University of Alberta

Mercury in the Lower Athabasca River and its Watershed

by

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Abstract

This study assessed the geographic distribution of mercury in water, and biota of the Athabasca River, and in snow and vegetation in its watershed. Mercury in the snowpack was significantly elevated within 46km of oil sands development relative to greater distances. Mercury was significantly higher in tributaries more disturbed by oil sands development relative to less disturbed watersheds. Mercury in vegetation was elevated near development, but was higher at moderate distances from development, likely due to differences in atmospheric speciation within upgrader plumes compared to speciation within the downwind atmosphere. Mercury concentrations were significantly higher in Walleye, Northern Pike, and Goldeye compared to Lake Whitefish. A large percentage (72-80%) of Northern Pike, Goldeye, and Walleye exceeded the Health Canada fish consumption guideline for frequent consumers. The spatial distribution of mercury within the Athabasca River and its watershed indicates oil sands development is a significant source of mercury within the region.

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"She insists that her narratives are rich, her supporting cast colourful, and her typeface bold." To all of my friends – I could not ask for a stronger, more amazing, or more colourful supporting cast. Thank you for providing me with rich narratives and for encouraging me to be bold, no matter what.

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Chapter 1: General Introduction

Large-scale resource extraction within the Athabasca oil sands area (OSA) began in the late 1960's and has expanded into the largest megaproject in the world. Much of this development has taken place in close proximity to the Athabasca River. As of 2008 (the year this study was conducted), 530 km^2 of land within Alberta's boreal forest was disturbed by oil sands mining operations and more than 130 km^2 of this area, approximately 25%, was covered by tailings ponds (Alberta Environment 2009). Bitumen production between 1995 and 2008 increased from 482,000 to 1.3 million barrels/day (ERCB 2009). Production rates are projected to more than double to 3.7 million barrels/day by 2021 (ERCB 2012). Oil sand contains natural contaminants of concern such as naphthenic acids, polycyclic aromatic compounds (PAC), and trace elements such as mercury. These compounds are released to surrounding environments during oil sands mining, processing, and upgrading activities; therefore, current and projected oil sands development represents a potentially significant source of mercury to the Athabasca River and its watershed. Limited independent and reliable studies of the concentration and distribution of mercury within the Athabasca River, its tributaries, and its watershed have been conducted, so the contribution of oil sands development to mercury within the region remains largely unknown. The purpose of this study is to assess the geographic distribution and deposition of mercury to the Athabasca watershed in snowpack and vegetation samples and to assess mercury concentrations in water of the Athabasca River and its tributaries, and in biota of the Athabasca River.

Oil sand is composed of bitumen, sand, shale, clay, carbonates, and/or water (ERCB 2009) as well as compounds such as naphthenic acids, polycyclic aromatic compounds (Kelly et al. 2009), and trace elements such as mercury, arsenic, and lead (Price 2008). Mining activity and the infrastructure required for oil sands mining and extraction (construction of facilities, land clearing, building of roads and pipelines, creation of tailings ponds, etc.) potentially increases loadings of mercury to the Athabasca watershed through increased erosion and sedimentation rates, the release and deposition of gaseous and particulate mercury to the landscape via stack emissions, and leaks, spills, and/or fugitive emissions from tailings ponds or facilities (Holroyd and Simieritsch 2009).

Mercury is a naturally occurring element; however, increased anthropogenic emissions of mercury have increased the mass of mercury within the global cycle relative to pre-industrial times. An estimated two-thirds of currently cycling mercury is from anthropogenic sources, while one third is from natural emissions (Hurley et al. 2007). Inorganic mercury may enter aquatic systems and be converted to methylmercury (MeHg) (Jensen and Jernelov 1969), the neurotoxic, bioavailable form that bioaccumulates and biomagnifies within organisms and food webs (Compeau et al. 1985). MeHg in fish is the primary exposure route for human populations (Agah et al. 2010) and is responsible for the majority of fish consumption advisories in North America (USEPA 1998). A fish consumption advisory is in place for walleye (*Sander vitreus*) in the Athabasca River downstream of oil sands development (Alberta Government 2012) and exceedances of Health Canada guidelines have been reported in larger

specimens of other predatory fish species within the region (northern pike, *Esox lucius*; Donald et al. 1996; RAMP 2009).

Monitoring within the region has been conducted by the Regional Aquatics Monitoring Program (RAMP), a multi-stakeholder industry-funded environmental monitoring program. Increases in mercury concentrations in water have been attributed to natural erosion of the McMurray formation (NREI 2003), and RAMP has consistently concluded that inputs from industrial development are negligible to low when compared to baseline conditions (RAMP 2009). However, "baseline conditions" are defined as 1997, the inception of the RAMP program. Because oil sands operations began in 1967, this baseline likely does not reflect actual baseline conditions (RAMP 2011). RAMP also consistently concludes that fish mercury concentrations are comparable to regional concentrations and are not influenced by oil sands development (RAMP 2009). However, different fish species are assessed at different locations and within different systems (ex. fish concentrations from the Athabasca River are compared to fishes from lakes within the region) (RAMP 2009). Spotty temporal and spatial coverage makes reliable assessment of fish mercury concentrations over time and in relation to oil sands development difficult (RAMP 2011; Evans and Talbot 2012).

Residents of Fort Chipewyan, a community located 250 km downstream of oil sands development, have voiced concern for decades over declining fish and wildlife populations, decreases in water and fish quality (deformities, tainting) (Timoney 2007), and increased rates of diseases such as rare cancers, thyroid

problems, and other diseases characteristic of immunosuppression (Holroyd and Simieritsch 2009; Timoney 2007; Chen 2009). An Alberta Health and Wellness study concluded that cancer rates in Fort Chipewyan were comparable to provincial averages (2006); however, a more detailed study by Alberta Health Services concluded that the incidence of overall cancer, biliary tract, and soft tissue cancers were higher than expected (Chen 2009). Limited independent studies have been conducted to assess the extent of mercury contamination within the region and potential linkages between mercury concentrations and emissions from oil sands development. Because of shortcomings of the regional monitoring program, reliable information on the linkages between contaminant distributions within the region and oil sands development does not exist, making any causal relationships between oil sands development and effects on wildlife populations or human health in the region tenuous and virtually impossible to reliably assess.

This study assessed deposition of mercury to the Athabasca watershed at sites located near oil sands development (within 46 km of upgrading facilities) and at sites far from development (between 46 and 150 km) in accumulated snowpack and vegetation. Mercury was assessed in water of the Athabasca main stem and in six tributaries at sites upstream and downstream of oil sands development. The geographic distribution of mercury was assessed in benthic invertebrates and fishes of the Athabasca River. The study design allowed inputs from natural sources (i.e., erosion of oil sands formations) to be assessed relative to inputs from oil sands development.

Literature Cited

Agah, H., M. Leermakers, Y. Gao, S.M.R. Fatemi, M.M. Katal, W. Baeyens, and M. Elskens. 2010. Mercury accumulation in fish species from the Persian Gulf and in human hair from fishermen. Environmental Monitoring and Assessment **169**:203-216.

Alberta Environment. 2009. Environmental Management of Alberta's Oil Sands.

Chen, Y. 2009. Cancer incidence in Fort Chipewyan, Alberta 1995-2006. Alberta Cancer Board, Division of Population Health and Information Surveillance, Alberta Health and Wellness, Government of Alberta.

Compeau, G.C., and R. Bartha. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. Applied Environmental Microbiology **50**:498-502.

Donald, D.B., H.L. Craig, J. Syrgiannis. 1996. Contaminants in environmental samples: mercury in the Peace, Athabasca and Slave River basins. Northern River Basins Study project report no. 105. Edmonton, Alberta.

Energy Resources Conservation Board (ERCB). 2009. Alberta's energy reserves 2008 and supply/demand outlook 2009-2018.

Energy Resources Conservation Board (ERCB). 2012. Alberta's energy reserves 2011 and supply/demand outlook 2012-2021.

Government of Alberta. 2012. Alberta guide to sportfishing regulations.

Holroyd, P., and T. Simieritsch. 2009. The Waters that Bind us - Transboundary Implications of Oil Sands Development. The Pembina Institute, Drayton Valley.

Hurley, J.P., D.P. Krabbenhoft, J.G. Wiener, and C.L. Babiarz. 2007. Preface to the Madison declaration and critical synthesis papers on mercury pollution - Eighth international conference on mercury as a global pollutant Madison, Wisconsin, USA - 6-11 August 2006. Ambio **36**:2-2.

Jensen, S. and A. Jernelov. 1969. Biological methylation of mercury in aquatic organisms. Nature **223**:753-754.

Kelly, E.N., J.W. Short, D.W. Schindler, P.V. Hodson, M. Ma, A.K. Kwan, and B.L. Fortin. 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences USA 106:22346-22351.

Northern Rivers Ecosystem Initiative (NREI). 2003. Northern River Ecosystem Initiative Key Findings. Government of Canada, Alberta, and Northwest Territories.

Price, M. 2008. 11 Million Litres a Day: The Tar Sands' Leaking Legacy. Environmental Defence, Toronto.

Regional Aquatics Monitoring Program. 2009. Final 2008 Technical Report. Hatfield Consultants, Stantec Consulting Ltd., Klohn Crippen Berger Ltd., and Western Resource Solutions.

Regional Aquatics Monitoring Program. 2011. 2010 regional aquatics monitoring (RAMP) scientific review. Integrated Water Management Program. Alberta Innovates - Technology Futures, Calgary, Alberta. 160 pp.

Timoney, K. 2007. A study of water quality as related to public health issues, Fort Chipewyan, Alberta. Treeline Ecological Research, Edmonton, Alberta.

U.S. Environmental Protection Agency. 1998. Fact sheet update: national listing of fish and wildlife consumption advisories. Environmental Protection Agency, Washington, DC, EPA Publication 823-F-98-009.

Chapter 2: Review of Relevant Literature

Section I: The Alberta Oil Sands

General Background

The Alberta oil sands are located in three major areas in the northeast and northwest corners of the province. The Athabasca, Cold Lake, and Peace River oil sand areas (OSAs) are comprised of 15 distinct deposits that occupy a total area of 142,200 km^2 (Alberta Environment 2009). As of 2008, the volume of crude bitumen in place was estimated at 1,731 billion barrels of oil (ERCB 2008). The deposits are estimated to contain 27 billion cubic meters of crude bitumen that are economically feasible to extract using current technologies, or an established reserve of 169.9 billion barrels of oil (ERCB 2008).

Oil sand is composed of bitumen (an extra-heavy, thick oil) within a matrix that may contain sand, shale, clay, carbonates, and/or water (ERCB 2009). Oil sand also contains naturally occurring contaminants of concern, such as naphthenic acids, polycyclic aromatic compounds (PAC), and trace elements such as mercury, arsenic, and lead (Price 2008).

The American Petroleum Institute (API) classifies liquid petroleum products based on how heavy or light they are in comparison to water (API gravity). If a liquid petroleum product has an API gravity greater than 10 degrees, it is lighter than water and will float, whereas if it has an API gravity of less than 10 degrees, it is heavier than water and will sink (Martinez-Palou 2011). Bitumen is considered an extra-heavy form of oil because it has an API gravity of less than 10 degrees (Martinez-Palou 2011). Therefore, it cannot be recovered through

methods used for lighter conventional oil, such as wells, as it does not flow. As a result, the two methods used to recover oil sand are surface/open pit mining and in situ mining. Approximately 20% (5.44 billion m^3) of the Alberta OSA is shallow enough that it can be recovered through surface or open pit mining (ERCB 2009). Surface mining has a large environmental footprint as, in order to access the underlying deposits, wetlands are drained, streams and rivers are diverted, and vegetation, trees and overburden (topsoil, mineral soil, muskeg) are removed. The remaining 80% (21.55 billion m^3) of the deposit is found deeper than 75 metres and must be recovered using in situ techniques, the most common of which is steam assisted gravity drainage, or SAGD (Alberta Environment 2009). During the in situ mining process, steam, water or chemical solvents are injected into the reservoir containing the oil sand deposit. This reduces the viscosity of the bitumen and allows it to flow vertically or horizontally to a well (Alberta Environment 2009).

To produce crude oil, bitumen must first be extracted from the oil sand. Present techniques are based on the hot water extraction method, developed by Dr. Karl Clark in the 1920's (ERCB 2009). The oil sand is first conditioned by breaking up large pieces and removing coarse material; after which the oil sand is mixed with water to produce a slurry. The slurry is transported from the mine to extraction facilities through hydrotransport pipelines that mix the slurry, breaking the bonds that bind the bitumen, water, and sand together. Additional hot water is added to the slurry during primary separation, which results in the formation of three layers: a floating impure bitumen froth, middlings (bitumen, sand, clay and

water), and a layer of sand at the bottom. An additional 2-4% of the bitumen is recovered from the middlings during secondary separation, which involves aerating the mixture to create additional bitumen froth. The bitumen froth is treated to remove water and solids using inclined plate settlers, which increase the rate of particle settling, and centrifuges. Primary and secondary separation recovers up to 98% of the bitumen contained in oil sand (OSDC 2011).

Bitumen extraction and processing results in the production of a by-product called tailings. Tailings contain water, sand, silt, and clay contaminated with toxic substances (Price, 2008). Because of this toxicity, companies operate under a "zero discharge" policy, so tailings waste must be stored on-site. Tailings are pumped into large impoundments called tailings ponds to allow solids to settle out and to facilitate recovery of water to be re-used in the extraction process (referred to as process-affected water). Coarse solids rapidly settle out and form a solid deposit, whereas fine solids remain suspended (Chalaturnyk et al. 2004). This mixture of fine solids (14% of the total volume) and water (86% of the total volume) is referred to as thin fine tailings, which, after a few years of settling and dewatering, are referred to as mature fine tailings (MFT).

Bitumen is proportionally higher in carbon compared to lighter hydrocarbons; therefore, it must be upgraded into synthetic crude oil through the removal of carbon or the addition of hydrogen. Extracted bitumen can be upgraded through four main processes: thermal conversion, catalytic conversion, distillation, and hydrotreating. Thermal conversion breaks long hydrocarbon molecules into shorter hydrocarbon molecules by heating them to approximately

500°C. Catalytic conversion is an enhanced form of thermal conversion, as it uses high temperatures to break down bitumen molecules; but also uses catalysts such as nickel/molybdenum or cobalt/molybdenum to produce an increased amount of the upgraded product. Distillation involves heating bitumen in a distillation tower that decreases in temperature from the bottom to the top, so the highest temperature occurs at the bottom, the coolest at the top. Lighter hydrocarbons have a lower boiling point so they travel as vapours to the top of the column, while heavier, denser hydrocarbons with higher boiling points collect lower in the tower. Hydrotreating is used to remove impurities and to stabilize the crude oil, this prevents further reactions and chemical changes from occurring during transportation to refineries. Bitumen is mixed with hydrogen and heated at high pressure to 300-400°C, this mixture then passes through towers containing catalysts (OSDC 2011).

