residence time compared to GEM, allowing for rapid deposition onto landscapes and waterbodies.[41-44] Hg(II) can undergo various biogeochemical transformations, including being reduced back to GEM and re-emitted to the atmosphere, or methylated to methylmercury (MeHg) via abiotic, or more commonly, biotic processes.[41-43, 45] Biotic Hg methylation is performed by microorganisms, such as sulfate- and iron-reducing bacteria, and primarily occurs in reducing conditions in lakes and wetlands.[41-43] MeHg is the form of mercury of greatest concern because it is a strong vertebrate neurotoxin (among other effects) and biomagnifies through aquatic foodwebs to concentrations in top predatory fish that may be toxic to consumers, including humans.[41, 46, 47]

1.3 Mercury in the AOSR

Mercury has become a contaminant of potential concern in the AOSR. For example, in 2009 the Regional Aquatics Monitoring Program (RAMP) with the Alberta Government released fish Hg consumption advisories for northern pike (*Esox lucius*), walleye (*Sander vitreus*), and lake trout (*Salvelinus namaycush*) in 10 watersheds.[48-50] In 2013, a study demonstrated the presence of elevated concentrations of Hg in colonial water birds ~ 200 km downstream of the oil sands developments.[51, 52] This study provided the foundation for Hg consumption advisories in gull (*Larus spp.*) and tern (*Sterna spp.*) eggs released later that year. [51, 52] A number of studies have also demonstrated concentrations and loadings of total Hg (THg; all mercury forms present in a sample), MeHg, and an array of metals in snowpacks increase with proximity to the major industrial developments of the AOSR.[37, 39, 53] For instance, the Canada-Alberta Joint Oil Sands Monitoring program (JOSM) began a series of long-term studies, one of which revealed that loadings of THg and MeHg were highest at sites closest to the major developments reaching

1420 and 19 ng/m^2, respectively, and decreasing to 103 ± 42 and 1.2 ± 0.2 ng/m^2, respectively at sites furthest away (>100 km).[39, 54] The JOSM program continues to monitor Hg levels in the AOSR in snowpacks, freshwater, fish, and other microorganisms. Though there is a large body of research supporting the concern of Hg contamination to the AOSR, there is a large gap in the understanding of the origins of the toxic form of Hg, MeHg, in atmospheric deposition and in fish and wildlife. To reduce Hg exposure in and downstream of the AOSR, we must understand its sources.

1.4 Study rational

To develop potential strategies to reduce Hg exposure in and downstream of the AOSR, we must first understand its sources. Thus, in Chapter 2, I examine concentrations of both THg and MeHg in four of the ~17 tailings ponds in the AOSR.[8, 10] To the best of my knowledge, this is the first study to examine THg or MeHg concentrations in tailings ponds of this region. This study also includes quantification of trace element concentrations and general water chemistry for the four tailings ponds to determine if OSTPs are environments conducive to methylation of inorganic Hg(II). Determining the composition of these ponds is particularly important as they leak into ground water and the nearby Athabasca River[55] and potentially other freshwater systems through the porous sand liner.[22, 56] This, in combination with the recent finding that THg concentrations increased up to 8-fold under ice in the Athabasca River downstream of tailings ponds and other developments,[37] suggests that determining THg and MeHg concentrations in tailings ponds could be of substantial importance.

In Chapter 3, I examine the potential for inorganic Hg(II) to be methylated to MeHg within snowpacks and melted snow, which is particularly important as MeHg in snow melt may enter local water bodies where it could become available for bioaccumulation during the spring pulse of biological activity. This was accomplished using unique Hg stable isotope tracer experiments. Concentrations of MeHg in particles (pMeHg) were also quantified as previous work suggested that MeHg is primarily particulate-bound in AOSR snowpacks.[39] I also analysed particle size distribution in snowpacks to potentially improve our understanding of the sources of pMeHg. Finally, I quantified concentrations of MeHg in a limited number of petroleum coke (petcoke) samples to determine if petcoke was a source of MeHg to snowpacks, since previous research suggested fugitive petcoke dust was a source of PAHs to the AOSR.[57]

1.5 Significance

This research expands knowledge on the extent of THg and MeHg contamination in the AOSR, and examines the origins of this THg and MeHg. Although it is difficult to determine the origins of THg and MeHg in various environmental compartments as the biogeochemical cycling in the environment is quite complex, my research closes some major knowledge gaps in the literature. Additionally, the potential for snowpack methylation has long been hypothesized, particularly in Arctic environments, but has never been tested. Thus, the novel experiments described in Chapter 3 provide an experimental method for quantifying potential Hg(II) methylation rates in other ecosystems and increase our understanding of Hg cycling in Northern environments. In the AOSR, source identification is crucial for future mitigation of anthropogenic releases of both Hg(II) and MeHg to the AOSR. This is particularly important for the many First Nation and Métis communities that reside close to and downstream of the major developments who rely heavily on fish and to a lesser extent piscivorous birds and their eggs as food sources, as well as for all wildlife affected by the toxicity of MeHg.[50]

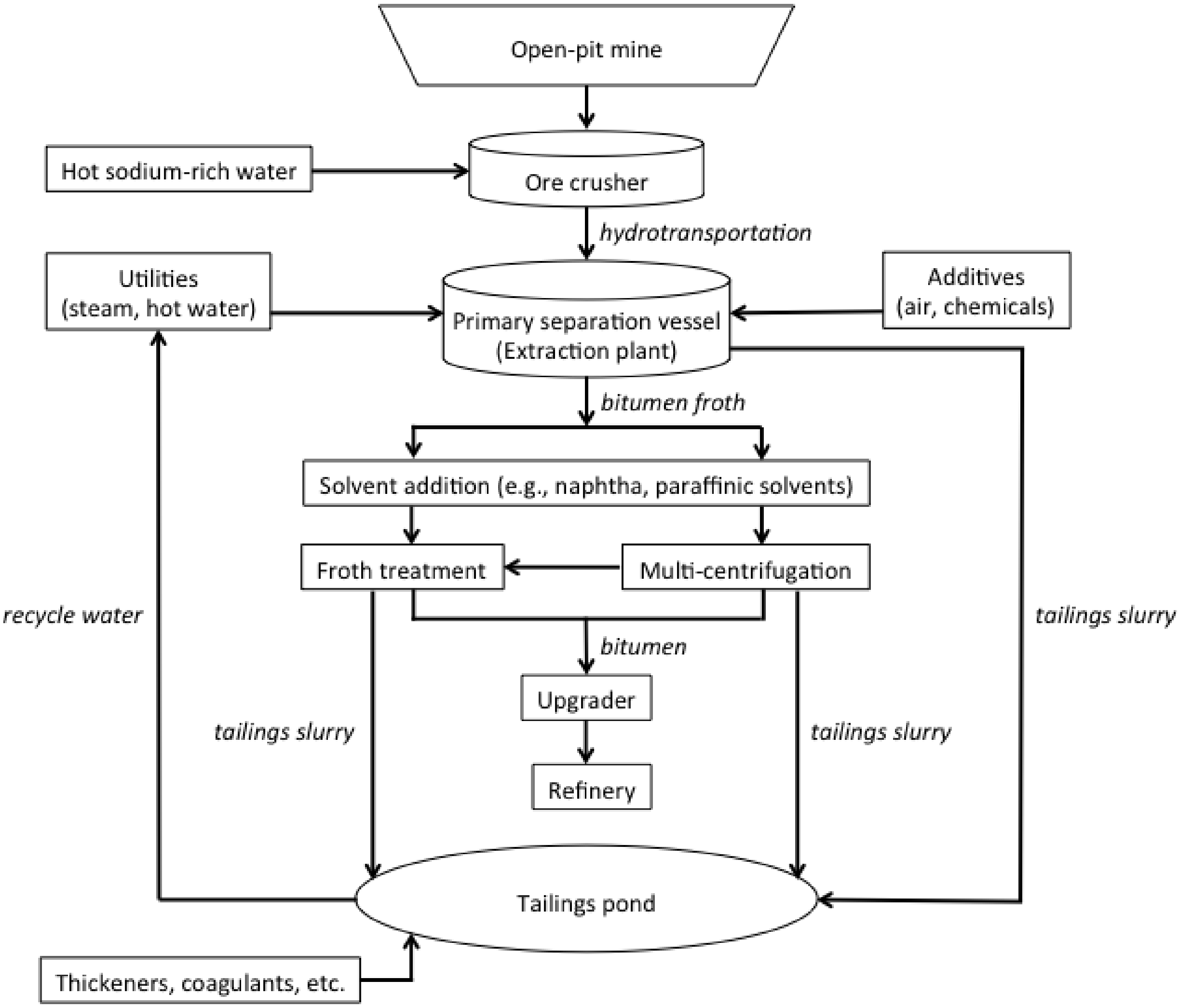

Figure 1.1 Processes involved in bitumen extraction from oil sands via open-pit mining ending with upgrading and refining. Tailings slurry includes solids (e.g., asphaltenes), process-affected water, unrecovered solvents and unrecovered bitumen. Note that multi-centrifugation and froth treatment do not necessarily both happen at all extraction plants. [14]

2 Measures of mercury, methylmercury, trace elements and other chemical parameters in tailings ponds of the Athabasca Oil Sands Region, Alberta, Canada

2.1 INTRODUCTION

There are ~170 billion barrels of economically recoverable oil in the Alberta Oil Sands Region (AOSR) of Canada, making it the world's largest bitumen reserve and third largest oil reserve following those in Saudi Arabia and Venezuela.[1, 2, 13] In the AOSR, bitumen is extracted either by *in situ* steam assisted gravity drainage (SAGD) or via open-pit mining.[1] SAGD involves injecting steam into the bitumen layer to decrease its viscosity, which then allows the bitumen to be pumped out of the ground.[10] 90% of the water from this process is recycled constantly, while the other 10% is treated and pumped into rock formations ~500 m underground.[58] Open-pit mining occurs when bitumen can be recovered from the top 75 m of terrain and constitutes ~20% of recovery operations in the AOSR.[59]

Bitumen recovered from open pit mining requires several processing steps to separate oil from the terrain, including primary separation, which involves oscillating crushed ore with hot water, as well as an assortment of secondary separation treatments, such as froth treatment flocculation and multi-centrifugation.[7, 8, 60] These processes collectively consume up to four barrels of water for each barrel of oil produced.[59, 61] Up to 90% of the oil sands process-affected water (OSPW) is recycled through various processes,[62] while the remainder is diverted to tailings ponds (1 Mm^3/day) along with waste slurry, called tailings, which result only from open-pit mining.[13, 63]

Oil sands tailings ponds (OSTP) currently cover a surface area of ~220 km^2 in the AOSR (142,200 km^2) and are generally constructed overtop native ground with only sand, and on occasion, some overburden separating the ground from the contents of the pond.[10, 63, 64] Tailings slurry is primarily composed of coarse and fine sediments, including sands, silts and clays, as well as residual bitumen, salts, and small amounts of unrecovered solvent (e.g., naphthenic or paraffinic solvents) from extraction processes.[62, 65, 66] A tiered stratum develops within the ponds as a result of varying densities of constituents (Figure 2.1). The stratification begins as the tailings slurry enters a pond from an outfall pipe, with heavier particles separating from the slurry along a gradual slope created both by the sand liner.[67] Fluid fine tailings (FFT; 15-30% m/v solid content), of which there is ~1 billion m^3 in the AOSR,[63] are pushed toward the center of the pond, where they slowly settle (1-2 years) and eventually become a highly viscous, tar-like layer referred to as mature fine tailings (MFT; solid content >30% m/v).[10, 67] The final stage of settling is expected to occur over decades to centuries.[13, 67]

Though the general composition of OSTPs is similar amongst ponds, the make-up of the stratigraphy in the AOSR is highly complex and varies considerably over short distances, thus resulting in varying chemical compositions of sediments within and among ponds.[8, 60] Further variability in OSTP composition is introduced by company proprietary chemicals (solvents, thickeners and coagulants),[60] the type and stage of pond production or recovery (e.g., unprocessed settling basin to highly processed end-pit lake), and the deposition of local fugitive dust and other particulates from the mining operations, as well as other atmospheric pollutants.

Determining the composition of these ponds is particularly important as they leak into ground water and the nearby Athabasca River[55] through the porous sand base as well as potentially other nearby freshwater systems and release volatile toxic compounds to the atmosphere.[22, 56] In fact, several studies have established the presence of toxic compounds in OSPW, including naphthenic acids,[60, 68] volatile organic compounds,[60, 69] and polycyclic aromatic hydrocarbons.[22, 56] Mercury (Hg), a pollutant of global concern,[40] has been found in elevated concentrations near developments in the AOSR.[37, 39, 54] Hg in aquatic ecosystems is especially concerning as inorganic Hg(II) can be methylated to MeHg, a potent neurotoxin.[47] Previous studies have shown that loadings of both total Hg (THg; all forms of Hg in a sample) and MeHg in snowpacks increased with proximity to major developments in the AOSR.[39, 54] This, in combination with the finding that THg concentrations increased up to 8-fold under ice in the Athabasca River downstream of tailings ponds and other developments,[37] suggests that determining THg and MeHg concentrations in tailings ponds could be of substantial importance. This is especially true for MeHg, as it biomagnifies through aquatic foodwebs to concentrations in top predatory fish that may be toxic to consumers, including humans.[46, 47] However, to the best of our knowledge, there are no published studies on Hg concentrations in the ~17 major tailings ponds produced by this regional industry.[8, 70]

Here we report concentrations of THg, MeHg, trace elements and other chemical parameters in OSPW, FFT and MFT in four different AOSR tailings ponds varying in composition, age, surface area, and volume. We also compare tailings ponds chemical concentrations to Canadian Water Quality Guidelines for the Protection of Aquatic Life and the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life set by the Canadian Council of Ministers of the Environment (CCME). This study can be used for assessments of potential risks associated with subaqueous pond leaking as well as provide insight for future remediation planning.

2.2 METHODS

2.2.1 Study sites

The four tailings ponds that we sampled in the AOSR included *Horizon* (Figure 2.2a) from Canadian Natural Resources Ltd. (CNRL), as well as *Southwest in-pit* (SWIP; Figure 2.2b), *Mildred Lake Settling Basin* (MLSB; Figure 2.2c) and *Southwest Sand Storage* (SWSS; Figure 2.2d) from Syncrude Canada Ltd. (Syncrude). Horizon, the only tailings pond in operation at CNRL, became operational in 2009.[71] The composition of this pond includes 36.2 Mm^3 of FFT, 25.8 Mm^3 of water, froth treatment tailings (product of a secondary extraction step where FFT are combined with a polymer to activate mineral binding causing rapid settling), MFT, recycled OSPW and residual bitumen.[71] SWIP became operational in 2007 and holds the least FFT at 13.2 Mm^3 and 28.6 Mm^3 of water.[72] Other constituents include coarse tailings (> 44μm) and composite tailings (FFT combined with sand and gypsum).[72] MLSB became operational in 1976 and is the oldest pond in the AOSR. This pond holds 196.5 Mm^3 of FFT and only 13.4 Mm^3 of water.[72] MLSB is also used to store froth treatment tailings, floatation tailings, coke solids (by-product of upgrading process) and recycled OSPW.[72] Finally, SWSS became operational in 1991 and holds 46.3 Mm^3 of FFT and 10.1 Mm^3 of water, as well as coarse tailings, interim FFT (temporary FFT storage), and some OSPW.[72]

2.2.2 Sample collection and preparation

A third party with appropriate on-site training completed all sampling. Site selection was based on accessibility and safety while trying to achieve distribution of sampling sites across each pond. Horizon was sampled between 29-30 October 2014, while the three Syncrude ponds were sampled between 27 August and 3 September 2015. At the two deepest points in the Horizon, SWIP and MLSB ponds, water samples were collected from the surface, mid-depth and just above the impenetrable MFT layer. Surface water was also collected from three additional sites on all ponds. At SWSS, only surface water samples were collected from three sites. At the two deepest points in SWIP and MLSB, duplicate solid MFT samples were also collected.

All samples were collected using the two person "clean hands, dirty hands" trace metal sampling protocol (EPA Method 1669)[73]. Surface water samples were collected by dipping bottles off the side of a boat. To avoid sampling surface films or floating materials, all bottles were uncapped, filled, and then recapped ~10 cm below the surface. Depth profile samples were collected using a Teflon coated Niskin sampler that was cleaned with 1% trace metal grade (TMG) HCl followed by a triple Milli-Q rinse between each sampling site and depth. Water samples for general water chemistry analyses were collected into a 1 L precleaned, quality certified, high-density polyethylene Nalgene™ bottle (Environmental Sampling Supply), whereas water samples for analyses of THg, MeHg, and trace elements were collected in duplicate into 250 mL pre-cleaned trace-level grade quality assured amber glass bottles (Environmental Sampling Supply). All depth profile sample bottles were rinsed three times prior to filling. MFT samples were collected using a Wildco 196-F65 tall Eckman Bottom Grab. MFT were removed from the center of the grab using a precleaned stainless steel scoop, and placed into Whirl-Pak® bags. A YSI 6-series sonde was used to measure temperature profiles (all other sensors on the sonde were immediately fouled in tailing pond waters and therefore unreliable). All samples were kept refrigerated, with the exception of solid MFT samples, which were stored frozen, until processing.

2.2.3 Sample analysis

Samples were delivered to the CALA accredited and internationally intercalibrated University of Alberta Biogeochemical Analytical Service Laboratory (BASL) within 24 hours of sampling for processing (Table 2.1). Water chemistry analyses were completed on all liquid samples using standard analytical protocols at the BASL. Due to the high turbidity, depth samples from Horizon were initially centrifuged to separate particles from the liquid and the supernatant was analyzed (Table 2.1). Water chemistry parameters measured included pH, colour, turbidity (Turb), total dissolved solids (TDS), total suspended solids (TSS), silica (SiO_2), total phosphorous (TP), total dissolved phosphorous (TDP), total dissolved nitrogen (TDN), particulate nitrogen (PN), ammonia (NH_3), nitrite (NO_2), dissolved organic carbon (DOC), particulate carbon (PC), and sulfate (SO_4).

Liquid samples were analyzed for concentrations of 46 trace elements at the CALA accredited National Laboratory for Environmental Testing (NLET) in Burlington, ON. Samples were first filtered through a 0.45 μm cellulose acetate filter paper, acidified to 2% v/v nitric acid (HNO_3), then analyzed 24 hours later by inductively coupled argon plasma-collision/reaction cell mass spectrometer (CRC-ICP-MS) by discrete sampling pneumatic nebulization. A suite of standard reference materials from SCP Science was used to test method accuracy. Samples from depth sites at Horizon were too particle-rich to analyze as liquid; therefore, samples were frozen and freeze-dried prior to analysis using a LABCONCO FreezeZone® 12 L freeze dry system. Once dried, samples were homogenized with an acid-washed (10% HCl) glass mortar and pestle, subsampled into new Whirl-Pak® bags, and stored in a desiccator until analysis. Similarly, MFT samples collected using the Eckman grab were also freeze-dried and homogenized. Herein when discussing sediment samples, Horizon freeze-dried depth samples and MFT samples will collectively be called sediment samples. Sediment samples were analyzed for concentrations of the same 46 trace elements using an Elan 6000 ICP-MS (PerkinElmer Sciex) at the Canadian Centre for Isotopic Microanalysis (CCIM) at the University of Alberta. ~ 0.2 g of sample was digested in 8 mL of concentrated HF and 2 mL of HNO_3 at 130°C until completely dry. 5 mL of HCl and 5 mL of HNO_3 were then added and digested at 140°C until completely dry. Subsequently, 10 mL of 8M HNO_3 was added and digested at 130°C for two hours. Finally, 0.1 mL HNO_3, internal standards (In, Bi, Sc), and 8 mL of deionized water were added to 1 mL of this solution, shaken and analyzed with an average recovery of 87.5 ± 15.6%. SRM BIR-1 (Icelandic basalt, USGS) and SRM BHVO-2 (Hawaiian basalt, USGS) were used as quality controls with recoveries between 67.5-113.5% and 63.3-114.5% respectively.

Immediately upon arrival at the laboratory (<1 hour), one of the duplicate THg and MeHg water samples was filtered through pre-cleaned, acid-washed (1% v/v TMG HCl) filter packs (Nalgene RapidFlow™). All THg and MeHg samples were then preserved via acidification to 0.2% v/v with concentrated TMG HCl. All THg and MeHg analyses were carried out at the BASL. Liquid samples were analyzed for THg concentrations using a Tekran© 2600 THg Analyzer. The method detection limit (MDL) was 0.03 ng/L, calculated as three times the standard deviation of the blanks using ~40 mL of sample. 10% of the THg samples were analyzed in duplicate and were within 10% of each other. Freeze-dried solid samples were analyzed for THg using a Milestone DMA-80 direct Hg analyzer. Concentrations of THg in standard reference material (SRM) MESS-4 (marine sediment) run alongside solid samples were always within the certified range (0.08 ± 0.06 μg/g THg) and duplicates were within <10% of each other.

To quantify concentrations of MeHg in liquid samples, samples were distilled with 1% APDC using a Tekran© 2750 distillation unit and analyzed using a Tekran© 2700 MeHg Analyzer coupled with a PerkinElmer Elan DRC-e ICP-MS (PerkinElmer Sciex).[74] $Me^{201}Hg$ was added to samples as a species-specific internal standard prior to distillation to correct for procedural recoveries. The MDL for this method was 0.016 ng/L using ~40 mL of sample. 10% of MeHg samples were analyzed in duplicate and 5% were analyzed in triplicate, and all were within 10% of each other. The same method was used for analyzing MeHg in sediment samples, except with distillation reagents H_2SO_4 (50%) and KCl (50%) and SRM SQC1238 (methyl mercury in sediment) run alongside samples to assess method accuracy. All sample duplicates were within 10% of each other and SRM samples were well within the certified range (10.0 ± 0.29 ng/g MeHg) and SRM duplicates were within 5% of each other.

2.3 RESULTS AND DISCUSSION

2.3.1 Water chemistry and trace elements in the tailings ponds

Pond temperatures were consistently slightly higher than air temperatures at the time of sampling, with no marked changes with depth, suggesting no thermal stratification. All ponds were slightly basic (pH 8.1-8.5 at all depths; Table 2.2) and relatively hard (7-29 mg/L Ca; 6-15 mg/L Mg; Tables 2.3), consistent with previous studies.[8, 60, 75, 76] As a result of the addition of salts[60] during primary separation, Na (779-1050 mg/L) and Cl (438-669 mg/L) concentrations in the tailings ponds were greatly elevated relative to Na (16 mg/L) and Cl (6 mg/L) concentrations in the nearby Athabasca River.[60] Turbidity and concentrations of TSS and PC predictably increased with depth due to the settling process. DOC concentrations were uniform across all ponds and depths (48.2-55.4 mg/L) and consistent with previous findings.[69, 76] SO_4 concentrations were also elevated in all tailings ponds (105-606 mg/L) likely because $CaSO_4$ is commonly used to accelerate tailings settling and consolidation processes.[60, 77] Concentrations of SO_4 were 4-5X lower in Horizon than in the Syncrude ponds, and were substantially higher (4-100X) in all ponds compared with those observed in regional lakes (1-6 mg/L) and the nearby Athabasca River (22 mg/L).[60, 78] TDN concentrations in OSTP surface waters ranged from 1.31-2.45 mg/L, and were 2-10X lower than concentrations at depth (3.66-13.6 mg/L). NH_3 was the primary component of TDN in the ponds (~70%), likely originating from ore-born nitrogen and a by-product of the extraction process.[69, 79] Concentrations of NH_3 in the ponds ranged from 1.04-12.4 mg/L, which is 8-24X the CCME guideline of 0.001 mg/L and 2-20X greater than in the nearby Athabasca River (0.06 mg/L) and regional lakes (<0.05-0.57 mg/L).[60, 80] Finally, NO_2, concentrations were below detection at most sites in Horizon, SWIP, and MLSB, but were 72-84 μg/L in SWSS suggesting that active nitrification occurs in this pond.

A vast array of trace elements were detected in the four tailings ponds, including 9 of the 13 designated priority pollutant elements under the Clean Water Act set by the US Environmental Protection Agency (Table 2.3).[81] When compared to the CCME guidelines for the protection of aquatic life in freshwater,[82] all four tailings ponds at all sites analyzed exceeded guidelines for dissolved concentrations of aluminum (Al; 1.6-6X the CCME guidelines of 0.1 mg/L) boron (B; 1.5-2X the guideline of 1.5 mg/L), cadmium (Cd; 1.5-2X the guideline of 0.00009 mg/L), selenium (Se; 2-15X the guideline of 0.001 mg/L), and zinc (Zn; 1.5-2.5X the guideline of 30 μg/L). In all Syncrude ponds, guideline limits were also exceeded for arsenic (As; 1.5-3X the guideline of 0.005 mg/L) and molybdenum (Mo; 1-2X the guideline of 0.07 mg/L). Trace elements that have previously been reported to exceed CCME guidelines in OSPW include Al, As, chromium (Cr), copper (Cu), iron (Fe), lead (Pb), nickel (Ni), and Zn, only three of which were exceeded in some or all of the ponds examined herein.[60] Numerous trace elements were also detected in the sediment samples (excluding SWSS, where sediment samples were not collected), though only Cu marginally exceeded (by 2.20 μg/g) the CCME guidelines (197 μg/g) for the Probable Effects Level (PEL) for freshwater sediment (Table 2.3).[83] All water column CCME guidelines exceeded are of concern for aquatic life downstream of the OSTP since the ponds are leaking into both groundwater and into the Athabasca River.[55] Cu in the solid MFT only marginally exceeded the guidelines and is likely considerably less mobile than in water and therefore does not likely pose a risk to downstream aquatic life.

2.3.2 THg and MeHg in the tailings ponds

Concentrations of unfiltered THg in surface waters averaged 0.35 ± 0.17 ng/L, and ranged between 0.16-0.50 ng/L (Table 2.4). Horizon and SWSS had average surface THg concentrations of 0.50 ± 0.19 ng/L and 0.40 ± 0.07 ng/L, respectively, while SWIP had concentrations that were 2.5-3X lower at 0.16 ± 0.04 ng/L. Concentrations of filtered THg in surface waters averaged 0.25 ± 0.13 ng/L, and ranged from 0.07-0.50 ng/L (Table 2.4). Filtered THg concentrations were lowest in surface waters of the Horizon (0.16 ± 0.07 ng/L) and SWIP (0.15 ± 0.03 ng/L) ponds, and 2-3X higher in the MLSB (0.32 ± 0.05 ng/L) and SWSS (0.48 ± 0.06 ng/L) ponds. While the majority of THg was particle bound in Horizon (69%), virtually none of the THg was particle bound in SWIP (6%) and SWSS (<1%). Average filtered sub-surface THg concentrations in MLSB were 0.40 ± 0.24 ng/L, while sub-surface waters in SWIP had low THg concentrations (0.24 ± 0.04 ng/L), of which virtually none was particle-bound (<1%). As previously mentioned, sub-surface samples taken at 5 and 8.5 m from Horizon were extremely particulate rich, and therefore freeze-dried and analyzed as sediments. Average THg concentrations in these Horizon pond sediments (31.4 ± 0.83 ng/g) were similar to those observed in MFT in SWIP (39.2 ± 1.88 ng/g); however, THg concentrations in MLSB MFT were ~3-4x higher (134 ± 69.1 ng/g).

THg concentrations measured in the water of tailings ponds were within the range observed in the Athabasca River upstream of the developments (<0.4 ng/L)[37] and in lakes across Canada (1.08-3.98 ng/L).[84] For example, average THg concentrations are <1.0 ng/L in the Laurentian Great Lakes region, with concentrations ranging from 0.29 ng/L in Lake Huron to 12 ng/L in Western Lake Erie.[85, 86] Filtered THg concentrations in the AOSR tailings ponds (0.15-0.48 ng/L) were also below the concentrations of filtered THg in a constructed wetland in the AOSR (0.33-5.2 ng/L)[87] and below the range of filtered THg concentrations found in four natural lakes in Northern Québec (0.77-2.90 ng/L).[88]

In 1996, THg concentrations in sediments along the Athabasca River from Fort McMurray to the Peace-Athabasca delta ranged between 30-63 ng/g,[89] which is similar to those measured in Horizon and SWIP, but lower than in MLSB. A more recent study (2000) of sediments in the Peace, Athabasca, and Slave river basins within the AOSR reported slightly higher concentrations (27-123 ng/g), which is similar to the tailings ponds analyzed herein (31.4-134 ng/g), with highest THg concentrations measured at MLSB.[90] THg concentrations in the tailings ponds sediments were also comparable to those in more than 135,000 lake sediment cores taken from across Canada, where average THg concentrations ranged from 35.7 to 104.4 ng/g.[91] Overall, THg concentrations in solid samples of Horizon, SWIP, and MLSB are similar to background levels in the AOSR and across Canada.[89-91]

Average unfiltered surface water MeHg concentrations were extremely low in Horizon (0.05 ± 0.01 ng/L), SWIP (<MDL), and SWSS (0.08 ± 0.00 ng/L) (Table 2.4). Conversely, average MeHg concentrations in MLSB surface waters were nearly 7X higher (0.32 ± 0.14 ng/L). Similarly, filtered MeHg concentrations in surface water samples were on average ~8X higher in MLSB (0.14 ± 0.07 ng/L) than in Horizon (0.02 ± 0.01 ng/L), SWIP (<0.01 ng/L), and SWSS (0.04 ± 0.01 ng/L). In all tailings ponds, MeHg in surface waters were predominantly particulate-bound (52-62%). Subsurface unfiltered and filtered MeHg concentrations were virtually non-detectable in SWIP (<MDL-0.02 ng/L) but were considerably higher in MLSB, where at mid-depth, average unfiltered and filtered concentrations were 0.53 ± 0.25 ng/L and 0.11 ± 0.02 ng/L, respectively, or ~80% particulate bound. As in the overlying water, concentrations of MeHg were considerably higher in MLSB solid samples (0.46 ± 0.04 ng/g) than in the solid samples of Horizon (0.15 ± 0.04 ng/g) and SWIP (0.16 ± 0.06 ng/g).