Environmental Impacts of the Oil Sands

Oil sands development (exploration, construction of infrastructure, etc.), mining, extraction, upgrading, and refining have various environmental impacts, including disturbance to the landscape and the associated impacts on wildlife populations and habitats, water use, and the production of tailings and process-affected materials.

Disturbance to the Landscape

Changes in land cover, and the associated loss and fragmentation of terrestrial habitat, represents one of the most significant global changes that affects ecosystems and biodiversity (Vitousek, 1994). As of 2008, 530 km^2 of land within Alberta's boreal forest was disturbed by oil sands surface mining operations and tailings ponds covered 130 km^2. In addition, more than 4046 km of pipelines connected oil sand operations in Fort McMurray to refineries in Edmonton (OSDC 2011), as well as an extensive network of roads, seismic lines, well pads, and compressor stations associated with oil sands operations. If surface mineable bitumen is extracted to exhaustion, a potential 4800 km^2 of Alberta's boreal forest will be impacted by open pit mining activity (Alberta Environment 2009).

During the period of surface mining operations, there is a complete loss of soil, terrain features, terrestrial vegetation, wetlands, forest resources, wildlife, and biodiversity in the impacted area (Grant 2008). While the area of the landscape disturbed by surface mining is relatively straightforward to quantify, the area affected by in situ extraction is more difficult to assess (Jordaan et al. 2009). Permanent structures related to in situ extraction, such as well pads, roads, seismic lines, and pipelines, represent a direct loss of habitat; however, these structures create edge habitats that alter habitat suitability. Some species, such as coyotes, deer and snowshoe hare exploit edge habitats and use them to their advantage, while other species such as Woodland Caribou, lynx, and wolves avoid them (Nielsen et al. 2007). In this way, linear anthropogenic structures

affect an area that extends past the directly impacted area. For example, Woodland Caribou in northern Alberta avoid areas adjacent to development compared to areas farther from development (Dyer et al. 2001; Dyer et al. 2002). Areas of reduced use were demonstrated up to 500 m away from developments (Dyer et al. 2001). Linear structures may represent physical barriers that restrict the movements of wildlife populations, causing fragmentation of populations. This may result in a reduction in local population sizes that may potentially lead to local extinctions.

During the initial stages of surface mining, wetlands and muskeg must be drained. Wetlands confer a variety of valuable ecosystem services such as food production for wildlife and human consumers, habitat for a diverse assemblage of species, water purification, nutrient retention, flood control, reduction of erosion and sedimentation, and recreational opportunities (Bronmark and Hansson 2005). Wetlands also recharge water tables during droughts and certain types of wetlands sequester carbon (Holroyd and Simieritsch 2009). As of 2008, the potential loss of wetlands due to oil sands development and extraction was estimated at 1300 km^2 (Grant 2008). As part of the mine reclamation process, developers are required to construct wetlands in order to adhere to the no net loss of wetlands policy.

To comply with the no net loss of wetlands policy, developers have proposed the "wet landscape" reclamation option that involves the creation of engineered water bodies referred to as Mature Fine Tailings (MFT) capped lakes and End Pit Lakes (EPLs). MFT capped lakes consist of a pit lined with MFT that is capped with process-affected water, fresh water, or a combination of both. End

pit lakes are similar to MFT capped lakes; however, they contain smaller amounts of tailings and may also contain various oil sand byproducts, such as lean oil sand (raw, un-processed oil sand), process-affected water or overburden (BGC Engineering 2010). EPLs were approved-in-principal in 1993; however, a successful field demonstration has not yet occurred and it is uncertain if viable, sustainable aquatic ecosystems will develop in the long term (RSC, 2010). Despite this fact, numerous projects listing this un-proven reclamation technique have been approved and, as of 2007, at least 25 EPLs were planned for the region over the next 60 years (Grant et al. 2008).

The purpose of EPLs are to serve as a remediation tool that relies on the passive bioremediation of contaminants by microbial communities to decrease the concentration of these compounds in the overlying cap water. Once passive bioremediation occurs and contaminant concentrations in the overlying cap water have decreased, the cap water will be released to surrounding environments, a viable ecosystem will develop, and the lakes will become permanent features of the post-reclamation landscape (BGC Engineering, 2010). However, for this to occur, the tailings layer and water cap must not mix, a requirement specifically outlined in their design. To prevent this, the depth of the water cap is designed to prevent mixing due to surface wave action; however, methane-producing bacteria have been active in Syncrude's experimental ponds since the 1990s (BGC Engineering Inc. 2010). The release of methane bubbles destabilizes the tailings-water interface, leading to mixing that potentially mobilizes compounds contained in the tailings to the water column (Fedorak et al. 2002). The rate of

bioremediation will depend on whether the conditions in the EPLs are aerobic or anaerobic, as some compounds are degraded effectively under aerobic conditions, but are more persistent under anaerobic conditions (Han et al. 2009). As a result, it is thought that some EPLs will remain acutely and chronically toxic until at least 2070 (CEMA 2007).

Water Use

The production of crude oil from oil sand is more resource intensive than conventional sources of crude oil. Surface mining, in situ extraction and upgrading of oil sand are all dependent on water that is derived from various sources (RSC 2010). On average, the production of 1 barrel of oil requires approximately 19.5 barrels of water, 16.4 (80-85%) of which are derived from recycled process water (Allen 2008). However, due to a gradual build-up of compounds that decrease bitumen recovery and lead to scaling and corrosion of extraction facilities, process water can only be recycled a finite number of times (Allen 2008). As a result, an average of 3.1 barrels of water are imported per barrel of oil produced (Allen 2008). The main source of this water, accounting for an estimated 50-75% of total water used by oil sands operations (CAPP 2009), is the Athabasca River, with groundwater comprising the remainder (Allen 2008). Oil sands mining accounts for 8% of all licenced surface water use in Alberta, with combined licences totaling up to 535,930 dam^3 (cubic decametres, equivalent to 1000 cubic metres) permitted to be consumed or lost (Schindler et al., 2007).

Water consumed for oil sands mining does not return to the Athabasca River within the life cycle of the mine (Phase 2 Committee Report 2010).

It is widely recognized that in order to maintain the ecological function of a river, a minimum amount of flow must be maintained, this minimum flow is referred to as instream flow needs (IFN). Flow within the Athabasca River varies widely across and within years (Phase 2 Framework committee report 2010). Typically, the river experiences high flows during spring and summer, with flow decreasing towards late summer, resulting in low fall and winter flows (Phase 2 Framework committee Report, 2010; Schindler et al. 2007). Therefore, withdrawals of equivalent volume will have varying impacts on the Athabasca River and Delta depending on the season or year. For example, a withdrawal during a "wet" year, when flow in the river is high, may reduce total flow by less than 0.5%, whereas an equivalent withdrawal during a low flow year may account for 10% of the river's flow. Similarly, a withdrawal during spring high flows may have less impact on total flow and ecosystem function compared to an equivalent withdrawal during winter low flows. Due to a reduction in flow following the construction of the Bennett Dam on the Peace River during the 1960s, the vulnerability of aquatic habitats and species during low flow events, the effects of climate change, and increasing demand on water resources from a rapidly expanding oil sands sector, concern and debate regarding the potential impacts of growing demand for water from the Athabasca River has increased.

In response to these growing concerns, Alberta Environment and the Department of Fisheries and Oceans established a water management framework

for the Lower Athabasca River to regulate the use of water in order to meet in-stream flow needs (AENV 2007). Phase 1 of the framework outlines 3 management zones corresponding to flow conditions. In the "green" zone, flows are above 140 m^3/s (cubic metres per second) and it is assumed that 15% of the river's flow can be withdrawn without causing significant impacts on the aquatic ecosystem. In the "yellow" zone, flows are between 100-140 m^3/s and it is assumed that a 15% withdrawal will cause stress to aquatic ecosystems, so withdrawals must be reduced accordingly. In the "red" zone, flow is below 100 m^3/s and it is assumed that the aquatic ecosystem is stressed, so withdrawals are minimized and companies must rely on the use of water stored on-site during high flow periods (AENV 2007). However, the framework received criticism as it did not account for reduced flows that are expected to occur more frequently as a result of climate change (Schindler et al. 2007; Mannix et al. 2010) and permitted a maximum cumulative withdrawal of up to 15 m^3/s during "red" zone/low flow conditions when the ecosystem may be stressed and impacts on fish habitat are likely to occur (AENV 2007).

Phase 2 of the framework consists of a review and update of phase 1 and is not yet complete, despite an implementation date of January 1, 2011. The framework is being developed under a full build-out scenario of future development (the "growth case" scenario of development), which includes water use for announced and potential future projects under consideration as of the end of 2006 (Water Management Framework 2010). Under this growth scenario, average water demand is equivalent to 16 m^3/s with an associated peak demand of

29 m^3/s (Water Management Framework 2010). The option currently being considered by the framework committee (option H) sets an ecosystem base flow (EBF) threshold of 87 m^3/s, as it is estimated that the lowest weekly average flow within the last 50 years was 88 m^3/s. Below this threshold, a maximum withdrawal of 4.4 m^3/s is permitted, a 50% reduction from the phase 1 framework. The maximum withdrawal of 4.4 m^3/s is comprised of water allocated through past licences to Syncrude and Suncor (2 m^3/s each), in addition to 0.2 m^3/s to Albian Muskeg River and Canadian Natural Horizon for freeze-protection of existing infrastructure. However, the EBF exemption is still under debate as the committee was unable to reach a consensus. Some committee members and stakeholders believed that the withdrawal cutoff of 4.4 m^3/s may not be adequate to protect the aquatic ecosystem during rare low flow events. Option H proposes a long-term water storage target of 104 million m^3 for all operations that would be robust to moderate climate change scenarios (Global Climate Model 1) but not more extreme scenarios (Global Climate Models 2 and 3).

Tailings and Oil Sands Process-Affected Materials

Due to the unique physical properties of oil sand tailings, tailings management and reclamation is one of the largest operational and environmental problems associated with oil sand operations. It is estimated that for every barrel of oil produced from oil sand, approximately 1.5 barrels of tailings are produced (Grant et al. 2008). At 2008 production rates, this equates to the production of 1.8

billion liters of tailings each day (Price 2008). As of 2008, tailings ponds covered approximately 130 km^2, containing a total volume of 5.5 trillion liters (Price 2008).

When the tailings stream is pumped into settling ponds, coarse particles settle out rapidly, while fine solids remain suspended. Estimates for the time to self-consolidation range from a few decades to up to 150 years (Eckert 1996). The fines consolidate slower than anticipated for numerous reasons. MFT exhibit low hydraulic conductivity, this prevents water from passing through pore spaces and separating from the fines (Chalaturnyk et al. 2004). During bitumen extraction, caustic soda containing sodium hydroxide is added to the slurry (BGC Engineering Inc 2010). Clay particles exhibit an increased negative surface charge in the presence of sodium ions, increasing dispersion of the particles and preventing self consolidation (BGC Engineering Inc. 2010). Also, fine tailings develop thixotropic strength over time (Chalaturnyk et al. 2004). Thixotropic materials become less viscous when a force is applied, and become more viscous when the force ceases. Therefore, over time, the tailings develop an intrinsic strength that is capable of resisting effective stress, preventing further self-consolidation of the material (Chalaturnyk et al. 2004). Research conducted over the last 40 years to characterize tailings material and develop dewatering techniques has led to improved tailings management (RSC 2010); however, a technically and economically feasible technique that works for all types of tailings has yet to be developed (BGC Engineering Inc. 2010). As a result, a vast inventory of legacy tailings has accumulated on the landscape.

Currently, the most extensively used tailings reclamation technology is the creation of non-segregating tailings, such as consolidated/composite tailings (CT) or thickened tailings (TT). The process involves mixing MFT with gypsum ($CaSO_4 \cdot 2H_2O$) or other thickening agents to increase the density of the tailings and speed up the dewatering process; the solids settle rapidly, reaching up to 80% solids within a few hours (Fedorak et al. 2002). However, due to variability in the properties of MFT, off-spec CT is sometimes produced, which has properties similar to MFT (BGC Engineering Inc. 2010). The "dry landscape" reclamation option involves mixing CT and TT with overburden, coke, sand or other materials to produce trafficable deposits that can be incorporated into the post-reclamation landscape.

Tailings and process-affected water contain contaminants of concern, including naphthenic acids, polycyclic aromatic compounds, and trace metals such as arsenic, lead and mercury (Price 2008). Therefore, the current and future volume of tailings and process-affected water produced through oil sands development represent a substantial source of toxic compounds that could potentially be released or mobilized to surrounding environments through catastrophic failure of tailings dykes or through seepage.

Tailings ponds are constructed out of materials that conduct water, often settled out coarse solids (Chalaturnyk et al. 2004), and on top of material that conducts water (Price 2008). As a result, tailings ponds leak through the base and sides of the impoundment (Bishay 1998). While the rate of leakage declines over time due to the accumulation of clay and silt at the bottom of the impoundments

and the formation of bitumen mats along the edges (referred to as "self-sealing"), it does not cease altogether. Interceptor ditches and wells are operated to minimize the volume of tailings that escape into the environment; however, these measures are imperfect (Price 2008). One study found that oil sand process affected water from Syncrude's Mildred Lake settling basin was seeping through a permeable toe-berm and reaching the lower Beaver Creek (Mackinnon et al. 2005). However, studies by Yasuda (2010) and Ferguson et al. (2009) found that implemented mitigation efforts, such as seepage collection ditches and interceptor wells, are effective at preventing leakage from reaching water bodies and migrating into off-lease environments (Yasuda 2010; Ferguson et al. 2009). Oil sand operators are required by the EPEA to report seepage rates of OSPW to ground and surface water; however, no comprehensive, reliable estimate of actual seepage rates for the oil sands region exists (RSC 2010). A regional estimate by Environmental Defense reports that, as of 2007, tailings ponds within the oil sands region leak at a rate of approximately 11 million litres per day, or approximately 4 billion litres per year (Price 2008).

Tailings and process-affected water and materials have been shown to be acutely toxic to a variety of organisms. An experimental release of a small volume of tailings into the Muskeg River, a tributary of the Athabasca River, resulted in a 60% reduction in the benthic invertebrate community due to increased fine sediments and toxicity of the tailings to sensitive species (Barton and Wallace 1979). Coke, another by-product of oil sands operations, may be incorporated into dry or wet reclamation landscapes. Toxicity tests have revealed that whole coke

leachates are acutely toxic to *Ceriodaphnia dubia* (Puttaswamy et al. 2010). In addition to acute toxicity to individuals, oil sands process-affected materials have the potential to cause a variety of negative impacts on benthic invertebrate populations or communities. The benthic invertebrate community found in constructed wetlands containing oil sands material is dominated by chironomid larvae (Diptera) and the species diversity is reduced compared to natural wetlands (Bendell-Young et al. 2000).