In the Canadian Mercury Science Assessment Report (2017), a multitude of studies of lakes across Canada documented average MeHg concentrations of 0.07 ± 0.10 ng/L.[43] This report also suggests that typically, MeHg concentrations are <0.10 ng/L in unimpacted Canadian freshwater systems.[43] Thus, MeHg concentrations in Horizon, SWIP, and SWSS are typical for lakes across Canada and fall within the range of unimpacted freshwater systems. In MLSB however, unfiltered MeHg concentrations are slightly elevated in surface water and in MFT, but are substantially elevated in the subsurface waters.

The percentage of THg that is MeHg (%MeHg) can be used to evaluate the potential for net production of MeHg from Hg(II) in freshwater systems.[43] Typically, %MeHg is <5% in Canadian lake surface waters,[43] between 0.5-3%[43] for freshwater sediments, and <0.5% in estuarine sediments, which are briny like the OSTPs.[78, 92-95] The %MeHg in both filtered and unfiltered surface waters from Horizon and SWSS and all depths in SWIP was between 2-19% MeHg, and were thus similar to or just slightly above the average range for Canadian freshwaters.[43, 96] In MLSB filtered samples, %MeHg was distinctly high (46-57%) at all depths, indicating the potential for net methylation throughout the water column in this tailings pond. %MeHg in sediment samples from all ponds were below the average range for Canadian freshwater sediments, ranging between 0.3-0.5% MeHg.[43, 78]

What are the potential sources of MeHg to the tailings ponds? For example, is MeHg discharged or deposited to the ponds directly or is it produced *in situ*? Overall, surface waters, FFT and the surface of the MFT layer do not have elevated MeHg concentrations with the exception of MeHg concentrations in FFT in MLSB. MLSB is considerably older (15+ years) than the other ponds, and has the highest FFT to water ratio (~15:1) in the upper 2 m of the four ponds examined, potentially allowing for anaerobic microbial communities capable of Hg(II) methylation to become established there. OSPW and MFT are known to be microbially active[75, 97-101] and sulfate-reducing bacteria, iron-reducing bacteria, and methanogens, are all known to be capable of Hg(II) methylation,[102] and have been found in the MFT of MLSB.[76] The presence of SO_4 is known to stimulate microbial Hg methylation by sulfate-reducing bacteria (SRB) when present in optimal concentrations.[100, 101] When there is an abundance of SO_4 (>29 mg/L), methylation is often inhibited as a result of sulfide binding to inorganic Hg(II), which is much less bioavailable for uptake by SRB.[43, 78] Therefore, in all four tailings ponds, *in situ* Hg(II) methylation by SRB is likely somewhat inhibited by elevated sulfate concentrations (470 ± 156 mg/L).

In the future, it would be valuable to determine MeHg concentrations throughout the anaerobic[13, 76] MFT layer, which may be conducive to anaerobic methylation activity. Additional investigations of the potential for *in situ* Hg methylation should also be examined using stable

Hg isotope tracer experiments since these ponds are known to be microbially active, and bacteria other than SRB are known to be involved in Hg methylation.[75, 97-101] Though these OSTPs are likely not a significant source of THg or MeHg to nearby groundwaters and surface freshwaters into which they leak, monitoring of MeHg concentrations in MLSB, where concentrations were highest, should be continued, especially when considering pond remediation.

2.4 TABLES AND FIGURES

Table 2.1 Description of how samples from each depth sampled in four tailings ponds, Horizon, Southwest In-Pit (SWIP), Mildred Lake Settling Basin (MLSB), and Southwest Sand Storage (SWSS) in the Alberta Oil Sands Region, Alberta, Canada were processed and analyzed. NA indicates sample not analyzed for that parameter. Grey shading indicates samples analyzed as sediments.

POND	Depth (m)	# Sites sampled	Mercury	Methylmercury	Chemistry	Trace elements
Horizon	0	5	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	5	2	Solid (Freeze-dried)	Solid (Freeze-dried)	Liquid (Centrifuged, dissolved species F, total and particulate species UF)	Solid (Freeze-dried)
	8.5	1	Solid (Freeze-dried)	Solid (Freeze-dried)	Liquid (Centrifuged, dissolved species F, total and particulate species UF)	Solid (Freeze-dried)
SWIP	0	5	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	3	2	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	6	2	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	MFT[a]	2	Solid (Freeze-dried)	Solid (Freeze-dried)	NA	Solid (Freeze-dried)
MLSB	0	5	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	1	2	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)
	2	2	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	NA
	MFT[a]	2	Solid (Freeze-dried)	Solid (Freeze-dried)	NA	Solid (Freeze-dried)
SWSS	0	3	Liquid (UF/F)	Liquid (UF/F)	Liquid (Dissolved species F, total and particulate species UF)	Liquid (F)

[*] UF – unfiltered; F – filtered; MFT[a] – mature fine tailings (>30% solid), impenetrable by Eckman grab.

Table 2.2 Averaged physical and chemical composition (± standard deviation) in the waters of four tailings ponds, Horizon, Southwest In-Pit (SWIP), Mildred Lake Settling Basin (MLSB), and Southwest Sand Storage (SWSS) in the Alberta Oil Sands Region, Alberta, Canada.

POND	**Depth (m)**	**pH**	**Temp. (°C)**	**Turb (NTU)**	**TSS (mg/L)**	**PC (mg/L)**	**DOC (mg/L)**	**SO_4 (mg/L)**	**TDN (mg/L)**	**NH3 (mg/L)**	**NO_2 (µg/L)**
Horizon	0	8.18 ± 0.02	5.02 ± 0.41	895 ± 218	531 ± 176	35.0 ± 5.82	51.3 ± 1.31	108 ± 2.42	1.78 ± 0.03	1.07 ± 0.03	NA
	5	NA	11.4 ± 2.11	NA	NA	NA	55.4$^{\Delta}$	NA	3.68$^{\Delta}$	1.93 ± 1.24	NA
	8.5	NA	11.9$^{\Delta}$	NA	NA	NA	50.3$^{\Delta}$	NA	3.66$^{\Delta}$	3.38$^{\Delta}$	NA
SWIP	0	8.19 ± 0.03	21.0 ± 0.53	212 ± 130	192 ± 85.0	13.1 ± 7.18	49.6 ± 1.13	594 ± 10.5	8.49 ± 0.17	5.21 ± 0.25	<MDL
	3	8.32 ± 0.03	20.4 ± 0.23	301 ± 66.5	262 ± 59.6	14.8 ± 4.38	50.4 ± 0.85	508 ± 1.15	8.43 ± 0.11	5.83 ± 0.25	2.51 ± 3.53
	6	8.15 ± 0.00	22.6 ± 0.08	5320 ± 3000	2460 ± 1530	72.2 ± 88.9	52.4 ± 0.92	598 ± 3.97	8.11 ± 0.44	6.85 ± 1.41	10.5 ± 14.8
MLSB	0	8.11 ± 0.01	21.8 ± 1.97	726 ± 335	419 ± 165	77.5 ± 58.3	50.3 ± 2.34	510 ± 8.59	14.1 ± 0.93	9.81 ± 1.49	6.61 ± 9.36
	1	8.14 ± 0.01	19.8 ± 1.27	2330 ± 2860	2120 ± 14.4	481 ± 61.8	50.0 ± 0.14	508 ± 4.70	13.5 ± 0.23	10.0 ± 0.55	1.51 ± 2.11
	2	8.12 ± 0.02	20.4 ± 0.79	1670 ± 1420	2065 ± 6.72	193 ± 97.3	50.6 ± 1.77	501 ± 19.7	13.6 ± 0.00	10.2 ± 1.69	<MDL
SWSS	0	8.54 ± 0.00	14.7 ± 0.36	302 ± 4.93	284 ± 11.7	14.2 ± 1.36	51.7 ± 1.15	431 ± 7.54	4.08 ± 0.18	2.71 ± 0.13	77.7 ± 6.03

$^{\Delta}$Only one site analyzed; MFT^{a} – mature fine tailings (>30% solid); <MDL – below method detection limit; Turb – turbidity; TSS – total suspended solids; PC – particulate carbon; DOC – dissolved organic carbon; SO_4 – sulfate; TP – total phosphorous; TDN – total dissolved nitrogen; NO_2 – nitrite

Table 2.3 Average concentrations of trace elements (± standard deviation) that are either known to be enriched in bitumen or exceeded the Canadian Council of Ministers of the Environment guidelines for the protection of aquatic life in freshwater and sediments, in four tailings ponds (Horizon, Southwest In-Pit (SWIP), Mildred Lake Settling Basin (MLSB), and Southwest Sand Storage (SWSS)) at varying depths in the Alberta Oil Sands Region, Alberta, Canada. Water samples were filtered prior to analyses. Grey shading indicates samples analyzed as solids (see Table 2.1).

POND	Depth (m)	Al (µg/L or mg/g)	As (µg/L or µg/g)	B (mg/L or mg/g)	Ca (mg/L or mg/g)	Cd (µg/L or µg/g)	Cl (mg/L)	Cu (µg/L or µg/g)	K (mg/L or mg/g)	Mg (mg/L or mg/g)	Mo (µg/L or µg/g)	Na (mg/L or mg/g)	Se (µg/L or µg/g)	V (µg/L or µg/g)	Zn (µg/L or µg/g)
Horizon	0	200 ± 77.9	2.64 ± 0.24	3.07 ± 0.04	8.17 ± 1.15	0.12 ± 0.00	660 ± 8.85	4.90 ± 2.16	18.0 ± 0.31	5.83 ± 0.29	67.0 ± 1.81	933 ± 16.1	2.73 ± 0.23	2.04 ± 0.22	43.5 ± 27.3
	5	189 ± 16.8	1.88 ± 0.22	0.15 ± 0.02	1.81 ± 0.44	0.13 ± 0.02	555$^{\Delta}$	14.8 ± 2.18	21.7 ± 1.16	5.82 ± 0.63	1.59 ± 0.12	5.79 ± 0.53	0.86 ± 0.16	142 ± 9.29	54.5 ± 3.57
	8.5	100 ± 10.3	1.68 ± 0.09	0.11 ± 0.00	2.27 ± 0.23	0.14 ± 0.01	570$^{\Delta}$	13.7 ± 0.91	22.0 ± 0.73	6.19 ± 0.15	1.84 ± 0.03	1.06 ± 0.36	1.06 ± 0.09	158 ± 5.10	48.5 ± 2.74
SWIP	0	161 ± 49.4	14.8 ± 1.78	2.69 ± 0.05	17.2 ± 0.62	0.16 ± 0.01	576 ± 11.8	3.57 ± 0.85	19.7 ± 0.25	10.5 ± 0.30	114 ± 2.45	1030 ± 11.4	2.19 ± 0.24	16.6 ± 0.92	61.8 ± 5.96
	3	169 ± 55.2	13.3 ± 0.57	2.66 ± 0.01	17.0 ± 0.64	0.17 ± 0.01	579 ± 1.25	2.98 ± 0.44	19.7 ± 0.14	10.3 ± 0.21	113 ± 2.12	1040 ± 14.1	2.27 ± 0.40	16.3 ± 0.50	58.4 ± 6.51
	6	204 ± 79.2	10.9 ± 5.87	2.59 ± 0.09	16.6 ± 0.07	0.16 ± 0.01	579 ± 3.70	3.70 ± 1.67	18.7 ± 1.34	10.0 ± 0.28	110 ± 4.95	985 ± 50.2	1.89 ± 0.13	13.2 ± 4.68	59.3 ± 13.9
	MFT^{a}	91.6 ± 2.27	2.52 ± 0.46	0.95 ± 0.00	1.97 ± 0.40	0.16 ± 0.01	NA	21.6 ± 2.29	16.0 ± 0.45	4.42 ± 0.10	3.25 ± 0.41	6.40 ± 3.36	1.02 ± 0.10	126 ± 2.60	64.2 ± 2.88
MLSB	0	227 ± 81.9	9.86 ± 1.74	2.20 ± 0.04	28.8 ± 0.33	0.17 ± 0.01	456 ± 9.24	2.64 ± 0.29	17.2 ± 0.29	14.6 ± 0.43	121 ± 3.70	806 ± 18.5	9.73 ± 2.97	16.6 ± 2.54	72.1 ± 6.69
	1	289$^{\Delta}$	12.8$^{\Delta}$	2.19$^{\Delta}$	27.9$^{\Delta}$	0.18$^{\Delta}$	453 ± 11.5	2.15$^{\Delta}$	17.4$^{\Delta}$	14.6$^{\Delta}$	119$^{\Delta}$	799$^{\Delta}$	14.6$^{\Delta}$	13.5$^{\Delta}$	66.4$^{\Delta}$
	2	NA	NA	NA	NA	NA	450 ± 16.3	NA	NA	NA	NA	NA	NA	NA	NA
	MFT^{a}	69.2 ± 32.2	3.91 ± 2.28	0.09 ± 0.01	112 ± 7.82	0.23 ± 0.06	NA	37.9 ± 18.3	11.4 ± 4.47	7.51 ± 3.63	5.40 ± 0.32	2.13 ± 0.68	2.45 ± 0.32	151 ± 19.4	117 ± 38.9
SWSS	0	601 ± 75.7	6.90 ± 0.17	2.47 ± 0.09	20.2 ± 0.36	0.13 ± 0.01	586 ± 11.9	1.93 ± 0.09	15.7 ± 0.31	10.7 ± 0.35	87.0 ± 1.82	967 ± 36.4	3.21 ± 0.08	11.1 ± 0.46	46.1 ± 2.59
								CCME Guidelines							
Freshwater (µg/L)		100	5.00	1500		0.09		4.00			70.0		1.00		30.0
ISQG (µg/g)			5.90			0.60		35.7							123
Sediment PEL (µg/g)			17.0			3.50		197							315

$^{\Delta}$Only one site analyzed; MFT^{a} – mature fine tailings (>30% solid); ISQG – interim sediment quality guideline; PEL – probable effects level.

Table 2.4 Filtered (F) and unfiltered (UF) THg and MeHg concentrations, and percent MeHg (%MeHg) in four tailings ponds, Horizon, Southwest In-Pit (SWIP), Mildred Lake Settling Basin (MLSB), and Southwest Sand Storage (SWSS), in the Alberta Oil Sands Region, Alberta, Canada. Grey shading indicates samples analyzed as sediments.