Several studies have shown that exposure to tailings and process-affected water and materials may have negative impacts on the normal endocrine function, reproductive function, and health of various organisms such as fish, amphibians and waterfowl. Yellow Perch (*Perca flavescens*) and Goldfish (*Carassius auratus*) exposed to water containing high levels of oil sands process-affected water for 3 weeks exhibited significant gill and liver histopathological changes, such as epithelial cell necrosis, mucous cell proliferation and hepatocellular degeneration (Nero et al. 2006). Goldfish caged for 19 days in experimental EPLs containing MFT or MFT and tailings water exhibited significantly reduced plasma testosterone and 17β-estradiol levels and significantly increased plasma cortisol levels (Lister et al. 2008). This suggests that oil sands affected water and materials have the potential to disrupt normal endocrine and reproductive function in fish species (Lister et al. 2008). Stickleback and Fathead Minnows transplanted to constructed wetlands from natural wetlands displayed increased hematocrit and decreased leucocrit levels, an indicator of an acute stress response that was often exhibited prior to death of the organism (Bendell-Young et al. 2000). Northern

Canadian Toad (*Bufo borealis*) and Wood Frog (*Rana sylvatica*) tadpoles exposed to water from wetlands formed by the intentional release of process-affected water (containing consolidated tailings) displayed high mortality (Pollet and Bendell-Young 2000). *R. sylvatica* also displayed high mortality when exposed to water from wetlands formed from tailings dike seepage (Pollet and Bendell-Young 2000). Of the individuals that survived, tadpoles from both species that were exposed to waters most affected by the oil sands mining process displayed higher incidences of deformities, as well as decreased growth and/or longer development times (Pollet and Bendell-Young 2000). Larger individuals metamorphose earlier, have higher survival rates and have an earlier age of first reproduction (Pollet and Bendell-Young 2000); therefore, exposure of tadpoles to oil sands process-affected waters may have negative impacts on their populations. Mallard (*Anas platyrhynchos*) ducklings reared on a natural wetland were larger and weighed more than ducklings reared on a wetland containing process-affected water (water formed from dewatering of a tailings dyke, the water composition is ~80% original tailings slurry) and from a constructed wetland (Gurney et al. 2005).

Contaminants contained in process-affected water and sediment can be mobilized through the food web; therefore, organisms can be negatively impacted through dietary exposure to contaminants. Various taxa within benthic invertebrate communities inhabit the sediment-water interface as larvae and metamorphose into terrestrial adults. Sediments act as a sink for contaminants and typically contain elevated levels of contaminants. Concentrations of PAHs in sediments have been found to be elevated in experimental wetlands compared to

reference or natural wetlands (Wayland et al. 2008). Due to the close association between benthic invertebrate communities and sediments, it is not surprising that concentrations of PAHs in larval aquatic insects have been found to significantly exceed those found in reference or natural wetlands (Wayland et al. 2008). This may have deleterious effects on higher trophic levels that utilize benthic invertebrates as dietary items, such as Tree Swallows, whose diet contains over 80% emergent insects (Smits et al. 2000). Tree Swallow (*Tachycineta bicolor*) nestlings bred on wetlands containing oil sands process-affected material had higher plasma T3 concentrations and higher T4 content within their thyroid glands compared to nestlings bred on natural wetlands (Gentes et al. 2007). These elevated hormone levels could be partly attributed to exposure to PAHs or other contaminants contained within oil sand effluent (Gentes et al. 2007). Pyrene and naphthalene (PAH metabolites) were found at significantly increased concentrations in the bile of ducklings reared on a wetland containing process-affected water from dewatering of a tailings dyke compared to a natural wetland (Gurney et al. 2005). This suggests that the ducklings reared on the constructed wetland were exposed to higher concentrations of the parent compounds found in oil sands effluent, possibly through ingestion of contaminated grit (Gurney et al. 2005) which is used to aid digestion in the gizzard.

Section II: Mercury

Mercury in the Environment

Mercury is a naturally occurring element that is released to water and the atmosphere through natural and anthropogenic processes. Natural sources include volcanic eruptions, evasion from soils, vegetation surfaces, forest fires, and outgassing from the Earth's mantle at divergent tectonic boundaries (as reviewed by Schroeder and Munthe 1998). It occurs naturally in cinnabar deposits within the Earth's crust and has been mined for approximately 500 years for use in the mercury-amalgamation process in the recovery of gold and silver (Lacerda et al. 1997). More recently, anthropogenic mercury emissions are predominantly derived from unintentional losses from mercury-cell chlor-alkali plants (Environmental Protection Agency 2011) and emissions from coal-fired power plants (CCME 2009). While awareness of the toxicity of mercury to wildlife and human populations has resulted in efforts to reduce mercury emissions from these sources, on-going emissions and release from historically contaminated sites are significant sources of mercury to the environment.

The Mercury Biogeochemical Cycle

Mercury exists in three oxidation states (0, 1+, and 2+) and cycles between four interconnected compartments (atmospheric, aquatic, terrestrial and biotic compartments) that are dominated by different forms of mercury.

Approximately 98% of the mercury in the atmosphere is present as gaseous elemental mercury, Hg^0, with the remainder comprised of inorganic divalent mercury, Hg(II), particulate phase mercury, Hg(p), and occasionally, trace amounts of methyl mercury (MeHg) and dimethyl mercury (DMM) (Downs et al. 1998). Hg^0 has an average atmospheric residence time of one year, so it is subject to long-range atmospheric transport and is a global pollutant (Wiener et al. 2003). Hg(II) and Hg(p) have shorter atmospheric residence times of a few days to a few weeks and are deposited a few tens to a few hundreds of kilometers from their source (Downs et al. 1998; Wiener et al. 2003). Hg^0 is oxidized by ozone or other oxidizing agents present within the atmosphere to form Hg(II), which is deposited to landscapes through wet and dry deposition processes (Schroeder and Munthe 1998; Downs et al. 1998). Particulate mercury in the atmosphere is derived from direct emission or from the sorption of Hg(II) to particulates and/or aerosols present in the atmosphere and is subject to wet and dry deposition (Schroeder and Munthe 1998; Downs et al. 1998).

Mercury deposited to the surface of water bodies is dominated by wet deposition, whereas mercury deposited to forested ecosystems is derived from both wet and dry deposition processes. Dry deposition in forested ecosystems occurs through three processes: adsorption and oxidation of gaseous Hg^0, Hg^0 is taken up through stomata, and/or Hg(II) and particulate Hg are adsorbed (Schroeder and Munthe 1998). Deposited mercury is then either washed off of plant surfaces by precipitation and deposited to the forest floor as throughfall or is incorporated into plant tissues and eventually deposited as litterfall. Deposited

mercury is sequestered in soils and may re-enter the atmosphere through evasion, be taken up by biota (Stemenkovic and Gustin 2009; Gnamus et al. 2000), or may be slowly mobilized and exported to aquatic systems in runoff (Hintelmann et al. 2002).

Hg(II)-ligand pairs account for the majority of mercury present in waters of aquatic systems, with MeHg and Hg^0 present at lower concentrations. The speciation of Hg(II) and MeHg in aquatic environments is highly influenced by the chemical composition of the water. In oxic waters, Hg(II) and MeHg ion-pair formation is dominated by dissolved organic matter (DOM) and chloride. Under anoxic conditions, such as within sediment pore-waters and the hypoliminia of lakes, sulphide or sulphydryl complex ion pairs of Hg(II) and MeHg dominate. This complexation of Hg(II) with sulphide can strongly influence the availability of mercury for methylation through microbial processes (Benoit et al. 1999). While some methylation of Hg(II) occurs within the water column, the majority of methylation occurs within the uppermost few centimeters of sediments, where sulphate reduction is highest.

Within sediments, Hg(II) is converted to MeHg by sulphur-reducing and iron-reducing bacteria. The concentration of MeHg within aquatic systems is dependent upon the methylation rate of sulphur-reducing bacteria and the rate of demethylating bacteria that convert MeHg to inorganic forms. In addition, methylation rates are influenced by various water chemistry parameters (Ullrich et al. 2001). For example, the activity of sulphur-reducing bacteria is enhanced in systems that contain high concentrations of bioavailable sulphates (Gilmour et al.

1992). Low pH values may lead to increased production of MeHg and a concomitant increase in MeHg concentrations in biota; however, low pH could result in many changes within aquatic systems and may not directly influence methylation rates. For example, increasing acidity has been shown to decrease the solubility of Hg, as binding of Hg to particulates increased under acidic conditions (Schindler et al. 1980). However, the bioavailability of particulate-bound mercury is dependent upon particle size, with mercury bound to small particles being more bioavailable than mercury bound to large or coarse particles (Ullrich et al. 2001).

MeHg is the bioavailable form of mercury and once converted, enters aquatic food webs. As MeHg strongly biomagnifies within food webs, concentrations can increase by millions between the base of the food web and higher trophic levels. Mercury levels in fish populations respond rapidly to increased deposition of emissions of mercury (Orihel et al. 2007; Harris et al. 2007), with fish consumption advisories in North America steadily increasing. Consumption of contaminated fish is the most significant source of MeHg exposure within human populations (Mergler et al. 2007); therefore, rising MeHg levels in fish may pose a significant health risk to human populations, as MeHg is a neurotoxin that targets the central nervous system and has both acute and chronic toxic effects.

Health Effects of Mercury

As a result of increased understanding of the health risks associated with mercury exposure, pathways of exposure to human populations have decreased,

so the only remaining pathway of significant exposure is through the ingestion of contaminated fish and seafood (Clarkson and Magos 2006). Fish consumption rates and MeHg concentrations in human blood exhibit a highly positive relationship (Mahaffey et al. 2004). Approximately 95% of ingested MeHg is absorbed into the bloodstream (WHO 1990). On average, 5% of the ingested mercury remains in the bloodstream, with concentrations in the brain approximately five times higher than concentrations in the bloodstream (Clarkson and Magos 2006).

The health effects of MeHg exposure are dose dependent. In adults, exposure can result in permanent damage to the central nervous system as neuronal cells are destroyed (Fitzgerald and Clarkson 1991), leading to sensory and motor impairment, adverse effects on the cardiovascular system (Park and Johnson 2006 and references contained therein), and parasthesis (Fitzgerald and Clarkson 1991), seizures (Myers and Davidson 2000), blindness (Myers and Davidson 2000), deafness (Murata et al. 2004), and cerebral palsy (Gilbertson 2004).

MeHg in maternal blood is readily transferred through the placenta and accumulates within the blood and brain of the developing fetus (Choi et al. 1978). MeHg has a high affinity for the fetal brain and is a potent neurotoxic teratogen as it interferes with neuronal cell development and migration. In the early 1970s, an outbreak of mercury poisoning occurred in Iraq as the result of the consumption of bread that was prepared from seed grain of wheat that had been treated with a methylmercury fungicide. In two cases, the developing fetus was exposed to very

high mercury levels in maternal blood (726 ng/ml and 1188 ng/ml) early in development (Choi et al. 1978). Autopsies of the infants revealed an incomplete or abnormal migration of neurons to the cerebellar and cerebral cortices, as well as deranged cortical organization of the cerebrum (Choi et al. 1978). The effects of prenatal exposure to mercury on child development include decreased ability to concentrate (Grandjean et al. 1997; Crump et al. 1998), diminished visual-spatial perception (Harada et al. 2005), adverse effects on cardiovascular function (Grandjean et al. 2004), and impaired motor function (Mckeown-Eyssen et al. 1983; Myers and Davidson 2000). More severe effects occur at higher exposures, such as mental retardation, cerebral palsy, and seizures (Myers and Davidson 2000). These effects have been observed in populations where children are exposed to high levels of mercury *in utero* resulting from maternal consumption of highly contaminated fish (10 ppm to 40 ppm) (Myers et al. 2000); however, the effects of chronic exposure to lower concentrations of mercury in fish (0.3 ppm) on development are more difficult to detect and assess (Myers et al. 2000).

Many indigenous populations within Canada depend on fish as a subsistence food source (Wheatley and Wheatley 2000). Because of the higher consumption rate of MeHg contaminated fish, individuals within Canadian indigenous populations are at a greater risk for the adverse health effects resulting from exposure to MeHg than the general population (Wheatley and Wheatley 2000).

Mercury in the Alberta Oil Sands

Within recent decades, oil sands development has become a significant source of mercury within the oil sands region. Emissions of mercury reported to the National Pollutant Release Inventory (NPRI) increased by approximately seven times between 2000 and 2010 (the most recent year with complete and reviewed data; NPRI 2012). Despite the large mass of mercury released by oil sands development, a limited number of independent studies of the fate, cycling, and concentration of mercury in biota of the region have been conducted.

Concentrations of mercury within predatory fish species (walleye, *Sander vitreus* and northern pike, *Esox lucius*) in the lower Athabasca River and Lake Athabasca are known to be high (Donald et al. 1996; RAMP 2009). A consumption advisory is in place for walleye in the Lower Athabasca River (Alberta Government 2012). Walleye up to 2 lbs are recommended as safe for consumption and 1 serving is equal to 75 g. Adults are permitted 8 servings per week, children between 5-11 years of age are permitted 1 serving per week, young children (1-4) are permitted 0.5 servings, and women are permitted 2 servings (Alberta Government 2012). Unfortunately, consumption advisories are often ignored, as people may be unaware of specific warnings, such as size or weight restrictions associated with advisories, vulnerable age groups, or when they are vulnerable (for example, women who may become pregnant) (Burger and Gochfeld 2006). Further, reliable assessments of mercury concentrations in all fish species consumed by communities within the region do not exist. As a result,

individuals within communities downstream of oil sands development may be at risk for the negative health effects associated with MeHg exposure.

A meta analysis of mercury concentrations in walleye from the Athabasca River concluded that mercury concentrations have increased by approximately 30% between 1976 and 2005 (Timoney and Lee 2009). A meta analysis of a more extensive fish database by Environment Canada found that mercury concentrations in walleye and lake whitefish from the Athabasca River and northern pike from Lake Athabasca have decreased over time and walleye and lake trout mercury concentrations in Lake Athabasca have remained unchanged (Evans and Talbot 2012). The authors found that mercury concentrations in lake trout in Lake Athabasca were significantly higher in 2007 compared to 2000 (Evans and Talbot 2012). However, both studies analyzed datasets that utilized different sampling protocols between years (for example, analysis of whole body fish in some years and fillets in other years), different analytical methods, and contained data from monitoring programs with sporadic sampling of a small number of fish (Evans and Talbot 2012); therefore, neither study can reliably assess the cause of the observed trends. While temporal trends of mercury in fish remain uncertain, a limited number of studies within the region indicate that mercury concentrations may be increasing over time and are significantly higher than pre-oil sands development levels.

A study of acidification of small lakes within the region also assessed mercury concentrations within sediment cores in order to assess industrial contamination from oil sands development (Curtis et al. 2010). While

concentrations of mercury within lake sediments did not display an obvious spatial trend, they found that mercury concentrations have been increasing in sediments since the 1880's with a sharp increase within the last 20 years (Curtis et al. 2010). The authors concluded it was unlikely that the cause of this sharp increase was increasing global emissions and instead attributed the increase to emissions from a local source combined with a recent increase in sedimentation (Curtis et al. 2010).

Mercury in aquatic bird eggs from sites located in receiving waters of the Athabasca River had greater mercury concentrations than eggs from sites on the Peace River (Hebert et al. 2011). Trophic position did not explain the differences between sites, suggesting an upstream source of mercury at the Athabasca River sites (Hebert et al. 2011). Further, mercury concentrations in eggs from sites on the Athabasca River were correlated with naphthalene concentration, which suggests a common contaminant source (Hebert et al. 2011). Further, the study found that mercury contaminant burdens in california gull (*Larus californicus*) eggs from a colony on Lake Athabasca increased by 40% between 1977 to 2009 (Hebert et al. 2011). Therefore, it is unlikely that mercury concentrations in piscivorous birds within the region are increasing over time, while concentrations in their prey have remained constant or are decreasing over time (Evans and Talbot 2012).

Literature Cited

Alberta Environment. 2007. Water management framework: instream flow needs and water management system for the Lower Athabasca River. February 2007. Phase 1.

Alberta Environment. 2009. Environmental Management of Alberta's Oil Sands.

Allen, E.W. 2008. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. Journal of Environmental Engineering and Science **7:**123-138.

Barton, D.R., and R.R. Wallace. 1979. The effects of an experimental spillage of oil sands tailings sludge on benthic invertebrates. Environmental Pollution **18**:305-312.

Bendell-Young, L.I., K.E. Bennett, A. Crowe, C.J. Kennedy, A.R. Kermode, M.M. Moore, A.L. Plant, and A. Wood. 2000. Ecological characteristics of wetlands receiving an industrial effluent. Ecological Applications **10**:310-322.

Benoit, J.M., C.G. Gilmour, R.P. Mason, and A. Heyes. 1999. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environmental Science and Technology **33**:951-957.

BGC Engineering Inc. 2010. Oil Sands Tailings Technology Review. Oil sands research and information network, University of Alberta, School of Energy and the Environment, Edmonton, Alberta. OSIRIN Report No. TR-1. 136 pp.

Bishay, F.S. 1998. The use of constructed wetlands to treat oil sands wastewater. Fort McMurray, Alberta, Canada. M.Sc. Thesis. University of Alberta, Canada.

Bronmark, C., and L. Hanson. 2005. The biology of lakes and ponds, 2nd edition. Oxford University Press, Oxford, New York.

Burger, J. and M. Gochfeld. 2006. A framework and information needs for the management of the risks from consumption of self-caught fish. Environmental Research **101**:275-285.

Canadian Association of Petroleum Producers (CAPP). 2009. Crude oil forecast, markets, and pipeline report.

Canadian Council of Ministers of the Environment (CCME). 2009. Canada-wide standard for mercury emission from coal-fired electric power generation plants. 2009 progress report. 47 pp.

Chalaturnyk, R.J., J.D. Scott, and B. Ozum. 2004. Oil sands tailings production for environmental disposal. Mining Science and Technology. Proceedings of the 5th international symposium on mining science and technology, Xuzhou, China. October 2004. pg. 653-658.

Choi, B.H., L.W. Lapham, L. Amin-Zaki, and T. Saleem. 1978. Abnormal neuronal migration, deranged cerebral cortical organization, and diffuse white matter astrocytosis or human fetal brain: a major effect of methylmercury poisoning *in utero*. Journal of Neuropathy and Experimental Neurology **37**:719-733.

Clarkson, T.W., and L. Magos. 2006. The toxicology of mercury and its chemical compounds. Critical Reviews in Toxicology **36**:609-662.

Crump, K.S., T. Kjellstrom, A.M. Shipp, A. Silvers, and A. Stewart. 1998. Influence of prenatal mercury exposure upon scholastic and psychological test performance: benchmark analysis of a New Zealand cohort. Risk Analysis **18**:701-713.

Cumulative Environmental Management Association (CEMA). 2007. Planned Pit Lakes in the Oil Sands Region. Cumulative Environmental Management Association. http://www.cemaonline.ca/index.php/research-library/cat_view/305-research-library/308- reclamation-working-group-rwg/310-rwg-research-and-reports/360-end-pit-lakes. RWG-EPL_pit_Lake_Map_with_EIAs[1].pdf

Donald, D.B., H.L. Craig, J. Syrgiannis. 1996. Contaminants in environmental samples: mercury in the Peace, Athabasca and Slave River basins. Northern River Basins Study project report no. 105. Edmonton, Alberta.

Downs, S.G., C.L. Macleod, and J.N. Lester. 1998. Mercury in precipitation and its relation to bioaccumulation in fish: a literature review. Water, Air, and Soil Pollution **108**:149-187.

Dyer, S.J., J.P. O'Neill, S.M. Wasel, and S. Boutin. 2001. Avoidance of industrial development by woodland caribou. Journal of Wildlife Management **65:**531-542.

Dyer, S.J., J.P. O'Neill, S.M. Wasel, and S. Boutin. 2002. Quantifying barrier effects of roads and seismic lines on movements of female woodland caribou in northeastern Alberta. Canadian Journal of Zoology **80:**839-845.

Eckert, W.F., J.H. Masliyah, M.R. Gray, and P.M. Fedorak. 1996. Prediction of sedimentation and consolidation of fine tails. AICHE Journal **42**:960-972.

Energy Resources Conservation Board (ERCB). 2009. Alberta's energy reserves 2008 and supply/demand outlook 2009-2018.

Environmental Protection Agency (EPA). 2003. National emission standards for hazardous air pollutants: mercury emissions from mercury cell chlor-alkali plants. 43 pp.

Environmental Resources Conservation Board (ERCB). 2008. Alberta's energy reserves 2008 and supply/demand outlook 2009-2018.

Evans, M.S. and A. Talbot. 2012. Investigations of mercury concentrations in walleye and other fish in the Athabasca River ecosystem with increasing oil sands developments. Journal of Environmental Monitoring DOI: 10.1039/c2em30132f.

Fedorak, P.M., D.L. Coy, M.J. Salloum, and M.J. Dudas. 2002. Methanogenic potential of tailings samples from oil sands extraction plants. Canadian Journal of Microbiology **48**:21-33.

Ferguson, G.P., D.L. Rudolph, and J.F. Barker. 2009. Hydrodynamics of a large oil sand tailings impoundment and related environmental implications. Canadian Geotechnical Journal **46**:1446-1460.

Fitzgerald, W.F., and T.W. Clarkson. 1991. Mercury and monomethylmercury: present and future concerns. Environmental Health Perspectives **96**:159-166.

Gentes, M., A. McNabb, C. Waldner, and J.E.G. Smits. 2007. Increased thyroid hormone levels in Tree Swallows (Tachycineta bicolor) on reclaimed

wetlands of the Athabasca oil sands. Archives of Environmental Contamination and Toxicology **53**:287-292.

Gilbertson, M. 2004. Male cerebral palsy hospitalization as a potential indicator of neurological effects of methylmercury exposure in Great Lakes communities. Environmental Research **95**:375-384.

Gilmour, C.C., E.A. Henry, and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environmental Science and Technology **26**:2281-2287.

Gnamus, A., A.R. Byrne, and M. Horvat. 2000. Mercury in the soil-plant-deer-predator food chain of a temperate forest in Slovenia. Environmental Science and Technology **34**:3337-3345.

Government of Alberta. 2012. Alberta guide to sportfishing regulations.

Grandjean, P., K. Murata, E. Budtz-Jorgensen, and P. Wiehe. 2004. Cardiac autonomic activity in methylmercury neurotoxicity: 14-year follow-up of a Faroese birth cohort. Journal of Pediatrics **144**:169-176.

Grant, J., S. Dyer, and D. Woynillowicz. 2008. Fact or fiction? Oil sands reclamation. The Pembina Institute, Drayton Valley, Alberta.

Gurney, K.E., T.D. Williams, J.E. Smits, M. Wayland, S. Trudeau, and L.I. Bendell-Young. 2005. Impact of oil-sands based wetlands on the growth of Mallard (*Anas platyrhynchos*) ducklings. Environmental Toxicology and Chemistry **24**:457-463.

Han, X.M., M.D. MacKinnon, and J.W. Martin. 2009. Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. Chemosphere **76**:63-70.

Harada, M., T. Fujino, T. Oorui, S. Nakachi, T. Nou, T. Kizaki, Y. Hitomi, N. Nakano, and H. Ohno. 2005. Followup study of mercury pollution in indigenous tribe reservations in the province of Ontario, Canada, 1975-2002. Bulletin of Environmental Contamination and Toxicology **74**:689-697.

Harris, R.C., J.W.M. Rudd, M. Amyot, C.L. Bablarz, K.G. Beaty, P.J. Blanchfield, R.A. Bodaly, B.A. Branfireun, C.C. Gilmour, J.A. Graydon, A. Heyes, H. Hintelmann, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S.E. Lindber, R.P. Mason, M.J. Paterson, C.L. Podemski, A. Robinson, K.A. Sandilands, G.R. Southworth, V.L. St. Louis, and M.T. Tate. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. Proceedings of the National Academy of Sciences **104**:16586-16591.

Hebert, C.E., D.V. Chip Weseloh, S. MacMillan, D. Campbell, and W. Nordstrom. 2011. Metals and polycyclic aromatic hydrocarbons in colonial waterbird eggs from Lake Athabasca and the Peace-Athabasca Delta, Canada. Environmental Toxicology and Chemistry **30**:1178-1183.

Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott, and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology **36**:5034-5040.

Holroyd, P., and T. Simieritsch. 2009. The Waters that Bind us - Transboundary Implications of Oil Sands Development. The Pembina Institute, Drayton Valley.

Jordaan, S.M., D.W. Keith, and B. Stelfox. 2009. Quantifying land use of oil sands production: a life cycle perspective. Environmental Resource Letters **4:**024004.

Lacerda, L.D. 1997. Global mercury emissions from gold and silver mining. Water, Air, and Soil Pollution **97**:209-221.

Lister, A., V. Nero, A. Farwell, D.G. Dixon, and G. Van Der Kraak. 2008. Reproductive and stress hormone levels in goldfish (*Carassius auratus*)

MacKinnon, M., G. Kampala, B. Marsh, P. Fedorak, and S. Guigard. 2005. Indicators for assessing transport of oil sands process-affected waters. *In* Bringing Groundwater Quality Research to the Watershed Scale. Edited by N.R. Thomson. IAHS Publication 297 (July 2005). ISBN 1-901502-18-X.

Mahaffey, K.R., R.P. Clickner, and C.C. Bodurow. 2004. Blood organic mercury and dietary mercury intake: national health and nutrition examination survey, 1999 and 2000. Environmental Health Perspectives **112**:562-570.

Mannix, A.E., D. Chokri, and W.L. Adamowicz. 2010. Water availability in the oil sands under projections of increasing demands and a changing climate: an assessment of the Lower Athabasca water management framework (Phase 1). Canadian Water Resources Journal **1**:29-52.

Martinez-Palou, R., M. de Lourdes Mosqueira, B. Zapata-Rendon, E. Mar-Juarez, C. Bernal-Huicochea, J.C. Clavel-Lopez, and J. Aburto. 2011.

Transportation of heavy and extra-heavy crude oil by pipeline: a review. Journal of Petroleum Science and Engineering **75**:274-282.

McKeown-Eyssen, G.E., J. Ruedy, and A. Neims. 1983. Methyl mercury exposure in northern Quebec II. neurologic findings in children. American Journal of Epidemiology **118**:470-479.

Mergler, D., H.A. Anderson, L. Hing Man Chan, K.R. Mahaffey, M. Murray, M. Sakamoto, and A.H. Stern. 2007. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio **36**:3-11.

Murata, K., M. Sakamoto, K. Nakai, P. Weihe, M. Dakeishi, T. Iwata, X. Liu, T. Ohno, T. Kurosawa, K. Kamiya, and H. Satoh. Effects of methylmercury on neurodevelopment in Japanese children in relation to the Madeiran study. International Archives of Occupational Health **77**:571-579.

Myers, G.J., P.W. Davidson, C. Cox, C. Shamlaye, E. Cernichiari, and T.W. Clarkson. 2000. Twenty-seven years studying the human neurotoxicity of methylmercury exposure. Environmental Research Section A **83**:275-285.

Myers, G.J., and P.W. Davidson. 2000. Does methylmercury have a role in causing developmental disabilities in children? Environmental Health Perspectives **108**:413-420.

Nero, V., A. Farwell, A. Lister, G. Van Der Kraak, L.E.J. Lee, T. Van Meer, M.D. MacKinnon, and D.G. Dixon. 2006. Gill and liver histopathological changes in yellow perch (*Perca flavescens*) and goldfish (*Carassius auratus*) exposed to oil sands process-affected water. Ecotoxicology and Environmental Safety **63:**365-377.

Nielsen, S.E., E.M. Bayne, J. Schieck, J. Herbers, and S. Boutin. 2007. A new method to estimate species and biodiversity intactness using empirically derived reference conditions. Biological Conservation **137**:101-113.

Orihel, D.M., M.J. Paterson, P.J. Blanchfield, R.A. Bodaly, and H. Hintelmann. 2007. Experimental evidence of a linear relationship between inorganic mercury loading and methylmercury accumulation by aquatic biota. Environmental Science and Technology **41**:4952-4958.

OSDC (Oil Sands Discovery Center). Facts about Alberta's oil sands and its industry. http://history.alberta.ca/oilsands/resources/docs/facts_sheets09.pdf accessed March 17, 2011.

Park, S., and M.A. Johnson. 2006. Awareness of fish advisories and mercury exposure in women of childbearing age. Nutrition Reviews **64**:250-256.

Pollet, I., and L.I. Bendell-Young. 2000. Amphibians as indicators of wetland quality in wetlands formed from oil sands effluent. Environmental Toxicology and Chemistry **19**:2589-2597.

Price, M. 2008. 11 Million Litres a Day: The Tar Sands' Leaking Legacy. Environmental Defence, Toronto.

Puttaswamy, N., D. Turcotte, and K. Liber. 2010. Variation in toxicity response of *Ceriodaphnia dubia* to Athabasca oil sands coke leachates. Chemosphere **80:**489-497.

Regional Aquatics Monitoring Program. 2009. Final 2008 Technical Report. Hatfield Consultants, Stantec Consulting Ltd., Klohn Crippen Berger Ltd., and Western Resource Solutions.

Royal Society of Canada (RSC). 2010. The Royal Society of Canada Expert Panel: Environmental and health impacts of Canada's oil sands industry. December 2010. Ottawa, Ontario.