Pond	Depth (m)	UF THg (ng/L or ng/g)	F THg (ng/L)	UF MeHg (ng/L or ng/g)	F MeHg (ng/L)	UF %MeHg	F %MeHg
Horizon	0	0.50 ± 0.19	0.16 ± 0.07	0.05 ± 0.01	0.02 ± 0.01	11.2	13.8
	5	30.0 ± 2.82	NA	0.16 ± 0.04	NA	0.53	NA
	8.5	31.4 ± 0.83	NA	0.13 ± 0.03	NA	0.41	NA
SWIP	0	0.16 ± 0.04	0.15 ± 0.03	0.01 ± 0.01	0.00 ± 0.01	3.88	2.00
	3	0.24 ± 0.03	0.23 ± 0.02	0.02 ± 0.01	0.01 ± 0.00	9.42	6.15
	6	0.23 ± 0.04	0.24 ± 0.06	0.01 ± 0.00	0.01 ± 0.01	5.78	2.06
	MFT[a]	39.2 ± 1.88	NA	0.16 ± 0.06	NA	0.41	NA
MLSB	0	NA	0.32 ± 0.05	0.32 ± 0.14	0.14 ± 0.07	NA	45.7
	1	NA	0.23 ± 0.02	0.53 ± 0.25	0.11 ± 0.02	NA	46.3
	2	NA	0.57 ± 0.33	NA	0.32 ± 0.30	NA	56.5
	MFT[a]	134 ± 69.1	NA	0.46 ± 0.04	NA	0.34	NA
SWSS	0	0.40 ± 0.07	0.48 ± 0.06	0.08 ± 0.00	0.04 ± 0.01	19.4	7.93

MFT[a] – mature fine tailings (>30% solid)

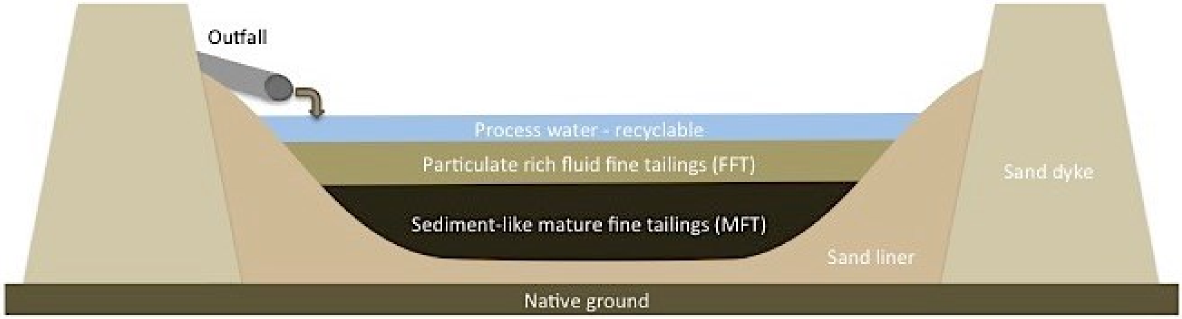

Figure 2.1 Cross-sectional view of a typical tailings pond in the Alberta Oil Sands Region, Alberta, Canada. Tailings ponds receive a slurry of mining process water and sediments of various sizes from an outfall located on the side of the pond. The surface water is often recycled back into the bitumen separation processes. The layer of fluid fine tailings is composed of process water and has a solid content between 15-30%, with the particles sizes typically ≤44 µm. The final layer is composed of mature fine tailings, which are highly viscous and contain particles >30 µm.

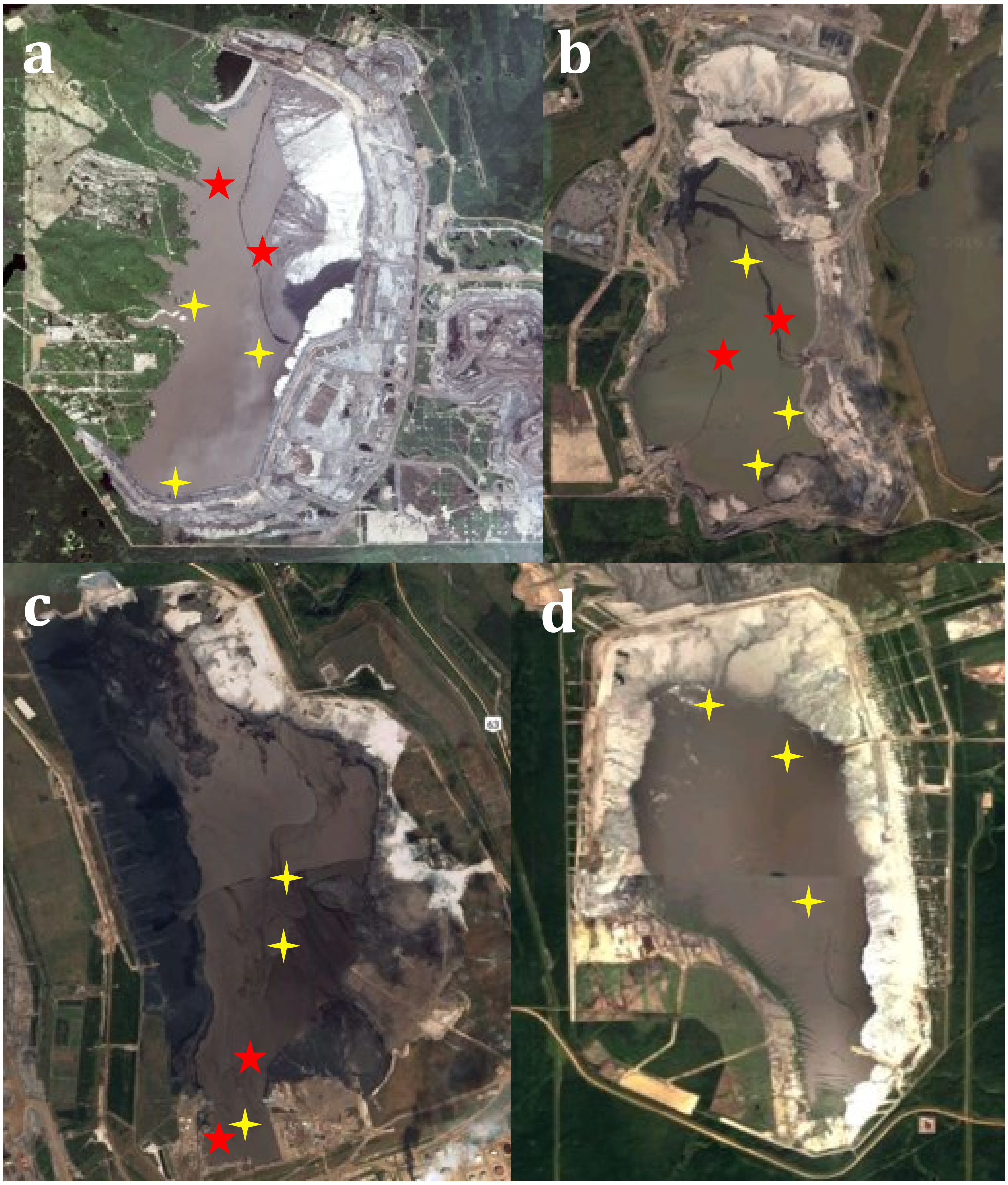

Figure 2.2 Tailings pond surface sampling sites (red and yellow) and depth profile sampling sites (red) at Canadian Natural Resources Limited (A) Horizon and at Syncrude ponds (B) Southwest In-pit, (C) Mildred Lake Settling Basin, and (D) Southwest Sand Storage, in the Alberta Oil Sands Region, Alberta, Canada. Adapted from Alberta Energy Regulator's Directive 074 Tailings Management Plan reports.

3 Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: A study of in situ methylation and particulates

3.1 INTRODUCTION

Exploitation of the world's third largest crude oil reserve in northern Alberta has recently been one of Canada's major economic drivers.[1] The Alberta Oil Sands Region (AOSR) is home to ~170 billion barrels of proven oil reserves[1] and from a combination of enhanced oil recovery strategies, produces ~2.3 million barrels of oil per day.[1, 103] Though the geolithology of the AOSR is rich in oil, it yields low recoveries, as the oil sands mixture is mainly composed of sand, clay, and other minerals with only ~4-6% bitumen, a highly viscous form of petroleum.[104]

As with most large-scale industrial activities, there are concerns about human and ecosystem health within the AOSR.[15-17] Contaminants in the AOSR are released from sources such as stack emissions and wastewaters,[18-21] tailings ponds,[22, 23] increased erosion,[24] blowing dust from landscape disturbance, road activity, and open-pit mines.[24, 25] Among these contaminants are an array of organic pollutants such as polycyclic aromatic hydrocarbons,[26-30] naphthenic acids,[31-33] sulphur dioxide and nitrogenous oxide species,[3, 34, 35] secondary organic aerosols,[36] and metals, including mercury (Hg).[37-39] Kelly et al.[26, 37] found that wintertime atmospheric deposition of the 13 elements (Ag, Ar, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sb, Tl, Zn) considered priority pollutants elements (PPEs) under the U.S. Environmental Protection Agency[105] increased with proximity to the major upgraders. The same pattern of elevated loadings near the major upgraders was demonstrated by Kirk et al.[39] for both total Hg (THg; all forms of Hg in a sample) and methylmercury (MeHg; a vertebrate neurotoxin that readily bioaccumulates in organisms and biomagnifies through foodwebs) in snowpacks. These finding are of concern because during snowmelt, MeHg may enter local water bodies where it could become available for bioaccumulation during the spring pulse of biological activity. Currently, the origin of the MeHg in these snowpacks is unknown, although previous studies showed that a large portion of the MeHg in snowpacks is particle-bound.[39] Is the particle-bound MeHg deposited into snowpacks, and/or is there *in situ* methylation of inorganic Hg(II) within snowpacks, after which the MeHg becomes bound to particles?

In this study, net Hg(II) methylation potential in snowpacks and melted snow was quantified at maximum snowpack depth in March using the addition of enriched Hg stable isotopes during incubation experiments. We also quantified concentrations of MeHg on snowpack particles (pMeHg), and determined particle size distributions to help understand the sources of pMeHg to AOSR snowpacks.

3.2 METHODS

3.2.1 Sample collection

Snow was collected between 4-14 March 2015 at 23 sites ranging in distance from the major AOSR upgraders for analyses of THg, MeHg, pMeHg, general water chemistry and multi-element concentrations and loadings to snowpacks (Figure 3.1). Snow for net potential methylation experiments was collected at four of the 23 sites, which were known to differ in THg, MeHg, and particulate loads,[37, 39] hereafter referred to as the four focus sites. These four sites were selected using data from 2013; site ST2 had high THg, MeHg, and particle-loadings, two sites (AR6 and MU3) had intermediate loadings of THg, MeHg, and particles, and one reference site (AR10) had low loadings of THg, MeHg, and particles. For the remainder of this paper, these four focus sites will be referred to by their distance from the major upgrading facilities: 0 km (AR6), 7 km (ST2), 25 km (MU3) and 134 km (AR10).

All sites were accessed by helicopter. Snow samples were collected in clearings approximately 50-100 m upwind of the landing site. Snow was collected behind the cleaned edge of a snow pit using HNO_3-washed stainless steel corers of 5 or 10 cm inner diameter (ID) and the two person "clean hands, dirty hands" Hg sampling protocol.[106] Snow samples for unfiltered and filtered THg and MeHg analyses, as well as pMeHg analyses, were transferred into 1 or 2 L trace-level grade quality assured containers guaranteed to be contaminant free following the OSWER Directive 9240.0-05A (referred to as ‘precleaned’ hereafter). Samples for water chemistry and multi-element analyses were collected into a pre-cleaned five-gallon high-density polyethylene (HDPE) container. Three precleaned amber glass jars of snow were collected at each of the four focus sites for particle size distribution analysis. To limit the impacts of post-depositional processes, only surface snow was collected for analysis of particle size distribution by dragging the jars across the top 5 cm of the fresh snowpack. All samples were stored frozen until analysis.

For Hg(II) methylation and MeHg demethylation experiments in snowpacks at the four focus sites, six intact snow cores were collected (at each site) into 1% HCl-washed polycarbonate core tubes (7.3 cm ID) with pre-drilled 1.25 mm injection ports every 1 cm along both sides of the tube. For Hg(II) methylation and MeHg demethylation experiments in melted snow, 12 1L precleaned glass jars were filled using the 5 cm (ID) stainless steel corer. Six of these samples were used to determine potential rates of Hg(II) methylation and MeHg demethylation in melted snow, whereas the other six samples were used for reactive Hg (RHg; defined as stannous chloride reducible Hg) analysis.

3.2.2 Sample analyses

Concentrations and loadings of THg, MeHg, general chemistry and multi-elements in snowpacks: Snowpack samples from all 23 sites were melted in the laboratory and analyzed for concentrations of THg and MeHg at the Low Level Hg Analytical Laboratory at the Canada Centre for Inland Waters (CCIW) as in Kirk et al.[39] (see SI for details).

Melted snow from all sites was also analyzed for a variety of chemical parameters, using standard protocols, at the Canadian Association for Environmental Analytical Laboratories (CAEAL) accredited National Laboratory for Environmental Testing (NLET) at CCIW in Burlington, ON, Canada (see SI for details). Loadings were calculated by multiplying concentration by snow-water equivalence (see SI, Eq[1]).

Potential rates of Hg methylation in snowpacks and melted snow. Establishing net methylation potentials required quantifying rates of MeHg demethylation and loss of Hg(II) substrate, or RHg, over time. To remove photodemethylation as a confounding factor, all net methylation experiments were completed in the dark. Potential rates of dark MeHg demethylation were quantified by measuring loss of $Me^{199}Hg$ in snow cores and melted snow over time, while potential rates of net Hg(II) methylation were quantified from the quantity of available $R^{198}Hg$ that was converted to $Me^{198}Hg$ over time, taking into account simultaneous rates of MeHg demethylation. All samples were analyzed for concentrations of $R^{198}Hg$, $Me^{199}Hg$, and $Me^{198}Hg$ at the CAEAL accredited and internationally intercalibrated University of Alberta Biogeochemical Analytical Service Laboratory (BASL). For analytical reasons, we were only able to quantify $R^{198}Hg$ in melted snow. Snow samples for $R^{198}Hg$ analyses were melted overnight in the dark, decanted to a volume of 350 mL and spiked with 4.1 ng $^{198}Hg(II)$ resulting in a calculated concentration of 11.7 ng/L $^{198}Hg(II)$, which was 2-10X higher than ambient THg concentrations in AOSR snowpacks. 30 mL subsamples were then analyzed for $R^{198}Hg$ at T = 0, 2, 4, 6, 8, 10, 24, 30, and 48 hrs. $R^{198}Hg$ was quantified by $SnCl_2$ reduction without prior oxidation using BrCl[107] using a Tekran© model 2600 Hg analyzer coupled to an Elan DRC-e ICP-MS (PerkinElmer Sciex).[74]

To determine potential rates of methylation in snowpacks, six snow cores from each site were injected with a solution of 1.05 ng/mL $^{198}Hg(II)$ and 0.0052 ng/mL $Me^{199}Hg$ immediately after collection. At 2 cm intervals over the whole length of the snow core, three 33.3 μL injections were made using a Hamilton gas tight syringe into each port on both sides of the core tube (total of 200 μL per interval). Injections were made in a fan-like pattern to evenly distribute the isotope. Two cores were immediately emptied into 2 L pre-weighed, precleaned, glass jars, acidified to 0.2% v/v with concentrated trace metal grade (TMG) HCl, shaken, and melted in a dark refrigerator, to obtain the T=0 measurement. The remaining four cores were incubated in a dark freezer (~ -8°C) for T=24 hours (two cores) and T=48 hours (two cores), after which they were processed as described for T=0 cores. All samples were kept refrigerated in the dark until analysis. To determine potential rates of Hg(II) methylation in melted snow, snow was melted overnight in the dark the same day of collection. The following morning, jars were decanted to 350 mL and spiked with 4.1 ng ^{198}Hg(II) and 0.02 ng Me^{199}Hg for calculated concentrations of 11.7 ng/L ^{198}Hg(II) and 0.57 ng/L Me^{199}Hg, which approximately doubled ambient THg and MeHg concentrations. Two jars were immediately acidified with TMG HCl to 0.2% v/v to stop methylation and demethylation (T=0). The remaining four jars were incubated in a dark fridge (~ 4^{o}C) for T=24 (two jars) and T=48 hours (two jars), after which they were processed as described for T=0 samples.