Schindler, D.W., R.H. Hesslein, and R. Wagemann. 1980. Effects of acidification on mobilization of heavy metals and radionuclides from the sediments of a freshwater lake. Canadian Journal of Fisheries and Aquatic Sciences **37**:373-377.

Schindler, D.W., W.F. Donahue, and J.P. Thompson. 2007. Running out of steam? Oil sands development and water use in the Athabasca River - Watershed: science and market based solution. Environmental Research and Studies Centre. University of Alberta. 58 pp.

Schroeder, W.H., and J. Munthe. 1998. Atmospheric mercury - an overview. Atmospheric Environment **32**:809-822.

Smits, J.E., M.E. Wayland, M.J. Miller, K. Liber, and S. Trudeau. 2000. Reproductive, immune, and physiological end points in tree swallows on reclaimed oil sands mine sites. Environmental Toxicology and Chemistry **19:**2951-2960.

Stemenkovic, J., and M.S. Gustin. 2009. Nonstomatal versus stomatal uptake of atmospheric mercury. Environmental Science and Technology **43**:1367-1372.

Timoney, K.P. and P. Lee. 2009. Does the Alberta tar sands industry pollute? The scientific evidence. The Open Conservation Biology Journal **3:**65-81.

Ullrich, S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: a review of factors affecting methylation. Critical Reviews in Environmental Science and Technology **31**:241-293.

Vitousek, P.M. 1994. Beyond global warming: ecology and global change. Ecology **75:**1861-1876.

Wayland, M., J.V. Headley, K.M. Peru, R. Crosley, and B.G. Brownlee. 2008. Levels of polycyclic aromatic hydrocarbons and dibenzothiophenes in wetland sediments and aquatic insects in the oil sands area of Northeastern Alberta, Canada. Environmental Monitoring and Assessment **136**:167-182.

Wheatley, B., and M.A. Wheatley. 2000. Methylmercury and the health of indigenous peoples: a risk management challenge for physical and social sciences and for public health policy. The Science of the Total Environment **259**:23-29.

WHO. 1990. Environmental health criteria 101: methylmercury. Geneva. International Program on Chemical Safety, World Health Organization.

Wiener, J.G., D.P. Krabbenhoft, G.H. Heinz, and A.M. Scheuhammer. 2003. Ecotoxicology of mercury in: Handbook of Ecotoxicology, 2nd edition. Lewis Publishers, Boca Raton. CRC Press. Pg. 409-422.

Yasuda, N., N.R. Thomson, and J.F. Barker. 2010. Performance evaluation of a tailings pond seepage collection system. Canadian Geotechnical Journal **47**:1305-1315.

Chapter 3: Mercury in the Athabasca River, its tributaries, and its watershed

Introduction

Rapid expansion of crude oil production from the Alberta oil sands has generated widespread concern regarding the potential impact of oil sands development on the Athabasca River and its watershed. Bitumen production increased from 482,000 to 1.3 million barrels/day between 1995 and 2008 and is expected to double by 2020 (ERCB 2009). As a result of increasing production, reported annual mercury emissions from oil sands operations have more than quadrupled within the last decade, increasing from 32 kg in 2000 to 140 kg in 2010 (NPRI 2012). The purpose of this study is to assess concentrations of total mercury (THg) in water of the Athabasca River and its tributaries and in snow and vegetation samples of the Athabasca watershed to determine the geographic distribution of mercury in the oil sands region.

Oil sand is composed of bitumen, sand, shale, clay, carbonates, and/or water (ERCB 2009) as well as toxic components such as naphthenic acids, polycyclic aromatic compounds (PAC), and trace elements such as arsenic, lead, and mercury (Price 2008). Mercury is released during all stages of oil sands development. It has been shown that increased loadings of polycyclic aromatic hydrocarbons to the Athabasca River and its tributaries are associated with landscape disturbance related to oil sands mining due to increases in erosion and sedimentation rates (Kelly et al. 2009); therefore, it is likely that landscape

disturbance also mobilizes mercury that has been sequestered in soils within the Athabasca watershed to the Athabasca River. During open-pit mining, peatlands are destroyed as they are removed as overburden (Rooney et al. 2012). The destruction of peatlands has been shown to exacerbate the effects of increased mercury loadings as the degradation of peatland and other land disturbances enhance dissolved organic carbon (DOC) flux to aquatic systems (Gueguen et al. 2011; Timoney and Lee 2011), which may lead to increased downstream mercury concentrations, as DOC mediates the transport of mercury through watersheds (Grigal 2002; Ward et al. 2010).

During the processing and upgrading of oil sands, mercury is released through coking, coke combustion, and through the production of wastes and fly ash that contain mercury (NPRI 2012). In 2008, the year this study was conducted, oil sands companies that were operational and reporting emissions released 85 kg of mercury (NPRI 2012), ranking oil sands as the fifth highest industrial emitter of mercury in Canada (RSC 2010). Land disturbance associated with oil sands development increases erosion and sedimentation, mobilizing contaminants sequestered in soils of the watershed to the Athabasca River (Kelly et al. 2009). In addition to these sources, tailings ponds leak an unknown volume of tailings wastes that contain mercury and other contaminants of concern directly into the Athabasca River (Price 2008).

Inorganic mercury that enters aquatic systems is available for conversion to methylmercury (MeHg) (Jensen and Jernelov 1969) and, once converted, enters the food web rapidly (Jernelov and Lann 1971). MeHg is a neurotoxic,

bioavailable form of mercury that bioaccumulates and biomagnifies within organisms and food webs (Compeau et al. 1985). Dietary intake of MeHg through consumption of fish is the primary exposure route for human populations (Agah et al. 2010) and is responsible for the majority of fish consumption advisories in North America (USEPA 1998). A fish consumption advisory is in place for walleye (*Sander vitreus*) in the Athabasca River downstream of oil sands development (Alberta Government 2012) and exceedances of Health Canada guidelines have been reported in larger specimens of other predatory fish species within the region (northern pike, *Esox lucius*; Donald et al. 1996; RAMP 2009).

At the time of this study, the Alberta government and oil sands companies claimed that oil sands development did not contribute substantial loadings of mercury to the region and that any increases in mercury in the Athabasca River and its tributaries were due to natural erosion of oil sand formations. To test these claims, an assessment of mercury concentrations in water of the Athabasca River, its tributaries, the Athabasca Delta and Lake Athabasca was conducted in the winter and summer of 2008. Deposition of mercury to the Athabasca watershed was assessed through the collection of integrated snowpack samples near the end of winter in 2008. An estimate of annual deposition was obtained through extrapolation of the data to the entire year to facilitate comparison to NPRI estimates. White spruce (*Picea glauca*) was sampled during the winter of 2008, and white spruce and willow (*Salix spp.*) were sampled during the summer of 2008 to further examine the distribution of mercury in the Athabasca watershed.

Materials and Methods

Study Design

The Athabasca River is exposed to the McMurray geologic formation 50 km upstream of Fort McMurray north to Eymundson Creek (Figure 3.1). Sites on the Athabasca River, Athabasca Delta, and Lake Athabasca were sampled upstream and downstream of oil sands mining and processing activity (Figure 1.1). All sites near oil sands development are exposed to the McMurray geologic formation, as this is where the richest oil sand deposits are located.

Using 2006 Landsat imagery, 3 sites were selected along each of 4 tributaries affected by oil sands development (Steepbank, Muskeg, Beaver and Tar Rivers) and along 2 undeveloped reference tributaries (Firebag and Ells Rivers). The Steepbank, Muskeg and Firebag tributaries drain from the east while the Beaver, Tar, and Ells tributaries drain from the west. Along each tributary, the first site was located upstream of oil sands development and the McMurray formation, the second site was located within the McMurray formation and upstream of oil sands development, and the third site was located at the stream mouth above the confluence with the Athabasca River, downstream of oil sands development and either downstream of or within the McMurray formation. This sampling design allowed inputs from oil sands development to be distinguished from natural inputs derived from erosion of oil sands formations and other natural processes.

Field Sampling

Snow

In March of 2008, an integrated snowpack sample was collected at each of 12 sites along the Athabasca River, Athabasca Delta, Western Lake Athabasca, and from 19 tributary sites to assess the spatial distribution of Hg deposition to the Athabasca watershed. Samples were collected close to the middle of the river, and a duplicate sample was collected at one site (site MU1). A plastic shovel was used to dig a pit at each sampling site to expose the snowpack from the surface to the river ice. A Teflon scraper was then used to remove the snow from the pit face that had come into contact with the shovel. A Teflon knife and scoop were used to transfer an integrated snow sample into acid-washed 2 L Teflon jars. Samples were transported to the lab and remained frozen until analysis. To calculate the aerial deposition rate of Hg, snow density, and snow water equivalents for each site, five integrated snow cores were collected in close proximity to the pit at each site and were weighed and measured.

Vegetation

To compare the spatial distribution of Hg in the Athabasca watershed across seasons, vegetation samples were collected in the winter and summer of 2008 along a northward transect beginning south of Fort McMurray and extending north to Fort Chipewyan. Vegetation sampling sites were co-located with water and snow sampling sites. The most recent year of growth, the growth extending

from the most terminal node, was collected from white spruce trees (*Picea glauca*) in March (n = 32) and July (n = 39). To determine if the spatial distribution of Hg differed between coniferous and deciduous species, willow trees (*Salix spp.*) were also sampled in July of 2008 (n = 39). Pruning shears were used to cut stems directly into Ziploc bags. Samples were placed on dry ice until transported to the laboratory and remained frozen until analysis.

Water

In February and June of 2008, unfiltered water samples were collected from the main stem of the Athabasca River (n = 17) at sites upstream of oil sands development (n = 3; AR17, AR2, AR3, Figure 3.1), at development (n = 7; AR16, AR4, AR5, AR6, AR7, AR8, AR15, Figure 3.1), downstream of oil sands development and in the Athabasca Delta (n = 6; AR9, AR10, AR18, AR11, AR14, AR12, Figure 3.1), and at one Lake Athabasca site (n = 1; AR13, Figure 3.1). Unfiltered water samples were also collected from tributary sites (n = 20) in February and June of 2008. The mouth of the Horse River was sampled in winter only and nine additional stream mouth sites were sampled in summer only (AR17down, AR17up, Clarke, Poplar, Mclean, Fort, and Eymundson Creeks and MacKay and Calumet Rivers; Figure 3.1).

All samples were collected using an ultraclean sampling protocol (St. Louis et al. 1995). Samples were collected using sterile amber glass bottles with Teflon-lined caps during the summer sampling campaign and in sterile Teflon bottles during the winter sampling campaign. All samples were acidified 500:1

with concentrated trace metal grade hydrochloric acid (HCl) in the field. Duplicates, a trip blank, and field blanks were included for both field trips.

Sample Preparation and Analysis

Water and Snow

In the laboratory, snow samples were melted in the dark to avoid photoreduction and subsequent loss of mercury from samples. The resulting melt water was shaken and 125 mL was poured into acid-cleaned amber glass bottles with Teflon-lined caps. The remainder was filtered using an acid-washed disposable Nalgene filter apparatus pre-fitted with a 0.45 μm cellulose nitrate filter. Filtered and unfiltered samples were acidified 500:1 with concentrated trace metal grade HCl. Total Hg in unfiltered water and snow samples and filtered snow samples was determined using cold vapour atomic fluorescence spectrometry (CVAFS) at the University of Alberta Low-Level Mercury Analytical Laboratory. All snow samples were analyzed in duplicate. 10% of water samples were analyzed in duplicate. The detection limit was 0.02 ng/L.

Vegetation

Hg concentrations differ among various plant tissues (Shaw and Panigrahi 1986), so only needles or leaves of vegetation samples were analyzed. Needles and leaves of spruce and willow samples were removed from stems using ethanol-rinsed sterile scissors. To obtain within-tissue concentrations only, needles and leaves were washed with distilled de-ionized water to remove particulates (Rea et

al. 2000). Because there was a high volume of precipitation throughout the summer field sampling campaign, particulate mercury was removed to control for the variability in mercury concentrations resulting from variability in precipitation between some sites (i.e., variability in removal of particulate mercury by precipitation). Winter samples received the same treatment. Willow leaves and spruce needles were freeze-dried for 48 and 96 hours, respectively. Samples were homogenized into a fine powder using an ethanol-rinsed sterile glass mortar and pestle.

A subsample of the resultant powder was analyzed for THg at the University of Alberta Low-Level Mercury Analytical Laboratory. Samples were weighed into Teflon bombs and 7 mL of a 7:3 trace metal grade HNO_3 and H_2SO_4 mixture was added. Bombs were wrench-tightened and baked for 2 hours in a 130°C oven. After cooling to room temperature, 19 mL of MilliQ water and 1 mL of BrCl was added to each bomb. Total mercury was measured using BrCl oxidation, $SnCl_2$ reduction, purge and trap, and cold vapour atomic fluorescence spectrometry (CVAFS) (modified (USEPA 1996, Olson et al. 1997)). The detection limit was 0.02 ng/L for snow and water, and 0.02 ng/g for vegetation. Sample blanks, spike recoveries, standard reference materials (National Research Council of Canada), and duplicates were included for all mercury analyses. The relative percent difference between duplicates was 10% or less.

GIS Analysis

Catchments were identified using a 50 m shuttle radar topography mission digital elevation model (Jarvis et al. 2008) and the area of the catchment was calculated for each site. Digital disturbance and geologic formation data were used to calculate the proportion of each catchment within the McMurray formation, overall surface land disturbance, and land disturbance attributable to oil sands development in 2008. Change analysis of forest ecozones within Alberta (1991-2001), Canada access data (roads, mines, forest fragments, and reservoirs buffered by 500 m), and extent of oil sands development in 2008 data from Global Forest Watch were extracted within each catchment and areas were calculated.

2008 Landsat imagery revealed that some midstream and stream mouth sites that had been classified as undeveloped based on Landsat 2006 imagery had been developed by 2008. Based on overall surface land disturbance data, each watershed was classified as either more disturbed (>25%) or less disturbed (<25%) to assess the effects of development on the Athabasca River and its tributaries.

Disturbance and geology data were only available for Alberta; however, the catchments of 19 sites extend outside of Alberta, so only the Alberta portion of the catchment was included in analyses. This was the case for the Firebag River and some Athabasca River sites that contain tributaries that originate in Saskatchewan (AR2, AR3, AR4, AR5, AR6, AR7, AR8, AR9, AR10, AR11, AR12, AR13, AR14, AR15, AR16, AR18, FR1, FR2, and FR3).

Statistical Analyses

All Data Sets

The distribution of all data sets was examined using Shapiro-Wilk and Kolmogorov-Smirnov tests in addition to visual inspection of histograms. Mercury concentrations in water, snow and vegetation pooled across all sites deviated from a normal distribution, and were natural log transformed to meet the assumptions of normality and equal variance for ANOVA.

Snow

The source of THg in accumulated snow was determined by graphing concentrations or deposition of dissolved and particulate THg vs. radial distance from site AR6 (location of upgrading facilities, distances were calculated using ArcGIS). Graphical inspection was then used to classify concentrations and loadings into four categories or distribution types: *(Type I Distribution)* exponential decline with increasing distance from AR6; *(Type II Distribution)* exponential decline with increasing distance from AR6 and additional local sources within the oil sands development area; *(Type III Distribution)* only local sources within the oil sands development area; or *(Type IV Distribution)* dissolved concentrations were below detection limits at all sites, so loadings were not calculated or particulates were not present, in which total THg minus dissolved THg would equal zero and there is no significant mercury loadings to our sampling locations resulting from oil sands development. These designations were

verified using exponential regression of mercury concentration with distance from AR6.

Calculation of the total mass of elements inferred from snowpack samples was completed in two steps, as described in Kelly et al. (2010). First, the samples results expressed on a mass per unit area (m^2) basis were regressed against distance from AR6 (which was calculated using ArcGIS), with distance as the independent variable. The functional relationship between element mass per unit area (m) and distance (x) was assumed to follow a declining exponential, expressed as:

$$m = A\exp(-kx) \qquad \textbf{(1)}$$

Here k is the decay constant indicating the rate that deposition per unit area declines with distance from AR6, and A is the deposition at AR6 (where x = 0).

The constants A and k are estimated by taking the natural logarithm of equation 1, giving $\ln m = \ln A - kx$), and then applying simple linear regression using our observed data for m and x. The constant A may then be obtained by taking the antilogarithm of the intercept of the regression equation estimated from the data, and k is the slope.

Second, the total deposition is calculated by finding the integrated deposition within a circle centered on site AR6 and extending to a distance where the data indicate the deposition is above background, usually 46 km. Assuming data is isotropic, this may be calculated by integrating the product of equation 1 above and the circumference of a circle distance x from AR6:

$$M = 2\,\pi A \int x e^{-kx}\, dx \qquad \textbf{(2)}$$

Where M is equal to the total mass deposited within the circle, that is usually 46 km. The result of the definite integral indicated in equation 2 is:

$$M = 2\,\pi A\,(1 - (kx + 1)e^{-kx}/k^2) \qquad \textbf{(3)}$$

The value for M then results from substituting x = 46 km (or whatever distance the data indicate that deposition is above background) into equation 3 (after expressing A in units of mg/km^2).

Sites within 46km of upgrading facilities located at AR6 were designated as near development (ND) and sites located outside of this radius were designated as background (BG) sites. The boundary between designation as ND or BG was defined as the point where a marked decrease in deposition was observed at sites ND and consistent deposition was observed at BG sites. If elevated concentrations were observed at sites located far from development, they were attributed to local sources unrelated to oil sands development, such as the airport in Fort Chipewyan, and were designated as BG. Two sample t-tests were used to compare concentrations and deposition of dissolved and particulate THg at BG and ND sites.

Vegetation

THg concentrations in spruce in summer and winter were compared using a two-sample t-test to examine seasonal differences in THg in vegetation. The within tissue concentrations of THg in willow and spruce were examined using a

two-sample t-test to compare differences in mercury uptake by deciduous versus coniferous species.

THg concentrations in tissues of vegetation were graphed and regressed against distance in km from AR6 (location of upgrading facilities, distances were calculated using ArcGIS). The same site designations that were used for snow samples were used to classify sites as background or near development. Two sample t-tests were used to compare THg concentrations at BG and ND sites.

THg concentrations in snow likely reflect deposition of particulate mercury as particulate mercury is efficiently scavenged by precipitating snow while gaseous mercury is inefficiently scavenged (Amos et al. 2012). Further, gaseous forms of mercury are deposited at greater distances from point sources than particulate mercury (Iverfeldt and Lindqvist 1986) and stack plumes within the region have been observed at distances greater than 46 km downwind of upgrading facilities (Lusis et al. 1979). For these reasons, THg concentrations in vegetation were examined further at a finer spatial resolution by comparing sites within 46 km of development, sites between 46 and 150 km, and sites more than 150 km downwind. Due to low sample sizes at this finer resolution scale, differences in vegetation THg concentrations could not be tested using formal statistics; therefore, general trends are described.

Water

THg concentrations were regressed against the proportion of the catchment within the McMF, overall land disturbance, and oil sands disturbance

to compare the relative inputs of natural erosion and mining development to THg concentrations within the Athabasca River and its tributaries. Statistical analyses were conducted for all tributary sites combined and separately for Athabasca River sites.

The relative contributions of natural erosion and land disturbance to THg concentrations were examined further in six tributaries using general linear models. THg concentrations at sites upstream of the McMF and oil sands development were compared to concentrations at midstream and downstream sites in winter and summer. A relative index of overall land disturbance based on the percentage of the catchment disturbed by development was used to classify midstream and downstream sites as more (>25%) or less (<25%) disturbed, and the effect of overall disturbance was compared. The effect of overall land disturbance on THg concentrations at midstream versus downstream sites was also assessed seasonally. To determine if THg concentrations at midstream and downstream tributary sites differed independently of overall land disturbance, THg concentrations were compared between all midstream and downstream sites in winter and summer.

The same approach was used to assess spatial patterns of THg concentrations in water from the Athabasca River. THg concentrations in the main stem of the Athabasca River at sites upstream of development, near development, and downstream of development were compared in winter and summer using a general linear model and one-way ANOVA.

Results

Mercury in Snowpack

Deposition of particulate THg displayed a type I deposition pattern (Figure 3.2a) while dissolved THg exhibited a type III pattern (Figure 3.2c). Deposition of particulate THg was significantly higher than deposition of dissolved THg ($p < 0.001$, $t = -8.415$, $df = 60$). Integrated annual deposition of particulate THg within a 46 km radius of AR6 totaled 1.1 kg compared to 0.16 kg of dissolved THg.

Deposition of particulate THg decreased exponentially with increasing distance from AR6 (Figure 3.2a) and was significantly higher at sites near development (sites located within 46 km of site AR6) compared to background sites ($p < 0.001$, $t = -4.101$, $df = 29$; Figure 3.3). Average particulate THg deposition was 5.6 times higher at sites near development relative to background sites (Figure 3.3). Concentrations of particulate THg displayed the same trend ($p = 0.003$, $t = -2.852$, $df = 29$; Figure 3.2c); however, because snow depth and density varied between sites, the site with the greatest deposition of particulate THg was not the site where the highest concentration of particulate THg was observed. The maximum deposition of particulate THg occurred at the site with the highest snow water equivalent, MU3, located 46 km north of site AR6 (861 ng/m^2), whereas the maximum concentration occurred at site AR16 (10.4 ng/L), 8 km south of AR6. Both the minimum deposition of particulate THg and the minimum concentration of particulate THg occurred at site AR18 (deposition = 20.2 ng/m^2, concentration = 0.4 ng/L), 160 km north of AR6.

Deposition of dissolved THg remained elevated at greater distances from AR6 compared to particulate THg (Figure 3.2b) and was significantly higher at sites near development compared to background sites ($p = 0.016$, $t = -2.227$, $df = 29$; Figure 3.3). Average dissolved THg deposition was 3.3 times higher at sites near development relative to background sites (Figure 3.3). Concentrations of dissolved THg were elevated near development and decreased with increasing distance from AR6 with the exception of one site near Fort Chipewyan, likely reflecting local sources of emissions unrelated to oil sands development (Figure 3.2d). Concentrations of dissolved THg were significantly higher at sites near development relative to background sites ($p < 0.001$, $t = -5.65$, $df = 29$). Similar to particulate THg, the site where the maximum deposition of dissolved THg was observed did not correspond to the site where the maximum concentration of dissolved THg was observed. The maximum deposition of dissolved THg occurred at site MU3 (71.61 ng/m^2), 14 km from AR6 while the maximum concentration occurred at site MU2 (0.633 ng/L), 41 km away from site AR6. The minimum deposition of dissolved THg occurred at site TR1 (4.95 ng/m^2), 63 km from AR6 while the minimum concentration (0.137 ng/L) was observed at site AR1, 33 km south of AR6.

Mercury in Vegetation

Mean concentrations of THg within spruce (9.14 ng/g) were significantly higher than in willow (7.39 ng/g; $p = 0.007$, $t = 2.762$, $df = 80$; Figure 3.4).

Concentrations in spruce did not differ significantly in winter (9.96 ng/g) and summer (9.14 ng/g; $p = 0.111$, $t = 1.615$, $df = 70$).

Patterns of THg concentrations in vegetation showed little association with distance from oil sands development. THg concentrations in vegetation were not significantly related to distance from upgrading facilities located at AR6 in white spruce in winter ($r^2 = 0.012$, $p = 0.554$, $df = 30$; Table 3.1) or summer ($r^2 = 0.01$, $p = 0.526$, $df = 40$; Table 3.1), or in willow in summer ($r^2 < 0.000$, $p = 0.560$, $df = 40$; Table 3.1).

Concentrations of THg at sites located near oil sands development were not significantly different from concentrations at background sites for white spruce in winter ($p = 0.117$, $t = -1.619$, $df = 28$) or summer ($p = 0.386$, $t = -0.880$, $df = 29$) or in willow in summer ($p = 0.141$, $t = -1.513$, $df = 29$).

When concentrations were compared at sites within 46 km, between 46 and 150 km, and greater than 150 km from AR6, mean concentrations of THg in the tissues of willow were relatively similar at all spatial scales (within 46 km = 7.04 ng/g; 46 - 150 km = 8.58 ng/g; >150 km = 7.67 ng/g; Figure 3.4). Concentrations of THg in white spruce in winter and summer were elevated within 46 km of oil sands development (9.48 ng/g and 8.62 ng/g, respectively) relative to sites more than 150 km downwind (9.96 ng/g and 6.61 ng/g, respectively); however, the highest concentrations occurred at sites between 46 and 150 km from AR6 (11.75 ng/g and 11.88 ng/g, respectiely; Figure 3.4).

Mercury in Water of the Athabasca River and its Tributaries

Concentrations of THg in the main stem of the Athabasca River were not significantly related to the proportion of McMurray formation within the catchment of the site (summer: $r^2 = 0.141$, $p = 0.286$, $df = 9$; winter: $r^2 = 0.072$, $p = 0.453$, $df = 9$; Table 3.2), overall land disturbance (summer: $r^2 = 0.132$, $p = 0.303$, $df = 9$; winter: $r^2 = 0.093$, $p = 0.391$, $df = 9$; Table 3.2), or to land disturbance attributable to oil sands development (summer: $r^2 = 0.310$, $p = 0.095$, $df = 9$; winter: $r^2 = 0.091$, $p = 0.396$, $df = 9$; Table 3.2).

THg concentrations in the Athabasca River were significantly greater in summer (7.47 ng/L) relative to winter (0.94 ng/L; General Linear Model, $p < 0.001$, $F = 198.547$, $df = 31$; Figure 3.6).

Mean THg concentration in Athabasca River water was 3.26 ng/L at sites upstream of development, 10.54 ng/L at sites at oil sands development, 6.58 ng/L at sites downstream of oil sands development and in the Athabasca Delta, and 3.94 ng/L at one Lake Athabasca site. In summer, THg concentrations in Athabasca River water displayed a significant spatial trend (one-way ANOVA, $p = 0.002$, $F = 10.969$, $df = 15$; Figure 3.6). THg concentrations were 3.2 times higher in water at sites at oil sands development relative to concentrations at sites upstream of development (Tukey's multiple comparison, $p = 0.002$). THg concentrations in water at sites downstream of development were twice as high as upstream sites; however, the increase was not statistically significant at an alpha = 0.05 (Tukey's multiple comparison, $p = 0.092$). The concentration of THg at the only site located on Lake Athabasca was 1.2 times higher than concentrations at

sites upstream of oil sands development. Mean THg concentration in the Athabasca River in winter was 0.67 ng/L at sites upstream of development, 1.11 ng/L at sites at sites near oil sands development, 0.97 ng/L at sites downstream of oil sands development and in the Athabasca Delta, and 0.43 ng/L at one Lake Athabasca site. In winter, THg concentrations along the Athabasca River did not display a significant spatial trend (one-way ANOVA, $p = 0.214$, $F = 1.741$, $df = 15$; Figure 3.6). However, relative to sites upstream of oil sands development, THg concentrations were 1.7 and 1.5 times greater near oil sands development and downstream of oil sands development, respectively.

Concentrations of THg in tributaries were not significantly related to the proportion of McMF within the catchment of the site (summer: $r^2 = 0.058$, $p = 0.217$, $df = 27$; winter: $r^2 = 0.004$, $p = 0.785$, $df = 19$; Table 3.3), overall land disturbance (summer: $r^2 = 0.005$, $p = 0.721$, $df = 27$; winter: $r^2 = 0.024$, $p = 0.517$, $df = 19$; Table 3.3), or to land disturbance attributable to oil sands development (summer: $r^2 = 0.009$, $p = 0.625$, $df = 27$; winter: $r^2 = 0.047$, $p = 0.357$, $df = 19$; Table 3.3).

Mean THg concentrations in tributaries in summer were 2.07 ng/L at upstream sites, 2.11 ng/L at midstream sites, and 4.17 ng/L at stream mouth sites. Mean THg concentrations in tributaries in winter were 1.36 ng/L at upstream sites, 1.53 at midstream sites, and 0.99 ng/L at stream mouth sites.

Concentrations of THg did not increase significantly from upstream sites outside the McMF to midstream and stream mouth sites within the McMF in summer or winter (general linear model, $p = 0.867$, $F = 0.143$, $df = 35$; Figure

3.7). At all sites combined, THg concentrations were higher in summer (3.87 ng/L) than in winter (1.32 ng/L; general linear model, $p = 0.004$, $F = 9.486$, $df = 35$; Figure 3.7). THg concentrations at midstream and stream mouth sites were not significantly different ($p = 0.867$, $F = 0.029$, $df = 34$). However, THg concentrations were significantly higher at midstream and stream mouth sites with >25% overall land disturbance relative to midstream and stream mouth sites with <25% overall land disturbance (general linear model, $p = 0.038$, $F = 4.719$, $df = 34$; Figure 3.8). Mean THg concentrations in winter were 0.7 ng/L at less disturbed sites and 1.46 ng/L at more disturbed sites. In summer, mean THg concentrations were 1.8 ng/L at less disturbed sites and 5.4 ng/L at more disturbed sites. THg concentrations at more disturbed sites were 2.1 times greater than less disturbed sites in winter, and were 3.0 times greater in summer (general linear model, $p = 0.002$, $F = 11.755$, $df = 34$).