Incubation samples were distilled using a Tekran$^{©}$ 2750 distillation unit and analyzed for Me^{198}Hg and Me^{199}Hg using a Tekran$^{©}$ model 2700 MeHg analyzer coupled with an Elan DRC-e ICP-MS (PerkinElmer Sciex). Me^{201}Hg was added to samples as a species-specific internal standard prior to distillation to correct for procedural recoveries. The instrument method detection limit (MDL) for MeHg was calculated as the average concentration of six method blanks added to three times the standard deviation of ten replicates of a low-level standard.[108] This low level standard was prepared to have a concentration of 3-5X higher than that of the MDL and resulted in a MDL of 0.01 ng/L using ~45 mL of sample. All samples were run in duplicate and were within 10% of each other.

To determine if acidification to 0.2% v/v with HCl resulted in any instantaneous Hg(II) methylation, MeHg analyses were carried out on acidified and non-acidified snow samples from our four focus sites within 6 hours of melting. Non-acidified samples were analyzed with additional distillation reagent (500-1000 µL) to compensate for the lack of HCl preservation and to ensure that ionic strength was high enough during the distillation procedure.

Rate constants for demethylation, the decline of RHg, and methylation were calculated as in Lehnherr et al.[109] (see SI for details).

pMeHg concentrations. Quartz fiber filters (AQFA 47 mm, 2.5 µm nominal pore size) were muffled overnight at 550°C, placed in an acid washed petri dish, and weighed to ± 0.1 mg. A known volume of melted snow was then filtered using an acid-washed Teflon filter tower, after which the filters were freeze-dried and immediately reweighed in the original petri dishes. The petri dishes were stored frozen in precleaned glass jars until analysis. Filters were distilled and analyzed for MeHg at the BASL as described above for the incubation samples, except that 11.7 ng/L of ^{198}Hg(II) was added to each still to quantify any analytical methylation artefacts by quantifying residual Me^{198}Hg formed[110-114]. This testing revealed virtually no Me^{198}Hg was produced (0.003±0.002 pg) during this step. MeHg recovery from certified reference material SQC1238 sediments analyzed alongside samples was within 5% of certified values.

Concentrations of MeHg and THg in petcoke. 0.1-0.2 g of petcoke, sourced from or nearby three different oil sands facilities (CNRL, Syncrude, and railroad near Anzac), were distilled and analyzed for MeHg as described above for pMeHg. All samples were run in duplicate and were within 10% of each other. Concentrations of THg in petcoke were determined using a Milestone DMA-80 direct Hg analyzer at the BASL. MeHg and THg recoveries from certified reference materials SQC1238 and MESS-3 (marine sediment), respectively, analyzed alongside samples were within the range of certified values.

Particle size distribution. Melted snow was analyzed at the Ariya Atmospheric and Interfacial Chemistry Laboratories at McGill University for particle size distribution as a function of hydrodynamic diameter. These analyses were completed by Nanoparticle Tracking Analysis (NTA) using a Malvern NanoSight NS500 with a laser wavelength of 532 nm and an Electron Multiplying Charge Coupled Device (EMCCD) camera.

3.3 RESULTS AND DISCUSSION

3.3.1 Concentrations and loadings of THg, MeHg, general chemistry and multi-elements in snowpacks

Here we discuss results at the four focus sites, although concentrations and loadings of measured parameters at the 23 sites are listed in Tables A1 and A2.

Concentrations of unfiltered and filtered THg ranged between ~0.79-9.01 and 0.32-0.60 ng/L, respectively, at the four focus sites, with highest concentrations measured at the 7 km site and lowest at the 134 km site (Table 3.1). Similarly, unfiltered MeHg concentrations were also highest at the 7 km site (0.28 ng/L) and lowest at the 134 km site (0.02 ng/L), while concentrations of filtered MeHg were below the MDL at all sites except the 7 km site (0.03 ng/L) (Table 3.1). THg and MeHg loadings followed similar patterns as concentrations, with loadings of unfiltered and filtered THg ranging between 50.4-644 and 20.3-42.7 ng/m^2, respectively, and unfiltered MeHg loadings ranging between 1.46-20.2 ng/m^2 (Table 3.1; 3.2).

The chemical and multi-element characterization of snowpacks demonstrated that the 0 and 7 km sites were most impacted by anthropogenic atmospheric deposition. At the 0 km site, concentrations and loadings of V, Mo, K, Chl a, TOC, POC, and several forms of nitrogen (PON, TDN, TN, NO_3, NO_2, and NH_3; Table 3.1, Table A1 and A2) were highest. When all 23 sites were included, the loadings of these parameters also decreased exponentially (R^2 = 0.23-0.97, $p < 0.05$) with distance from the upgraders, suggesting that the upgrading facilities and other developments located adjacent to the 0 km site may be their source. In fact, both nitrogenous species and V are emitted in large quantities from upgrading facilities.[115-117] The 0 km site was also located nearby to large exposed petcoke piles, which may explain the elevated POC deposition at this site. At the 7 km site, concentrations and loadings of ~90% of the 35 elements examined, including all 13 PPEs,[105] were highest, suggesting that this site is influenced by slightly different sources than the 0 km site. Due to high concentrations of a complex mixture of chemicals at the 7 km site, potential Hg interaction effects may exist, such as effects on Hg cycling in snowpacks (see below).

While each of the four focus sites showed unique chemical and multi-element profiles, the predominant elements at all sites were crustal (Al, Fe, Ca, Na, K, and Mg), indicative of lithogenic sources originating from the underlying McMurray formation, which is composed primarily of quartzitic sandstone.[118]

Normalization of trace elements concentrations to Al concentrations has been used to examine inputs of lithogenic material in various environmental archives[119-121] and was recently used to examine changes in sources of trace elements to the AOSR.[122] The crustal ratio of Hg:Al is ~1:163000,[123] which is similar to the Hg:Al ratios found at sites 0 and 134 km (1:200000). The 7 and 25 km sites exhibited Hg:Al ratios of 370X and 37X higher than the average crustal composition, clearly demonstrating non-lithogenic Hg inputs at these two sites. It is important to note that Al concentrations are elevated at the 0, 7, and 25 km sites, which may potentially affect the exact ratio, though the conclusion still remains viable.

3.3.2 Net Hg(II) methylation in snowpacks and melted snow

Demethylation: Concentrations of added $Me^{199}Hg$ decreased significantly over time in snowpack cores from all four sites (R^2 = 0.68-0.91, p ≤0.05) (Figure 3.2a). k_d was highest at the 134 km site (0.42/d) followed by the 7 km (0.23/d), 25 km (0.14/d), and 0 km (0.07/d) sites (Table A3). In contrast to demethylation in the snowpacks, concentrations of added $Me^{199}Hg$ did not change significantly over time in melted snow, and k_ds were <MDL of 0.003/d at all four sites examined (Table A3, Figure 3.2b). These results suggest that demethylation in the absence of UV radiation occurs preferentially within snowpacks rather than in the snowmelt phase.

k_ds measured here were higher than those measured in a freshwater lake at the Experimental Lakes Area (ELA; NW Ontario) under dark conditions (~5.36×10^{-3}/d), but comparable to those measured under light conditions (~0.17/d).[124] k_ds under dark conditions in Canadian Arctic (0.28–0.42/d)[109] and Mediterranean (0.06/d)[125] seawaters were comparable to those reported here for snowpacks.

Demethylation occurring in snowpacks in the absence of UV radiation was most likely the result of a microbial process, as has been observed in lake and seawaters, as well as sediments.[126-129] For example, Monperrus et al.[125] concluded that certain microorganisms associated with particulate matter were likely responsible for demethylation in the absence of UV radiation in seawater. Previous investigations have shown that such microorganisms in water and sediments possess the *mer*B gene which encodes for the enzyme organomercurial-lyase and cleaves MeHg, forming methane and Hg(II).[127, 130, 131] To date, mechanisms for snowpack demethylation in the absence of UV radiation have not been examined, thus no direct comparison can be made. The lack of demethylation in melted snow samples suggest that conditions such as temperature and redox potential change,[132-134] potentially rendering the environment less conducive to demethylating microbial communities.

RHg: Concentrations of added inorganic ^{198}Hg(II) available for methylation in melted snow samples decreased exponentially over time at all four focus sites ($R^2 = 0.99$, $p < 0.0001$; Figure 3.3). However, the loss of R^{198}Hg(II) was considerably slower in melted snow from the 7 km site than at all other sites. More specifically, in melted snow from the 0, 25, and 134 km sites, ~85% of the added ^{198}Hg(II) was no longer reactive within two hours, whereas it took nearly 24 hours for the same decrease in reactivity to occur in melted snow from the 7 km site. The slower loss of R^{198}Hg(II) at the 7 km site could be attributed to elevated concentrations of Fe, and potentially reduced S, at that site, both of which would preferentially bind to each other, thus leaving Hg unbound. Fe concentrations at the 7 km site (4720 mg/L) were approximately 3, 9, and 57 times higher than at sites 25 km, 0 km, and 134 km, respectively, though reduced S was not measured. Additionally, the complex mixture of chemicals at the 7 km site could affect availability of RHg substrate for methylation. In comparable experiments with Arctic seawater, ~78% of added ^{198}Hg(II) spike was lost after 24 hours,[109] which was similar to the timeframe observed at the 7 km site.

Methylation: Less than 1% of the newly added ^{198}Hg(II) in both snowpacks and melted snow was instantaneously methylated, as observed in the T=0 samples at all four sites (Table A4). Lehnherr et al.[109] also observed instantaneous methylation in Arctic seawater and Ramamoorthy et al.[135] suggested that availability of methyl group donors and methylation of Hg(II) by dead bacterial cells may influence instantaneous methylation. It has also been suggested that instantaneous methylation could result from sample preservation by acidification.[136,137] All snowpack and melted snow samples were acidified to 0.2% v/v with TMG HCl to stop methylation and demethylation at the end of each incubation period. No significant differences were found in MeHg concentrations between samples that were either acidified or not prior to distillation (*paired t-test*, $t = 0.07$, $p = 0.94$, $n = 24$), suggesting acidification did not cause instantaneous methylation.

Snowpack methylation was detectable but low at all four sites, with a rate constant (k_m) ranging from 0.001-0.004/d (Table A3, Figure 3.2c). There was no relationship between snowpack k_m and distance from the AOSR upgraders. In melted snow, however, methylation was non-detectable at three sites and just over the MDL at the 7 km site (0.007/d; Table A3, Figure 3.2d). The k_m obtained in AOSR snowpacks were over an order of magnitude lower than in freshwater systems such as oligotrophic (0.071/d) and eutrophic (0.087/d) boreal lakes at the ELA,[84] as well as in Mediterranean seawater (0.02-0.038/d),[125] but similar to rates in Arctic seawaters (0.007/d).[109]

The rate constants obtained here provide a measure of the potential for methylation and demethylation in snowpacks, rather than absolute rates, but are useful for quantifying the relative importance of both processes. By comparing the product of $k_\mathrm{m} \times$ [Hg(II)] (i.e., methylation rate) and $k_\mathrm{d} \times$ [MeHg] (i.e., demethylation rate) at each of our four focus sites, we estimate that the methylation to demethylation ratio (M:D) in AOSR snowpacks varied between 0.3-1.5. Those values were calculated using dissolved Hg(II) and MeHg concentrations (if <MDL, assigned half MDL of 0.008 ng/L) measured in snowpacks, as dissolved Hg species are likely more (bio)available for methylation and demethylation. Using unfiltered Hg(II) and MeHg concentrations instead, to acknowledge that these processes could also be associated with particulate matter, resulted in M:D values ranging between 0.3 and 1.[138] In both cases, the lowest M:D ratio was observed at the 134 km site, with the greatest M:D observed at the 7 km and 25 km sites, where snowpack Hg(II) concentrations were also highest. This suggests that snowpacks can be net sources of MeHg (i.e., when M:D >1), particularly where Hg deposition is elevated, but that in most cases methylation and demethylation seem to be in balance, and therefore snowpack methylation is likely not the primary source of MeHg to snowpacks near and far from the AOSR.

3.3.3 pMeHg and total snowpack MeHg loadings

As previously suggested, most of the MeHg in snowpacks is on the particles themselves.[39] Although unfiltered MeHg loads in snowpacks exponentially decreased with distance ($R^2 = 0.09$, $p = 0.16$; $R^2 = 0.21$, $p = 0.003$; Figure 3.4d), filtered MeHg loads remained fairly constant or below MDL across the 134 km sampling range. pMeHg concentrations ranged from 0.53-6.85 ng/g in the 23 snowpacks sampled within 0-134 km of the major AOSR upgraders. Surprisingly, pMeHg concentrations increased linearly with distance from those upgraders ($R^2 = 0.71$, $p < 0.0001$; Figure 3.4a). However, MeHg loadings in snowpacks due solely to pMeHg decreased exponentially over this same distance ($R^2 = 0.56$ $p < 0.0001$; Figure 3.4c) as a result of snowpacks close to the AOSR upgraders having high particle loadings ($R^2 = 0.49$, $p = 0.0002$, Figure 3.4b). Hence, at 134 km away from the major AOSR upgraders, despite pMeHg concentrations being their highest, total MeHg loadings in snowpacks were low due to low particle loadings (Figure 3.4). Therefore, the major upgraders of the AOSR are a source of particles; however, these particles are less rich in MeHg than those deposited further away.

Others have suggested that fugitive petcoke dust may be an important source of PAC contaminant deposition to the AOSR,[57] and thus could be considered as a potential source of pMeHg. Therefore, to further explore origins of pMeHg to snowpacks of the AOSR, we analyzed petcoke, collected as in Zhang et al.,[57] sourced from or nearby three different oil sands facilities (CNRL, Syncrude, and railroad near Anzac) for concentrations of MeHg, as well as THg. Petcoke MeHg concentrations were very low (0.02 ± 0.01 ng/g) compared to snowpack pMeHg concentrations (2.47 ± 0.56 ng/g), suggesting that petcoke dust is not an important source of pMeHg to the AOSR. Concentrations of THg in petcoke were also quite low; with the most elevated concentrations found in samples form CNRL (2.32 ng/g) followed by samples from ANZAC (0.75 ng/g) and Syncrude (0.65 ng/g).

The majority of observed snowpack particles were nano-sized (<1 micron), with the highest density found in the 200-600 nm size range (1.25×10^7 particles/L). The 7 km site had the highest concentration of particles ≥400 nm (3.31×10^6 particles/L), while the 0 km site had the highest concentration of particles <400 nm (6.68×10^6 particles/L) and the most particles overall (8.96×10^8 particles/L) (Figure A2). The variation in particle size distribution among sites suggests that there are numerous different sources within a fairly small spatial scale (<25 km). This is supported by the distinctions in chemical and multi-elemental profiles in the snowpacks. For example, the composition of snow from the 0 km site exhibited elevated concentrations of V, La, and nitrogenous species, consistent with nearby upgrading facilities as the source of those species, whereas the chemical profile of the 7 km site suggests lithogenic sources from mining activities with distinctively elevated concentrations of Al (Table 3.1). Due to such immense variation in particle size, with a great deal of overlap in particle size distributions between sites, it is not clear where the pMeHg is originating.