Discussion

Mercury in the Athabasca Watershed

The results of the current study indicate that oil sands upgrading facilities are a significant source of mercury within the Athabasca watershed. Concentrations and deposition of particulate mercury in snow declined exponentially with increasing distance from AR6. The efficient scavenging of particulate mercury by precipitating snow and the high gravitational deposition of heavier particles results in a bull's-eye pattern observed around upgraders and smelters (Goodarzi et al. 2002), with concentrations declining exponentially with

increasing distance from the point source. Deposition of particulate mercury was 5.6 times higher at sites near development relative to background sites, and an estimated annual deposition of 1.1 kg of particulate mercury was deposited within a 46 km radius of AR6. While concentrations and total deposition of particulate mercury decreased exponentially with increasing distance from AR6, concentrations and deposition of dissolved mercury remained elevated outside the 46 km radius impacted by oil sands development. The source of this mercury is likely local/secondary sources related to oil sands development, such as road dust, mining, land clearing, and other emissions, or mercury sorbed to fine particles or aerosols that can be deposited 100's of kilometers from their source.

Snow surveys conducted during 1978 and 1981 in the oil sands region concluded that increased deposition of heavy metals 25 km north and south and 10 km east and west of upgrading facilities were attributable to the rapid deposition of non-volatile flyash constituents, while over 98% of volatile oxides were deposited outside of this boundary (Barrie and Kovalick 1980; Murray 1981). In the current study, significant deposition of particulate mercury was observed near upgrading facilities; however, the estimate of annual mercury deposition integrated within a 46 km radius centered on AR6 was 96% lower than reported annual emissions in 2008 (NPRI 2012). This suggests that only a small portion of emitted mercury is deposited in the immediate vicinity of development, while more volatile forms produced within stacks are deposited outside of this radius, which is consistent with the known long-range atmospheric transport of mercury (Schroeder and Munthe 1998).

Studies of mercury speciation in flue gases suggest that the mercury emitted to the atmosphere is roughly equally partitioned between elemental mercury (Hg°) and divalent forms (Hg(II)) (as reviewed by Galbreath and Zygarlicke 1996). As the composition and partitioning of mercury species within emission plumes released from oil sands upgraders has not been assessed, it was assumed that the partitioning of mercury within upgrader stack plumes would be similar to other emission plumes. Hg(II) compounds are non-volatile and partition between the gas and particulate phases (Amos et al. 2012) and are subsequently removed from the atmosphere through dry and wet deposition (Schroeder and Munthe 1998). Hg(II) readily adsorbs to particulates and aerosols within the atmosphere and is deposited locally. Precipitating snow efficiently scavenges particulate Hg(II) and inefficiently scavenges gas-phase Hg(II) (Amos et al. 2012). Furthermore, up to 54% of deposited gaseous Hg(II) may be volatized and re-emitted to the atmosphere by photoreduction within 24 hours of a snowfall event (Lalonde et al. 2002) with concentrations decreasing by up to two-thirds with increasing time to re-emit mercury to the atmosphere (Nelson et al. 2008). Therefore, mercury concentrations and deposition in snow likely more reliably reflect deposition of particulate mercury than gaseous mercury (Nelson et al. 2010); this is likely the cause of the discrepancy between the current study's estimate of mercury deposition relative to reported NPRI emissions for the region (NPRI 2012).

The difference in mercury concentrations between spruce and willow are consistent with other studies that have reported species-specific differences in

mercury concentration (Rasmussen 1995; Hall and St. Louis 2004; Millhollen et al. 2006). These differences are likely due to other factors that differ between coniferous and deciduous species, such as physiology and geometry or structure (Obrist et al. 2012). Coniferous species are more structurally complex and the configuration of needles captures mercury species in the air more efficiently than the broad leaves of deciduous plants. Furthermore, the retention of captured mercury is higher for coniferous species as their cuticle sorbs mercury more strongly than the broad leaves of deciduous species that are efficiently washed by precipitation runoff.

Concentrations of mercury within the tissues of spruce and willow were not significantly related to distance from AR6 and concentrations near development were not significantly different from background sites. However, plume chemistry and dispersion studies conducted during the 1970s within the region reported plumes from Suncor's upgrading facilities extending more than 50 km downwind of the source (Lusis et al. 1978). When sites within 46 km of AR6 were compared to sites between 46 and 100 km and sites greater than 150 km downwind, tissue concentrations in both species and in winter and summer were elevated at sites within 46 km of development. However, tissue concentrations at sites between 46 and 150 km downwind were higher than concentrations at sites near development and near Lake Athabasca. While the simplest explanation for the observed trend is increased concentrations of atmospheric mercury derived from sources other than oil sands development downwind of development relative to sites located near development, this is unlikely given the mass of mercury

emitted by oil sands development (NPRI 2012). Alternatively, the trend may be attributable to differences in atmospheric composition between the two areas and its subsequent effects on mercury speciation.

While studies of mercury speciation within flue gas prior to emission suggest that emitted mercury is approximately equally partitioned between gaseous Hg° and Hg(II) species (as reviewed by Galbreath and Zygarlicke 1996), ambient downwind measurements suggest this composition is not retained within the emission plume (Edgerton et al. 2006). Immediately downwind of the stack, a reducing atmosphere is present as a result of high emissions of NO_x and SO_2 (NPRI 2012). High emissions of NO_x cause a decreased concentration of ozone (O_3) due to chemical scavenging, this results in the reduction of emitted Hg(II) to Hg^0 by SO_2 (Lohman et al. 2006; Vijayaraghavan et al. 2008). Reduction of Hg(II) to Hg° by SO_2 decreases wet and dry deposition by up to 40% in the immediate vicinity of the source (Vijayaraghavan et al. 2008). Downwind of the plume, increased concentrations of O_3 (Lusis et al. 1978) result in the oxidation of Hg° to Hg(II) (Iverfeldt and Lindqvist 1986; Hall 1995; Vijayaraghavan et al. 2008). Reactive gaseous mercury (RGM, all forms of gaseous Hg(II), such as $HgCl_2$, $Hg(OH)_2$, etc.) is highly surface reactive and is rapidly transferred to surface vegetation by both dry and wet deposition (Lindberg and Stratton 1998). Therefore, it is possible that lower concentrations of mercury within plant tissues near oil sands development compared to higher concentrations in vegetation at moderate distances from development is the result of decreased atmospheric concentrations and deposition of RGM to vegetation at sites near development.

The mechanism promoting these differences in atmospheric concentrations and deposition to the landscape is likely the presence of a reducing atmosphere at distances close to development compared to the presence of an oxidizing atmosphere at moderate distances (Figure 3.5).

In addition, THg concentrations in vegetation near development may also be lower than concentrations at moderate distances as a result of increased deposition of emitted Hg(II) as particulate mercury. Particulate mercury deposited to vegetation surfaces can be partially removed by subsequent precipitation events. In both winter and summer, a haze of particulates/aerosols was observed over the development area (personal observation and Figure S7 in Kelly et al. 2009). Hg(II) readily adsorbs to particulates/aerosols. Gas-particle partitioning modeling indicates that over 90% of Hg(II) partitions to the particulate phase in cold air containing high aerosol (Amos et al. 2012). Therefore, due to a high concentration of aerosols within the development area and northern climate, the majority of Hg(II) not reduced by SO_2 likely partitions into the particulate phase and is deposited locally (Figure 3.5). Subsequent precipitation events would remove a portion of this dry-deposited particulate mercury from vegetation (Rea et al. 2000). The loss of deposited particulate mercury from vegetation surfaces during precipitation events combined with a lower concentration (and therefore deposition) of gaseous Hg(II) near development may partially explain the lower concentration of THg in vegetation at sites near development compared to sites at greater distances from development. Further, our snow results indicated that only 4% of emitted mercury is deposited within a 46 km radius of oil sands

development. Therefore, the majority of emitted mercury is deposited at greater distances from development, which is consistent with the finding of higher concentrations of THg in vegetation at sites located further from development. This is consistent with the majority of emitted mercury being deposited outside of the immediate development area as a result of the long-range transport of Hg^0.

Mercury in the Athabasca River and its Tributaries

Prior to 2008, industry and government maintained that oil sands development had not resulted in increased concentrations of mercury and other contaminants of concern within the Athabasca River, and attributed any observed increases to natural inputs from erosion of the McMurray oil sand formation. However, in both main stem and tributary sites, THg concentrations were not significantly related to the proportion of the McMurray formation contained within the catchment of each site. Furthermore, concentrations of THg in tributaries did not increase significantly as water flowed through the McMurray formation from sites upstream of the deposit to midstream and stream mouth sites in either winter or summer (Figure 3.8). A comparison of heavy metal concentrations in bottom and suspended sediments at headwater, midstream, and stream mouth sites in three tributaries exposed to oil sands formation but not impacted by oil sands development showed that concentrations did not increase significantly as tributaries flowed through oil sands formations (Conly et al. 2007), consistent with the results of the current study. Therefore, it is likely that

natural erosion of the McMurray formation contributes only low loadings of THg to the Athabasca River and its tributaries.

Instead, results from the current study indicate that oil sands development is a significant source of THg to the Athabasca River and its tributaries. At tributary sites, THg concentrations were not significantly different at midstream sites relative to stream mouth sites; however, when midstream and stream mouth sites were classified by overall development within the catchment and compared, THg concentrations in tributaries with a greater extent of development were significantly higher than concentrations in less developed tributaries (Figure 3.8; Tukey's $p = 0.038$). If natural erosion of oil sands formations contributed substantial loadings of mercury to tributaries, water sampled from both midstream and stream mouth sites would show an increase in THg concentrations during winter, when atmospheric deposition and runoff cannot contribute to mercury loading in water bodies. Instead, THg concentrations in water decreased slightly from midstream to stream mouth sites during winter, though this difference was not statistically significant (Figure 3.7), likely due to low statistical power. In contrast, concentrations of mercury in summer almost double at stream mouth sites relative to midstream sites (Figures 3.7 and 3.8), implicating substantial inputs derived from oil sands related land disturbance and atmospheric deposition of emissions.

In the Athabasca River, THg concentrations under ice in winter did not display a significant spatial trend (Figure 3.6). However, in summer, when the river is not sealed off to atmospheric deposition of mercury and also receives

inputs from the watershed, concentrations near development increased significantly relative to upstream sites (Figure 3.6) and concentrations at downstream sites and one site in Lake Athabasca remained elevated relative to upstream sites (Figure 3.6). The distribution of THg in Athabasca River water corresponds to deposition of THg in snow and vegetation on the adjacent landscape, indicating possible substantial linkages between deposition of airborne emissions of THg to the Athabasca watershed and THg concentrations in Athabasca River water.

Forest soils represent a significant sink for mercury, as mercury deposited to forested areas is deposited as throughfall (Graydon et al. 2006; Graydon et al. 2012) and is also retained within the tissues of trees, which is subsequently deposited to forest soil as litterfall (Graydon et al. 2006; Graydon et al. 2012). Mercury sequestered in soils can be mobilized by runoff and act as a source of mercury to adjacent aquatic systems. Significant masses of contaminants emitted by oil sands development to the Athabasca region for over 40 years (Barrie and Kovalick 1980; Murray 1981) have increased mercury concentrations within aquatic sediments (Curtis et al. 2010) and have likely increased soil mercury concentrations within the region. The elevated concentrations of mercury in river water near oil sands development are likely derived from high inputs of historically and recently deposited mercury mobilized by land disturbance related to oil sands development, in addition to direct atmospheric deposition of emitted mercury to surface waters. However, due to an absence of long-term monitoring of concentrations of heavy metals and mercury in soil and ambient concentrations

in air within the region, the extent of these increases and subsequent impacts on river water concentrations over time is difficult to assess.

Despite past recommendations to Alberta Environment to regularly monitor contaminants in air and snow within the oil sands region (Barrie and Kovalick 1980; Murray 1981), heavy metals and mercury in air have not been regularly monitored (RSC 2010). While snow is sampled for hydrologic monitoring, contaminant concentrations within snow samples are not assessed (RAMP 2009). A limited number of studies conducted within the region indicate that concentrations of contaminants have increased over time. Concentrations of polycyclic aromatic hydrocarbons in Athabasca Delta sediments (Timoney and Lee 2011) and sediments in lakes within the region (Kurek et al. 2013) have increased since exploitation of the oil sands began. Increased mercury concentrations and fluxes in lake sediments within the last 20 years have also occurred (Curtis et al. 2010). However, a lack of reliable long-term monitoring of the emission, cycling, and fate of mercury within the oil sands region makes it difficult to determine to what extent oil sands development has increased mercury concentrations above background or pre-development levels.

Concentrations of mercury in some snow and water samples from tributary and Athabasca River sites near development exceeded guidelines for the protection of aquatic life. While mercury concentrations did not exceed drinking water quality guidelines, increased mercury deposition to the Athabasca River and its watershed may pose a health risk for human populations that fish and hunt within the region (Wheatley and Paradis 1995). Elsewhere, mercury

concentrations in fish have been shown to respond rapidly to increases in mercury deposition (Harris et al. 2007; Orihel et al. 2007), with Hg(II) that was deposited directly to aquatic systems entering the food web as methylmercury within weeks (Orihel et al. 2007). While this suggests fish may respond rapidly to decreased mercury inputs, newly deposited mercury is sequestered in soils shortly after deposition, but is exported from catchments slowly (Harris et al. 2007); therefore, 40 years of increased mercury deposition to soils within the oil sands region may be a significant source of mercury to aquatic food webs within the region for many years. Increased mercury concentrations in vegetation may result in higher tissue concentrations in consumer species such as deer and moose (Gnamus et al. 2000). The low efficiency of converting plant biomass into protein causes a higher consumption rate in terrestrial herbivores that can intensify metal intake and bioaccumulation in food webs within contaminated regions (Gnamus et al. 2000). Therefore, monitoring of contaminants within vegetation and wildlife species regularly consumed by people within downstream communities is essential.

Literature Cited

Agah, H., M. Leermakers, Y. Gao, S.M.R. Fatemi, M.M. Katal, W. Baeyens, and M. Elskens. 2010. Mercury accumulation in fish species from the Persian Gulf and in human hair from fishermen. Environmental Monitoring and Assessment **169**:203-216.

Amos, H.M., D.J. Jacob, C.D. Holmes, J.A. Fisher, Q. Wang, R.M. Yantosca, E.S. Corbitt, E. Galarneau, A.P. Rutter, M.S. Gustin, A. Steffen, J.J. Schauer, J.A. Graydon, V.L. St. Louis, R.W. Talbot, E.S. Edgerton, Y. Zhang, and E.M. Sunderland. 2012. Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition. Atmospheric Chemistry and Physics **12**:591-603.

Barrie, L.A., and J. Kovalick. 1980. A wintertime investigation of the deposition of pollutants around an isolated power plant in Northern Alberta. Prepared for the Alberta Oil Sands Environmental Research Program by Atmospheric Environment Service. AOSERP Report 90. 115 p.

Compeau, G.C., and R. Bartha. 1985. Sulfate-reducing bacteria: Principal methylators of mercury in anoxic estuarine sediment. Applied Environmental Microbiology **50**:498-502.