Net methylation within snowpacks of the AOSR was low but detectable; suggesting that *in situ* production of MeHg is possible under certain conditions. However, the majority of the MeHg in snowpacks is associated with the particles themselves. Further characterization of snowpack particles, including examination of structure and compositional material, could provide insight on the origin of the particles within the AOSR snowpacks. This information would also be valuable for understanding the bioavailability of pMeHg in receiving aquatic ecosystems following melt.

3.4 TABLES & FIGURES

Table 3.1 Summary of water chemistry and multi-elemental concentrations and loadings at the four focus sites, varying in distance from AR6 (0 km), the most proximal site to the major upgraders, in the Alberta Oil Sands Region, Alberta, Canada. ND signifies non-detectable, while UF indicates unfiltered and F denotes filtered.

Parameter†		Concentrations					Loadings			
	Units	0 km	7 km	25 km	134 km	Units	0 km	7 km	25 km	134 km
THg (UF)	ng/L	2.85	9.01	5.69	0.79	ng/m^2	208	644	259	50.4
THg (F)	ng/L	0.35	0.60	0.49	0.32	ng/m^2	25.2	42.7	22.2	20.3
MeHg (UF)	ng/L	0.11	0.28	0.12	0.02	ng/m^2	8.19	20.2	5.37	1.46
MeHg (F)	ng/L	ND	0.03	ND	ND	ng/m^2	ND	1.8	ND	ND
TSS	mg/L	127	268	180	8.65	g/m^2	29.5	23.2	11.1	0.06
pH		7.65	7.53	7.12	7.07					
$CaCO_3$	mg/L	19.7	20.6	12.7	11.2	g/m^2	1.44	1.47	0.58	0.72
TOC	mg/L	29.2	7.17	4.49	2.25	g/m^2	2.13	0.51	0.20	0.14
PON	µg/L	590	93.0	56.0	17.0	mg/m^2	43.1	6.60	2.50	1.10
TDN	mg/L	0.43	0.31	0.40	0.21	mg/m^2	31.1	21.8	18.2	13.2
SO_4	mg/L	2.08	1.25	1.60	2.65	mg/m^2	152	89.0	73.0	170
Al	mg/L	0.18	1.57	0.89	0.04	g/m^2	13.4	112	40.5	2.87
Ca	mg/L	4.11	10.4	4.73	2.01	g/m^2	0.30	0.74	0.22	0.13
Fe	mg/L	0.51	4.72	1.98	0.08	mg/m^2	37.0	337	90.0	5.34
K	mg/L	5.67	0.26	0.18	0.12	mg/m^2	413	19.0	8.00	7.50
Mg	mg/L	0.22	0.48	0.19	0.74	mg/m^2	16.0	34.0	9.00	47.0
Na	mg/L	0.56	1.05	0.34	1.88	mg/m^2	41.0	74.5	15.0	120
Cl	mg/L	0.42	0.35	0.29	1.74	mg/m^2	31.0	25.0	73.0	170
V	µg/L	120	8.68	4.39	0.23	mg/m^2	8.76	0.62	0.20	0.01

† See Tables S1 and S2 for water chemistry and multi-elemental concentrations and loadings at all 23 sites.

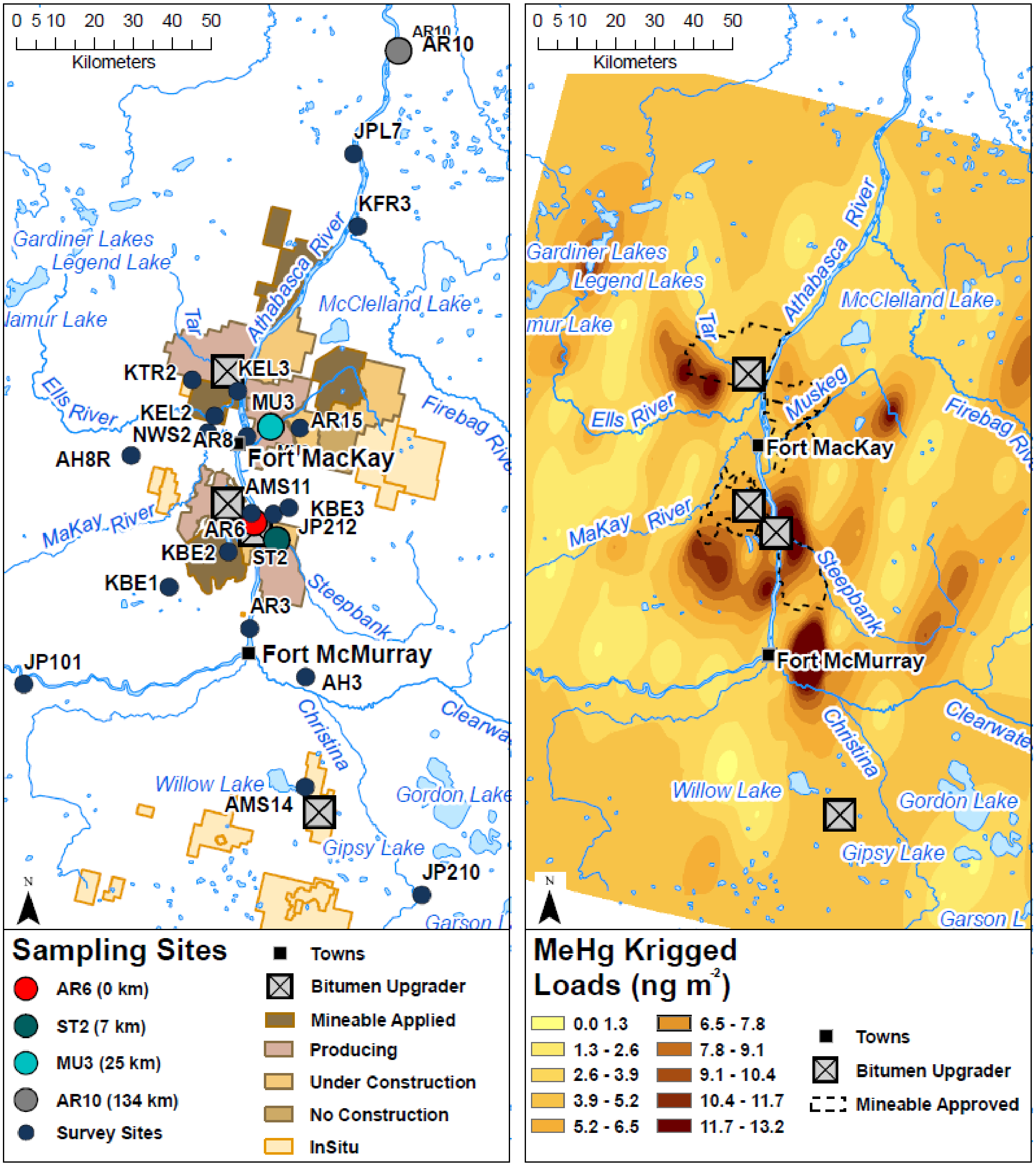

Figure 3.1 23 sampling sites, including four focus site used for *in-situ* net methylation experiments (left) and 2015 snowpack MeHg loadings (right) in the Alberta Oil Sands Region, Alberta, Canada. Interpolation of MeHg loads was produced using ArcGIS Geostatistical Analyst software as in Kirk et al.[1]

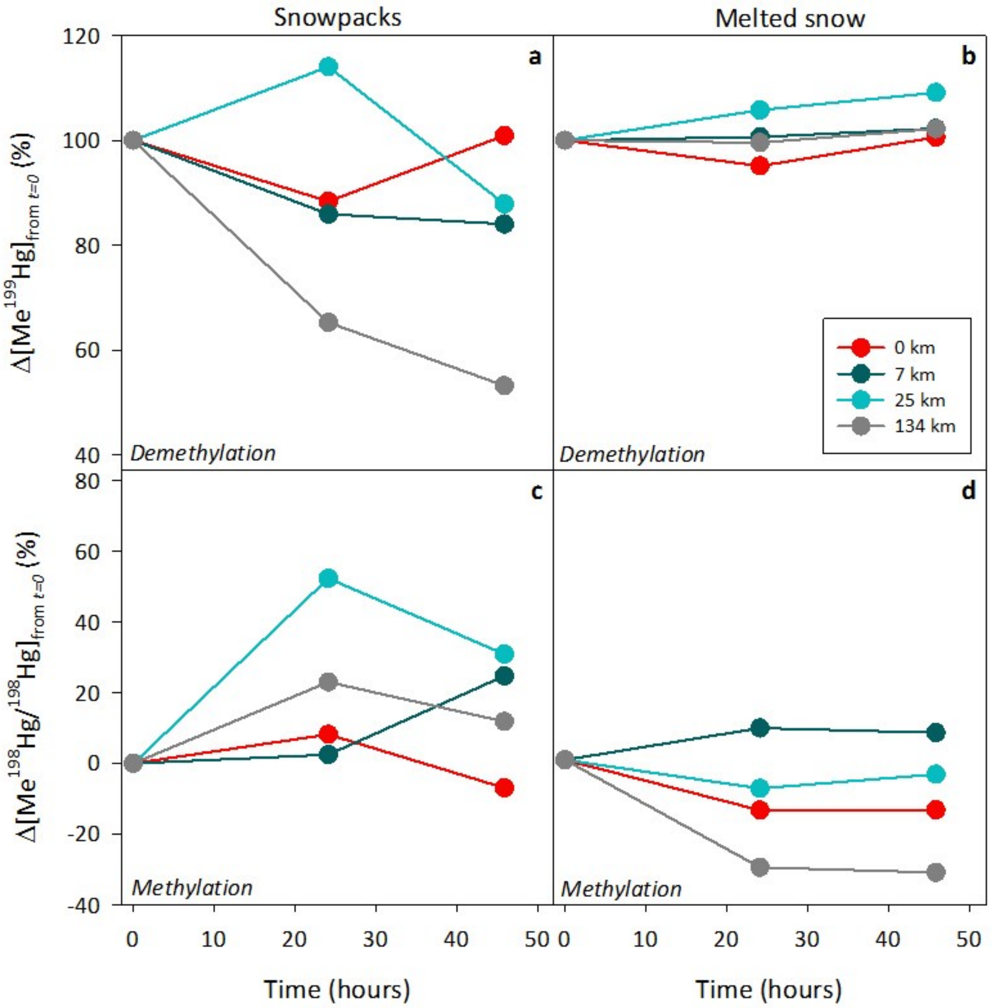

Figure 3.2 Loss of $\mathrm{Me}^{199}\mathrm{Hg}$ in the dark in snowpacks (a) and melted snow (b), shown as the percent of spike remaining from the initial concentration of $\mathrm{Me}^{199}\mathrm{Hg}$ measured at time zero. Net production of $\mathrm{Me}^{198}\mathrm{Hg}$ in snowpacks (c) and in melted snow (d), shown as the percent of spike remaining from the initial concentration of $\mathrm{Me}^{198}\mathrm{Hg}$ produced instantaneously at time zero. Each data point is the mean of two replicates, each of which were analyzed in duplicate. Error bars showing standard deviation among analytical replicates are too small to be visible.

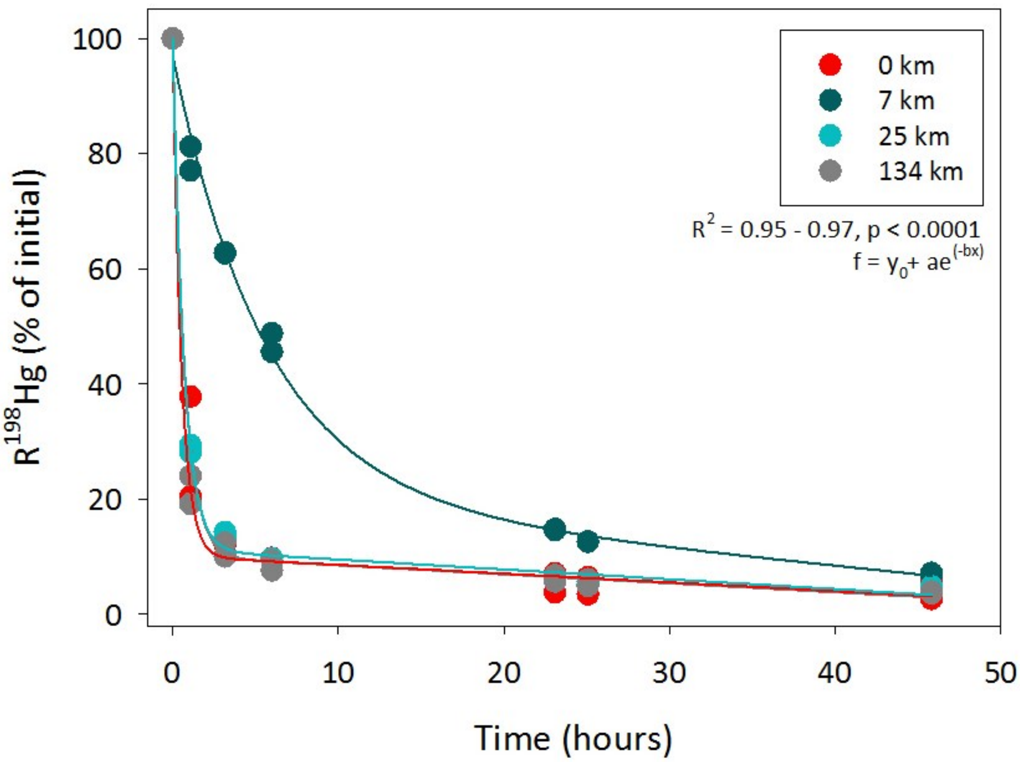

Figure 3.3 Percent of ^{198}Hg(II) available for methylation (R^{198}Hg) in melted snow at the four focus sites, measured in duplicate over a 48-hour period.

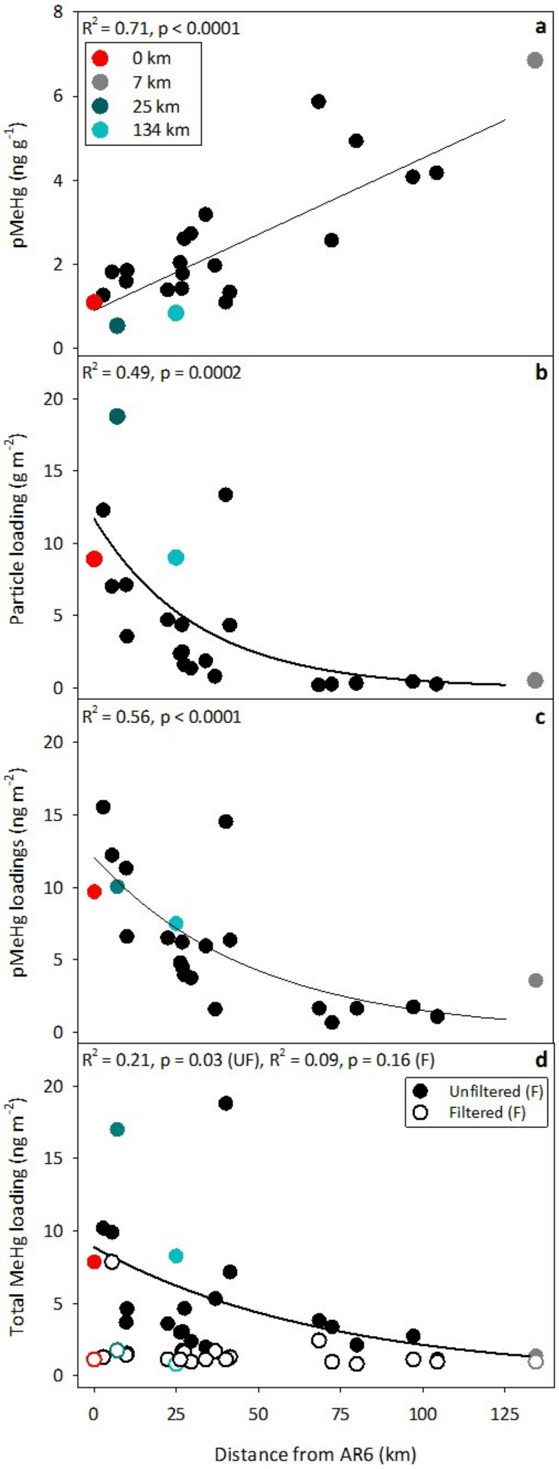

Figure 3.4 Concentrations of methylmercury on particles (pMeHg) (a), particle loadings (b), pMeHg loadings (c), and unfiltered and filtered MeHg loadings (d) in snowpacks in relation to distance from AR6 (0 km), the most proximal site to the major upgraders, in the Alberta Oil Sands Region, Alberta, Canada. Some filtered MeHg concentrations were <MDL of 0.016 ng/m^2 and therefore assigned as half of the MDL (0.008 ng/m^2) prior to calculating loadings.

4 Conclusions

4.1 Research conclusions

The primary purpose of the studies herein was to provide insight on sources of mercury (Hg) and methylmercury (MeHg; a neurotoxin that biomagnifies through foodwebs) in the Alberta Oil Sands Region (AOSR) of Alberta, Canada.

In Chapter Two we present our research findings on concentrations of total mercury (THg; all forms of Hg in a sample) and MeHg, as well as trace elements and various water chemistry parameters, within four oil sands tailings ponds (OSTPs) in the AOSR. These ponds have been previously shown to contain numerous contaminants, such as polycyclic aromatic hydrocarbons and naphthenic acids. However, despite elevated concentrations of both total mercury (THg; all forms of Hg in a sample) and MeHg in river waters downstream of the AOSR developments, and high loadings of THg and MeHg in snowpacks near the developments, to date there are no studies of Hg in the OSTPs themselves. Parameters for which concentrations in tailings ponds exceeded guidelines for the protection of aquatic life in water included aluminum, arsenic, boron, cadmium, molybdenum, ammonia, selenium, and zinc, while only copper exceeded sediment probable effects level guidelines in the mature fine tailings.[83] Concentrations of SO_4, Na, and Cl, used in bitumen processing, were also elevated in tailings ponds compared with those in nearby freshwaters. Surface water concentrations of THg (unfiltered 0.16-0.50 ng/L; filtered 0.15-0.57 ng/L) and MeHg (unfiltered <0.02-1.92 ng/L; filtered <0.02-0.32 ng/L) were low in all ponds, with highest concentrations observed in the oldest pond, Mildred Lake Settling Basin at Syncrude Canada Ltd. In the mature fine tailings that settle out in the ponds, concentrations of THg (37.0-197 ng/g) and MeHg (0.10-0.52 ng/g) were also low, with highest concentrations also observed at Mildred Lake. Overall, these ponds are likely not a major source of Hg of MeHg to downstream freshwater ecosystems into which they leak; though they may be potential sources for chemical parameters including those exceeded the CCME guidelines for the protection of aquatic life.

In Chapter Three we examine sources of MeHg to snowpacks in the AOSR. Snowpacks in the AOSR have been previously shown to contain elevated loadings of MeHg.[39] At sites ranging from 0-134 km from the major AOSR upgrading facilities, we examined sources of MeHg by quantifying potential rates of MeHg production in snowpacks and melted snow using Hg stable isotope tracer experiments, as well as quantifying concentrations of MeHg on particles in snowpacks (pMeHg). At four sites, methylation rate constants were low in snowpacks (k_m=0.001–0.004 d^{-1}) and non-detectable in melted snow, except at one site (k_m=0.0007 d^{-1}). The estimated ratio of methylation to demethylation varied between 0.3-1.5, suggesting that the two processes are in balance and that *in situ* production is unlikely an important source of MeHg to AOSR snowpacks. pMeHg concentrations increased linearly with distance from the upgraders (R^2=0.71, p <0.0001), however, snowpack total particle and pMeHg loadings decreased exponentially over this same distance (R^2=0.49, p=0.0002; R^2=0.56, p <0.0001). Thus, at near-field sites, total MeHg loadings in snowpacks were high due to high particle loadings, even though particles originating from industrial activities are not MeHg rich compared to those originating from natural sources at distant sites. More research is required to identify snowpack particle sources.

4.2 Suggested future research directions

Several aspects of the OSTP sampling could have been improved. For example, *in situ* microbial production of MeHg is known to fluctuate based on temperature/season;[43, 84, 139] therefore, it would be ideal to sample the ponds periodically throughout the year. Although no thermal stratification was detected at the time we sampled the OSTPs, looking at temperature and dissolved oxygen (DO) profiles throughout the year would clarify whether or not stratification occurs seasonally. Unfortunately, the viscous residual bitumen adhered to the dissolved oxygen probe on our YSI 6-series sonde causing it to malfunction, so a new technique should be used to measure this parameter in the future. This data would be useful when examining net Hg(II) methylation potential within the OSTPs since microbial Hg(II) methylation is thought to occur primarily in anaerobic conditions and often peaks at oxic-anoxic interfaces in water columns. [43, 84, 140] Moreover, expanding to other ponds with focus on older ponds, as well as increasing the number of depth profiles, and number of depths sampled, on each pond would enhance our understanding of physical and chemical variation throughout the ponds. We would also recommend further research at MLSB to provide insight as to why that pond had elevated MeHg concentrations in the water column when compared to the three other ponds examined. For example, it would be interesting to now conduct Hg(II) methylation and MeHg demethylation experiments using Hg stable isotopes on OSTP water and sediments to determine which sites are most important for net MeHg production.

I would suggest new research directions to further understand atmospheric sources of MeHg and THg to AOSR snowpacks. For example, because MeHg in AOSR snowpacks is primarily particulate-bound,[39] future research should focus on determining the source(s) of the particles to ultimately help determine the source of the MeHg itself, including in distant regions where particles contain the highest concentrations of MeHg. Some such potential sources may include fugitive dusts from open-pit mines, landscape disturbance, haul roads, and tailings sand, as well as particle emissions from upgrader stacks. To examine spatial and temporal trends in Hg deposition dated lake sediment cores from hydrologically simple lakes could be taken from varying distances from the major developments. Using this technique, Kurek et al. examined trends in polycyclic aromatic carbon (PACs) deposition, which led to the conclusion that PAC deposition has increased significantly since the 1960s, when the AOSR developments began.[28] I would also recommend sampling dry deposition of MeHg and THg loadings in litterfall and throughfall under forest canopies because forest canopies are known to scavenge Hg from the atmosphere.[141] Sampling of MeHg and THg dry deposition would also give us a more comprehensive measure of regional Hg loadings in the AOSR.

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Appendix I

Supplementary Information for "Sources of methylmercury to snowpacks of the Alberta Oil Sands Region: A study of in situ methylation and particulates"

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Supplementary Information

Included in the Supplementary Information are additional methodological details, four tables, and one figure.

Additional Methodological Details

Concentrations and loadings of THg, MeHg, general chemistry and multi-elements in snowpacks: Chemical parameters examined for all 23 snow sites included total nitrogen (TN), total dissolved nitrogen (TDN), particulate organic nitrogen (PON), nitrate and nitrite ($NO_{3,}$ NO_2), ammonia (NH_3), total phosphorus (TP), total organic carbon (TOC), particulate organic carbon (POC), chlorophyll a (Chla), chloride and sulphate (SO_4), alkalinity ($CaCO_3$), silicon dioxide (SiO_2), conductivity and pH, as well as 45 elements including numerous crustal and rare earth elements and the 13 metals considered priority pollutants elements (PPEs) under the US EPA Clean Water Act.[81]

Melted snow was analyzed for total Hg (THg) concentrations by BrCl oxidation, $SnCl_2$ reduction, dual gold trap amalgamation, and detection by cold vapor atomic fluorescence spectrophotometry (CVAFS)[107] using a Tekran© model 2500 Hg analyzer. Methylmercury (MeHg) in melted snow was analyzed by distillation, aqueous phase ethylation, and detection by CVFAS[142, 143] using a Brooks Rand MERX automated MeHg analyzer. For THg and MeHg analyses, the method detection limits (MDLs), calculated as three times the standard deviation of the blanks, were 0.03 and 0.015 ng/L, respectively, using ~ 40 mL of sample. Samples where MeHg concentrations were <MDL were assigned concentrations of 0.015 ng/L for statistical purposes. All THg samples and 20% of MeHg samples were analyzed in duplicate and were within 10% of each other with spike recoveries > 90% for both analyses.

SWE: To determine average aerial water volume, also known as snow-water equivalence (SWE), 8 – 10 cores were collected at each site using the 10 cm ID stainless steel corer. The weight and

ID radius of each core was then used in Equation [1] to calculate SWE, assuming 1 L of water weighs 1 kg.

$$SWE\left(\frac{kg}{m^2}\right) = \frac{snow\ core\ weight\ (kg)}{\pi[corer\ radius\ (m)]^2} \qquad [1]$$

SWE (kg/m^2) were then multiplied by parameter concentrations to determine areal loadings at each site.

Potential rates of Hg methylation in snowpacks and melted snow. Rate constants for demethylation (k_d), the decline of reactive mercury (RHg), and methylation were calculated as in Lehnherr et al.[109] Briefly, k_d, the rate constant of MeHg demethylation was calculated from the slope of the characteristic first-order decay kinetic plot for the Me^{199}Hg concentration time-series (Ln(Me^{199}Hg)$_t$ versus time):

$$\mathrm{Ln}(\mathrm{Me}^{199}\mathrm{Hg})_t = \mathrm{Ln}(\mathrm{Me}^{199}\mathrm{Hg})_0 - k_\mathrm{d} \times t \qquad [2]$$

k_m, the rate constant of ^{198}Hg(II) methylation, was obtained from the Me^{198}Hg concentration time-series data. The net rate of Me^{198}Hg production is the sum of inorganic mercury (^{198}Hg(II)) methylation and Me^{199}Hg demethylation, which can be expressed by the following differential equation:

$$\mathrm{d}[\mathrm{Me}^{198}\mathrm{Hg}]/\mathrm{d}t = k_{\mathrm{m}}[^{198}\mathrm{HgII})] - k_{\mathrm{d}}[\mathrm{Me}^{198}\mathrm{Hg}] \quad [3]$$

Concentrations of ^{198}Hg(II) available for methylation (i.e., R^{198}Hg) during the incubations decreased exponentially over time (Figure 3.2), suggesting that we cannot assume Hg(II) concentration to be constant when solving equation [3], even though only a small proportion of the added ^{198}Hg(II) is converted to Me^{198}Hg. Furthermore, because we cannot assume that equation [3] has a y-intercept of zero (i.e., Me^{198}Hg was detected in T=0 samples due to instantaneous methylation), equation [3] was solved by integration, with respect to time (*t*), to obtain equation [3b].

$$\mathrm{Me}^{198}\mathrm{Hg}(t) - \mathrm{Me}^{198}\mathrm{Hg}_0 = k_{\mathrm{m}} \int_0^t {}^{198}\mathrm{Hg(II)}(s)\mathrm{d}s - k_{\mathrm{d}} \int_0^t \mathrm{Me}^{198}\mathrm{Hg}(s)\mathrm{d}s \quad [3b]$$

Where *s* denotes time in the function describing the declining concentration of R^{198}Hg(II), which has the form $^{198}\mathrm{Hg(II)}(s)\mathrm{d}s = y_0 + a exp(-bs)$

The first integral term in equation [3b] then becomes $\int_0^t \mathrm{Hg(II)}(s)\mathrm{d}s = y_0 t + a/b)(1 - \exp(-bt))$, and from the Me^{198}Hg time-series we can evaluate the second integral term $\int_0^t \mathrm{Me}^{198}\mathrm{Hg}(s)\mathrm{d}s = S(t)$, as sums using the midpoint rule, such that

$$S(0) = 0,\ \ S(\Delta \mathrm{t}) = \frac{\mathrm{MeHg}_0 + \mathrm{MeHg}_1}{2}\Delta t, \ldots,$$

$$S(n\Delta t) = S\big((n-1)\Delta t\big) + \frac{\mathrm{MeHg}_{n-1} + \mathrm{MeHg}_{n}}{2}\Delta$$

k_m was then evaluated using a multiple-linear-regression model by inputting the integral terms as independent variables and constraining the model using the k_d value.

Method detection limit (MDL) calculations. The quantity of enriched stable-isotope spikes added to incubation samples were established based on a MDL calculated using prior knowledge of snow MeHg concentrations in the Alberta Oil Sands Region (AOSR) and estimations based on methylation and demethylation rates found in sediments, seawater, and lake water. The MDL for ^{198}Hg(II) methylation (Eq. [4]) and Me^{199}Hg demethylation (Eq. [5]) were calculated based on the following equations from Hintelmann et al.:[112]

$$\mathrm{c}_{new} \geq \mathrm{bg} \times \mathrm{A} \times 3\mathrm{RSD} \qquad [4]$$

where:

c_{new}= concentration of newly generated methylated species from spike

bg = background concentration of species of interest

A = natural abundance of tracer isotope, and

RSD = relative standard deviation of isotope ratio (i.e., tracer isotope/reference isotope).

Using equation [3], we determined that the lowest concentration of Me^{198}Hg(II) produced from methylation of the added of ^{198}Hg(II) spike that could be detected was 0.0025 ng/L.

$$\Delta \geq (\mathrm{A} + \mathrm{y}) \times \mathrm{bg} \times 3\mathrm{RSD} \qquad [5]$$

where:

Δ = decrease in concentration of added spike,

y = spike addition in multiples of background species concentration,

Therefore, the smallest concentration decrease in Me^{199}Hg due to demethylation that could be detected was 0.0034 ng/L.

Table A1 Summary of chemical and multi-element concentrations at 23 sites, varying in distances from AR6, the most proximal site (<1 km) to the major upgraders in the Alberta Oil Sands Region, Alberta, Canada. ND signifies below detection.

Parameter†	Units	AR6	AMS11	JP 212	ST2	KBE3	KBE2	AR8	MU3	NW-S2	AR3	AR15	KBE1	KEL2	KEL3	AH8-R	KTR2	AH 3	AMS14	JP 101	KFR3	JPL7	JP 210	AR10
		0 km	3 km	5 km	7 km	10 km	10 km	22 km	25 km	26 km	26 km	27 km	28 km	29 km	34 km	37 km	40 km	41 km	68 km	72 km	80 km	97 km	104 km	134 km
UF THg	ng/L	2.85	4.61	4.01	9.01	2.50	2.69	1.32	5.69	2.20	1.91	1.23	0.86	1.33	1.02	0.80	9.54	1.00	0.84	1.06	0.71	1.17	1.22	0.79
F THg	ng/L	0.35	0.52	0.55	0.60	0.70	0.40	0.31	0.49	0.37	0.35	0.26	0.27	0.46	0.29	0.34	0.25	0.18	0.45	0.27	0.19	0.38	0.27	0.32
UF MeHg	ng/L	0.11	0.13	0.11	0.28	0.05	0.05	0.06	0.12	0.04	0.03	0.04	0.06	0.04	0.04	0.09	0.27	0.09	0.08	0.06	0.03	0.04	0.02	0.02
F MeHg	ng/L	ND	ND	0.09	0.03	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	0.03	ND	ND	0.05	ND	ND	ND	ND	ND
TSS	g/L	127	154	78.2	268	79.2	44.7	67.3	180	33.9	43.7	35.8	16.1	22.8	26.7	13.5	191	54.3	3.93	4.32	6.64	6.18	4.39	8.65
pH		7.65	7.20	7.03	7.53	7.93	6.88	7.28	7.12	6.38	6.84	6.54	6.24	6.76	6.48	9.01	6.71	5.87	7.41	5.63	5.74	6.10	5.68	7.07
$CaCO_3$	mg/L	19.7	14.6	11.1	20.6	44.7	4.31	13.0	12.7	1.71	3.88	1.94	1.38	3.83	1.77	30.2	3.06	0.73	9.87	0.65	0.61	0.87	0.70	11.2
TOC	mg/L	29.2	4.00	2.83	7.17	3.51	3.18	4.02	4.49	2.85	1.81	2.24	1.84	3.29	3.19	5.18	3.23	2.72	5.31	1.52	0.85	2.40	2.72	2.25
PON	mg/L	0.59	0.07	0.04	0.09	0.06	0.04	0.03	0.06	0.04	0.02	0.01	0.03	0.04	0.05	0.05	0.03	0.03	0.06	0.02	0.01	0.03	0.03	0.02
TDN	mg/L	0.43	0.44	0.21	0.31	0.63	0.25	0.35	0.40	0.18	0.24	0.22	0.24	0.22	0.19	0.24	0.26	0.18	0.42	0.15	0.15	0.15	0.15	0.21
SO_4	mg/L	2.08	1.47	0.70	1.25	1.52	0.89	3.48	1.60	0.49	0.79	1.30	0.70	23.5	0.57	2.95	1.00	0.33	0.44	0.21	0.33	0.29	0.26	2.65
Al	mg/L	184	186	263	1570	1610	214	268	891	235	111	4.10	36.8	780	184	27.1	529	48.2	26.9	6.80	15.2	28.8	29.8	44.9
Ca	mg/L	4.11	2.62	2.88	10.4	15.7	2.35	3.15	4.73	0.75	1.75	0.87	0.49	5.04	0.90	7.58	0.85	0.34	2.29	0.22	0.21	0.19	0.18	2.01
Fe	mg/L	0.51	0.35	0.46	4.72	2.60	0.75	0.46	1.98	0.43	0.19	0.01	0.09	0.10	0.36	0.30	0.6	0.09	0.16	0.01	0.03	0.05	0.06	0.08
K	mg/L	5.67	2.91	0.10	0.26	0.62	0.11	0.22	0.18	0.10	0.07	0.09	0.25	0.36	0.06	0.24	0.13	0.05	0.37	0.04	0.03	0.04	0.12	0.12
Mg	mg/L	0.22	0.17	0.11	0.48	2.27	0.12	0.88	0.19	0.10	0.11	0.29	0.09	2.11	0.11	1.69	0.32	0.05	0.64	0.03	0.05	0.03	0.05	0.73
Na	mg/L	0.56	0.32	0.22	1.05	0.77	0.22	2.49	0.34	0.25	0.33	0.88	0.17	3.63	0.24	4.37	0.81	0.18	1.63	0.17	0.18	0.18	0.19	1.88
Cl	mg/L	0.42	0.31	0.20	0.35	0.46	0.20	2.19	0.29	0.22	0.38	1.11	0.16	0.29	0.23	0.51	0.25	0.16	2.01	0.13	0.16	0.17	0.18	1.74
V	µg/L	120	60.3	1.63	8.68	5.08	2.95	1.93	4.39	1.25	0.74	0.26	0.30	0.61	1.04	0.26	1.91	0.32	4.38	0.05	0.12	0.17	0.22	0.23

[†] Parameters measured but not shown here included H^+, Chl a, SRP, TP, F, SiO_2, As, B, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sn, Sr, Ti, U, W, Y, Zn.

Table A2 Summary of chemical and multi-element loadings at 23 sites located varying distances from AR6, the most proximal site (<1 km) to the major upgraders in the Alberta Oil Sands Region, Alberta, Canada. ND signifies below detection.

Parameter†	Units	AR6	AMS11	JP 212	ST2	KBE3	KBE2	AR8	MU3	NW-S2	AR3	AR15	KBE1	KEL2	KEL3	AH8-R	KTR2	AH 3	AMS14	JP 101	KFR3	JPL7	JP 210	AR10
		0 km	3 km	5 km	7 km	10 km	10 km	22 km	25 km	26 km	26 km	27 km	28 km	29 km	34 km	37 km	40 km	41 km	68 km	72 km	80 km	97 km	104 km	134 km
UF THg	ng/m^2	208	351	377	644	216	214	91.8	259	159	201	84.2	89.2	84.0	69.0	49.1	649	77.8	46.2	67.1	32.3	82.7	71.1	50.4
F THg	ng/m^2	25.2	39.6	52.1	42.7	60.7	32.0	21.6	22.2	26.6	36.6	17.7	27.8	29.2	19.7	21.0	17.1	14.5	24.7	17.4	8.60	27.1	15.8	20.3
UF MeHg	ng/m^2	8.19	9.68	10.3	20.2	4.56	4.08	4.18	5.37	3.09	2.63	2.97	5.99	2.51	2.68	5.42	18.3	7.00	4.15	3.58	1.38	2.75	1.10	1.46
F MeHg	ng/m^2	ND	ND	8.21	1.78	ND	1.50	ND	ND	ND	ND	ND	ND	ND	ND	1.73	ND	ND	2.66	ND	ND	ND	ND	ND
TSS	g/m^2	32.7	16.0	18.5	29.7	246	3.68	17.7	15.4	1.66	19.2	3.00	18.2	4.13	1.63	10.6	16.7	0.74	0.70	2.50	3.66	0.55	8.54	3.29
$CaCO_3$	g/m^2	1.44	1.11	1.04	1.47	3.87	0.34	0.91	0.58	0.12	0.41	0.13	0.14	0.24	0.12	1.84	0.21	0.06	0.54	0.04	0.03	0.06	0.04	0.72
TOC	g/m^2	2.13	0.30	0.27	0.51	0.30	0.25	0.28	0.20	0.21	0.19	0.15	0.19	0.21	0.22	0.32	0.22	0.21	0.29	0.10	0.04	0.17	0.16	0.14
PON	mg/m^2	43.1	5.02	4.14	6.64	4.85	3.41	2.37	2.55	3.11	1.78	0.96	3.31	2.21	3.59	3.11	1.70	2.66	3.28	1.02	0.55	2.40	1.92	1.09
TDN	mg/m^2	31.1	33.6	20.1	21.8	54.1	20.0	24.5	18.2	13.2	25.2	15.3	24.8	13.6	12.8	14.8	17.3	14.3	23.0	9.34	6.96	10.7	8.77	13.2
SO_4	mg/m^2	152	112	65.8	89.3	132	70.6	243	72.8	35.4	82.9	88.8	72.3	1490	38.7	180	68.0	25.8	24.1	13.3	15.1	20.4	15.1	170
Al	mg/m^2	13.4	14.2	24.7	112	139	17.0	18.7	40.5	17.0	11.6	0.28	3.80	4.93	12.5	1.65	36.0	3.77	1.47	0.43	0.70	2.03	1.73	2.87
Ca	mg/m^2	300	199	271	743	1360	187	220	215	54.4	184	59.1	50.9	319	61.0	463	57.9	26.4	125	13.7	9.52	13.3	10.4	129
Fe	mg/m^2	37.0	26.6	42.9	337	225	59.1	31.8	90.0	31.3	19.5	0.40	8.92	6.52	24.2	18.3	40.7	6.90	8.64	0.69	1.40	3.66	3.54	5.33
K	mg/m^2	414	221	9.63	18.7	53.4	8.89	15.2	8.00	7.23	7.39	6.38	26.3	23.1	3.83	14.8	9.08	3.60	20.3	2.67	1.56	2.99	7.00	7.39
Mg	mg/m^2	16.0	12.6	10.4	34.3	196	9.29	61.2	8.64	7.38	11.6	19.7	9.55	133	7.26	103	21.5	3.75	35.1	2.10	2.38	1.97	2.84	47.0
Na	mg/m^2	40.7	24.2	21.0	74.6	66.3	17.6	173	15.3	18.1	34.6	60.1	17.8	229	16.4	267	55.3	13.8	89.1	10.6	8.31	12.8	10.7	120
Cl	mg/m^2	30.7	23.6	18.8	25.0	39.8	15.9	153	13.2	15.9	39.9	75.8	16.5	18.3	15.6	31.1	17.0	12.5	110	8.30	7.30	12.0	10.5	111
V	mg/m^2	8.76	4.59	0.15	0.62	0.44	0.23	0.13	0.20	0.09	0.08	0.02	0.03	0.04	0.07	0.02	0.13	0.03	0.24	0.00	0.01	0.01	0.01	0.01

†Parameters measured, but not shown here because loadings at all sites were below 0.03 mg/m^2, included H^+, Chl a, SRP, TP, F, SiO_2, As, B, Ba, Be, Cd, Ce, Co, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sn, Sr, Ti, U, W, Y, Zn.

Table A3 Average rate constants of net Hg methylation (k_m) and demethylation (k_d) in snowpacks and melted snow at four focus sites in the Alberta Oil Sands Region, Alberta, Canada. ND signifies below detection.

Site (km)	**Snowpack** $\boldsymbol{k_d}$ (/d)	**Melted snow** $\boldsymbol{k_d}$ (/d)	**Snowpack** $\boldsymbol{k_m}$ (/d)	**Melted snow** $\boldsymbol{k_m}$ (/d)
0	0.07	ND	0.001	ND
7	0.23	ND	0.004	ND
25	0.14	ND	0.003	0.0007
134	0.42	ND	0.003	ND

Table A4 Percentage of ^{198}Hg(II) spike instantaneously methylated (T = 0) in snowpacks and in melted snow, as well as percentage of ambient THg that was methylated (unfiltered MeHg/ unfiltered THg * 100) in snowpacks from the four focus sites in the Alberta Oil Sands Region, Alberta, Canada.

Site (km)	**Snowpacks** **Spike methylated** (%)	**Melted snow** **Spike methylated** (%)	**Ambient %MeHg**
0	0.387	0.300	3.930
7	0.573	0.452	3.143
25	0.164	0.381	2.077
134	0.121	0.001	2.889

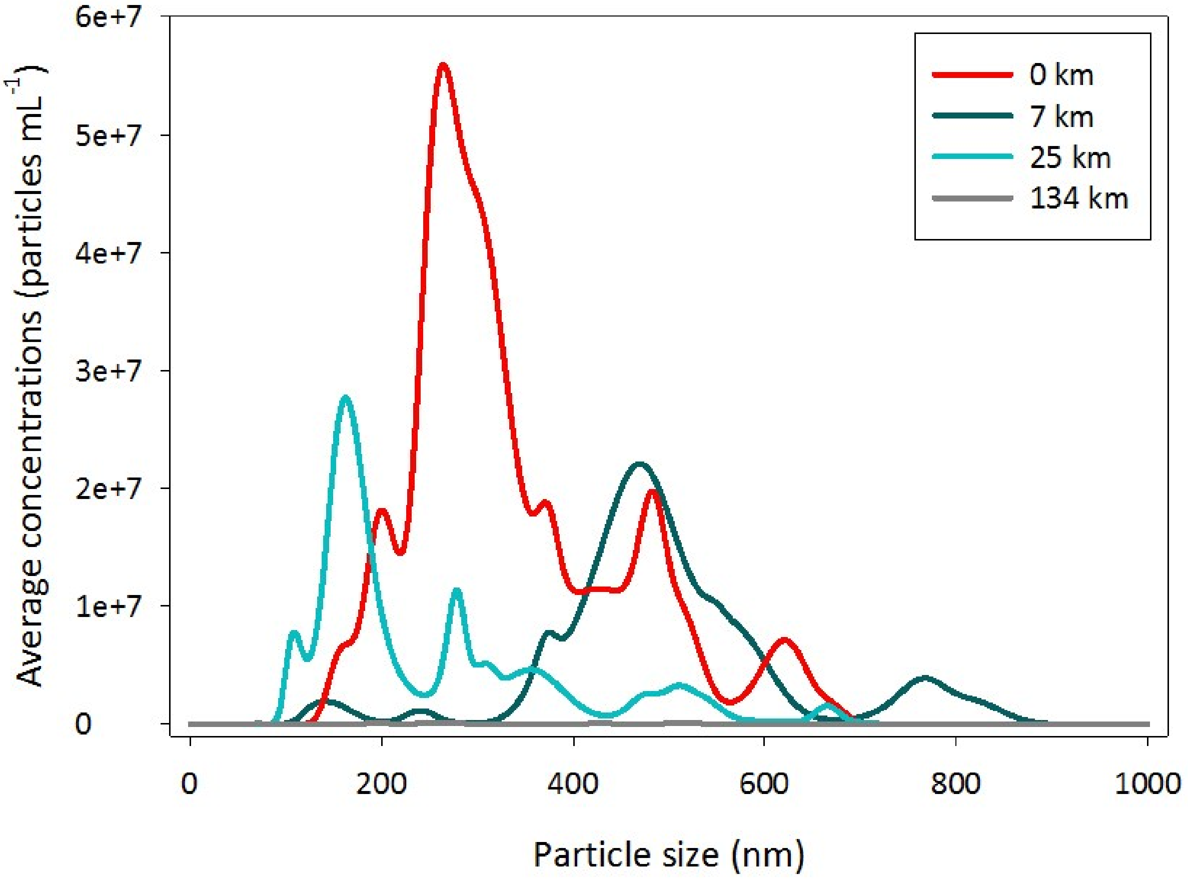

Figure A1 Size distribution (nm) of particles in surface snow collected from four sites located varying distances from AR6, the most proximal site (<1 km) to the major upgraders in the Alberta Oil Sands Region, Alberta, Canada.