Conly, F.M., R.W. Crosley, J.V. Headley, and E.K. Quagraine. 2007. Assessment of metals in bed and suspended sediments in tributaries of the Lower Athabasca River. Journal of Environmental Science and Health Part A **42**:1021-1028.

Curtis, C.J., R. Flower, N. Rose, J. Shilland, G.L. Simpson, S. Turner, H. Yang, and S. Pla. 2010. Palaeolimnological assessment of lake acidification and

environmental change in the Athabasca Oil Sands Region, Alberta. Journal of Limnology **69(Suppl. I):**92-104.

Donald, D.B., H.L. Craig, J. Syrgiannis. 1996. Contaminants in environmental samples: mercury in the Peace, Athabasca and Slave River basins. Northern River Basins Study project report no. 105. Edmonton, Alberta.

Edgerton, E.S., B.E. Hartsell, and J.J. Jansen. 2006. Mercury speciation in coal-fired power plant plumes observed at three surface sites in the southeastern U.S. Environmental Science and Technology **40**:4563-4570.

Energy Resources Conservation Board (ERCB). 2009. Alberta's energy reserves 2008 and supply/demand outlook 2009-2018.

Galbreath, K.C., and C.J. Zygarlicke. 1996. Mercury speciation in coal combustion and gasification flue gases. Environmental Science and Technology **30**:2421-2426.

Gnamus, A., Byrne, A.R., and M. Horvat. 2000. Mercury in the soil-plant-deer-predator food chain of a temperate forest in Slovenia. *Environmental Science & Technology* **34**:3337-3345.

Goodarzi, F., H. Sanei, M. Labonte, and W.F. Duncan. 2002. Sources of lead and zinc associated with metal smelting activities in the Trail area, British Columbia, Canada. Journal of Environmental Monitoring **4**:400-407.

Government of Alberta. 2012. Alberta guide to sportfishing regulations.

Graydon, J.A., St. Louis, V.L., Lindberg, S.E., Hintelmann, H., D.P. Krabbenhoff. 2006. Investigation of mercury exchange between forest canopy

vegetation and the atmosphere using a new dynamic chamber. *Environmental Science & Technology* **40**:4680-4688.

Graydon, J.A., St. Louis, V.L., Lindberg, S.E., Sandilands, K.A., Rudd, J.W.M., Kelly, C.A., Harris, R., Tate, M.T., Krabbenhoft, D.P., Emmerton, C.A., Asmath, H., M. Richardson. 2012. The role of terrestrial vegetation in atmospheric Hg deposition: pools and fluxes of spike and ambient Hg from the METAALICUS experiment. *Global Biogeochemical Cycles* **26**:GB1022.

Grigal, D.F. 2002. Inputs and outputs of mercury from terrestrial watersheds: a review. Environmental Reviews **10**:1-39.

Gueguen, C., O. Clarisse, A. Perroud, and A. McDonald. 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). Journal of Environmental Monitoring DOI: 10.1039/c1em10563a.

Hall, B. 1995. The gas phase oxidation of elemental mercury by ozone. Water, Air, and Soil Pollution **80**:301-315.

Hall, B. and V.L. St. Louis. 2004. Methylmercury and total mercury in plant litter decomposing in upland forests and flooded landscapes. Environmental Science and Technology **38**:5010-5021.

Harris, R.C., J.W.M. Rudd, M. Amyot, C.L. Bablarz, K.G. Beaty, P.J. Blanchfield, R.A. Bodaly, B.A. Branfireun, C.C. Gilmour, J.A. Graydon, A. Heyes, H. Hintelmann, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S.E. Lindber, R.P. Mason, M.J. Paterson, C.L. Podemski, A. Robinson, K.A. Sandilands, G.R. Southworth, V.L. St. Louis, and M.T. Tate. 2007. Whole-ecosystem study shows rapid fish-mercury response to changes in

mercury deposition. Proceedings of the National Academy of Sciences **104**:16586-16591.

Iverfeldt, A, and O. Lindqvist. 1986. Atmospheric oxidation of elemental mercury by ozone in the aqueous phase. *Atmospheric Environment* **20**:1567-1573.

Jarvis A., H.I. Reuter, A. Nelson, E. Guevara, 2008, Hole-filled seamless SRTM data V4, International Centre for Tropical Agriculture (CIAT) [digital data]. Available from http://srtm.csi.cgiar.org.

Jensen, S. and A. Jernelov. 1969. Biological methylation of mercury in aquatic organisms. Nature **223**:753-754.

Jernelov, A. and H. Lann. 1971. Mercury accumulation in food chains. Oikos **22**:403-406.

Kelly, E.N., J.W. Short, D.W. Schindler, P.V. Hodson, M. Ma, A.K. Kwan, and B.L. Fortin. 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences USA 106:22346-22351.

Kurek, J., J.L. Kirk, D.C.G. Muir, X. Wang, M.S. Evans, and J.P. Smol. 2013. Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems. Proceedings of the National Academy of Sciences USA 10.1073/pnas.1217675110.

Lalonde, J.D., A.J. Poulain, and M. Amyot. 2002. The role of mercury redox reactions in snow on snow-to-air mercury transfer. Environmental Science and Technology **36**:174-178.

Lindberg, S.E., and W.J. Stratton. 1998. Atmospheric mercury specitation: concentrations and behavior of reactive gaseous mercury in ambient air. Environmental Science and Technology **32**:49-57.

Lohman, K., C. Seigneur, E. Edgerton, and J. Jansen. 2006. Modeling mercury in power plant plumes. Environmental Science and Technology **40**:3848-3854.

Lusis, M.A., K.G. Anlauf, L.A. Barrie, and H.A. Wiebe. 1978. Plume chemistry studies at a northern Alberta power plant. Atmospheric Environment **12**:2429-2437.

Millhollen, A.G., M.S. Gustin, and D. Obrist. 2006. Foliar mercury accumulation and exchange for three tree species. Environmental Science and Technology **40**:6001-6006.

Murray, W.A. 1981. The 1981 snowpack survey in the AOSERP study area. Prepared for the Alberta Oil Sands Environmental Research Program by Atmospheric Environment Service. AOSERP Report 125. 137 p.

National Pollutant Release Inventory (NPRI). 2012. www.ec.gc.ca/inrp-npri/. Accessed March 13, 2012.

Nelson S.J., K.B. Johnson,K.C. Weathers, C.S. Loftin, I.J. Fernandez, J.S. Kahl, and D.P. Krabbenhoft. 2008. A comparison of winter mercury accumulation at forested and no-canopy sites measured with different snow sampling techniques. Applied Geochemistry **23**: 384–398.

Nelson, S.J., I.J. Fernandez, and J.S. Kahl. 2010. A review of mercury concentration and deposition in snow in eastern temperate North America. Hydrological Processes **24**:1971-1980.

Obrist, D., D.W. Johnson, and R.L. Edmonds. 2012. Effects of vegetation type on mercury concentrations and pools in two adjacent coniferous and deciduous forests. Journal of Plant Nutrition and Soil Science **175**:68-77.

Olson, M.L., L.B. Cleckner, J.P. Hurley, D.P. Krabbenhoft, and T.W. Heelan. 1997. Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades. Fresenius Journal of Analytical Chemistry **358**:392-396.

Orihel, D.M., M.J. Paterson, P.J. Blanchfield, R.A. Bodaly, and H. Hintelmann. 2007. Experimental evidence of a linear relationship between inorganic mercury loading and methylmercury accumulation by aquatic biota. Environmental Science and Technology **41**:4952-4958.

Price, M. 2008. 11 Million Litres a Day: The Tar Sands' Leaking Legacy. Environmental Defence, Toronto.

Rasmussen, P.E. 1995. Temporal variation of mercury in vegetation. Water, Air, and Soil Pollution **80**:1039-1042.

Rea, A.W., Lindberg, S.E., Keeler, G.J. 2000. Assessment of dry deposition and foliar leaching of mercury and selected trace elements based on washed foliar and surrogate surfaces. *Environmental Science & Technology* **34**:2418-2425.

Regional Aquatics Monitoring Program. 2009. Final 2008 Technical Report. Hatfield Consultants, Stantec Consulting Ltd., Klohn Crippen Berger Ltd., and Western Resource Solutions.

Rooney, R.C., S.E. Bayley, and D.W. Schindler. 2012. Oil sands mining and reclamation cause massive loss of peatland and stored carbon. Proceedings of the National Academy of Sciences **109**:4933-4937.

Royal Society of Canada (RSC). 2010. The Royal Society of Canada Expert Panel: Environmental and health impacts of Canada's oil sands industry. December 2010. Ottawa, Ontario.

Schroeder, W.H., and J. Munthe. 1998. Atmospheric mercury - an overview. Atmospheric Environment **32**:809-822.

Shaw, B.P., and A.K. Panigrahi. 1986. Uptake and tissue distribution of mercury in some plant species collected from a contaminated area in India: its ecological implications. *Archives of Environmental Contamination and Toxicology* **15**:439-446.

St. Louis, VL, Rudd, J.W.M., Kelly, C.A., and L.A. Barrie. 1995. Wet deposition of methyl mercury in northwestern Ontario compared to other geographic locations. *Water Air and Soil Pollution* **80**:405-414.

Timoney, K.P., and P. Lee. 2011. Polycyclic aromatic hydrocarbons increase in Athabasca River Delta sediment: temporal trends and environmental correlates. Environmental Science and Technology **45**:4278-4284.

U.S. Environmental Protection Agency, 1996, Draft Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: EPA 821-R-96-012, Office of Water, 32 p.

U.S. Environmental Protection Agency. 1997. Mercury study report to Congress: Volume I executive summary. Report No. EPA-452/R-97-003. U.S.

Environmental Protection Agency, Research Triangle Park, North Carolina.

U.S. Environmental Protection Agency. 1998. Fact sheet update: national listing of fish and wildlife consumption advisories. Environmental Protection Agency, Washington, DC, EPA Publication 823-F-98-009.

Vijayaraghavan, K., P. Karamchandani, C. Seigneur, R. Balmori, and S. Chen. 2008. Plume-in-grid modeling of atmospheric mercury. Journal of Geophysical Research **113**:D24305.

Wheatley, B., and S. Paradis. 1995. Exposure of Canadian Aboriginal peoples to methylmercury. Water, Air and Soil Pollution **80**:3-11.

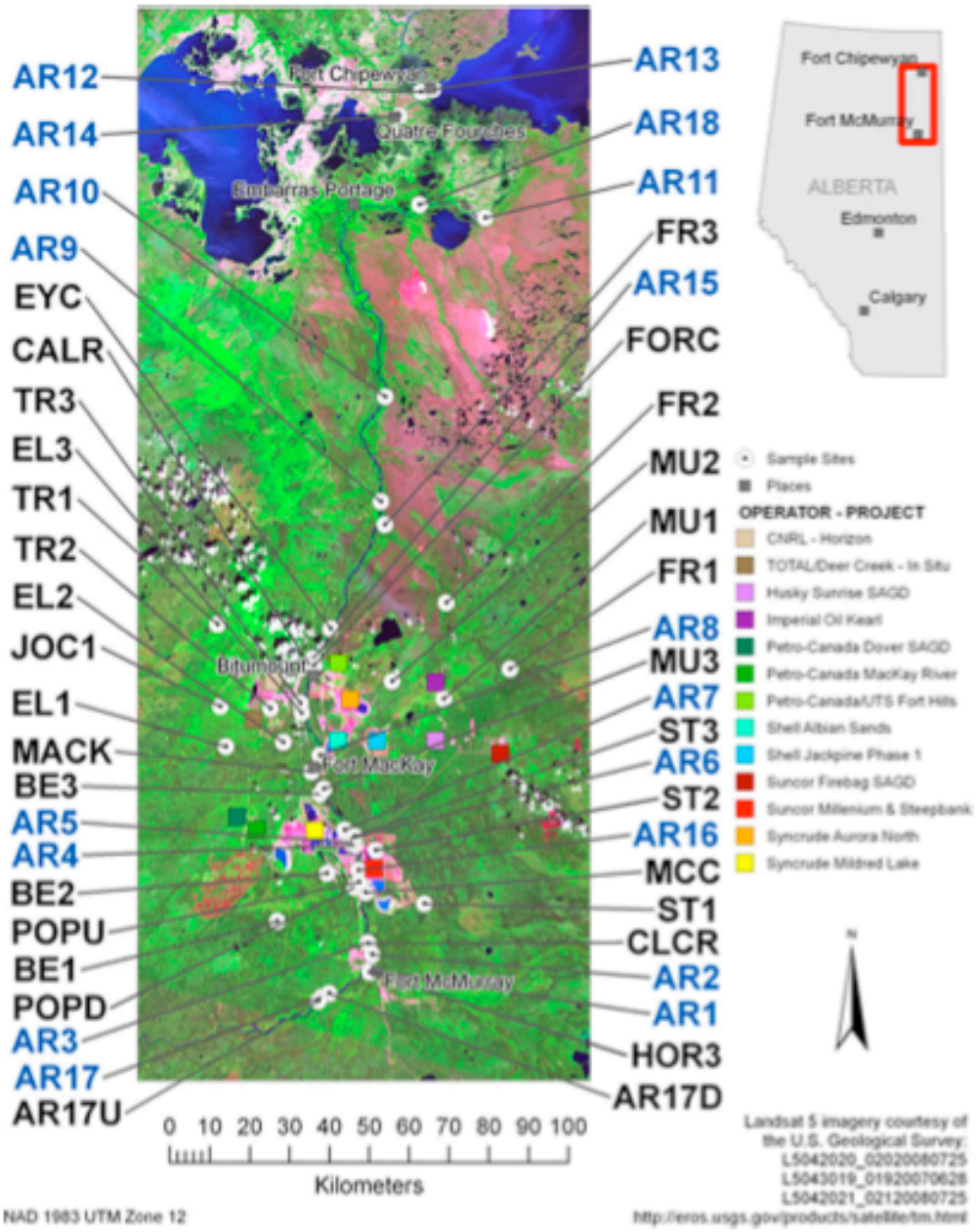

Figure 3.1 Map of study area and sampling sites. Athabasca River (AR) main stem sites: blue, tributary sites: black. Tributary abbreviations: AR17U, unnamed creek; AR17D, unnamed creek; POP, Poplar Creek; BE, Beaver River; ST, Steepbank River; MCC, McLean Creek; MACK, MacKay River; EL, Ells River; JOC, Jocelyn Creek; MU, Muskeg River; FR, Firebag River; FOR, Fort Creek; TR, Tar River; CALR, Calumet River; EYC, Eymundson Creek. For tributary sites: 1, upstream; 2, midstream; 3, stream mouth. Existed and approved oil sands projects are denoted by squares. Landsat 5 image: blue, water; green, vegetation; pink, non-vegetated or developed areas. From Kelly et al. (2009)

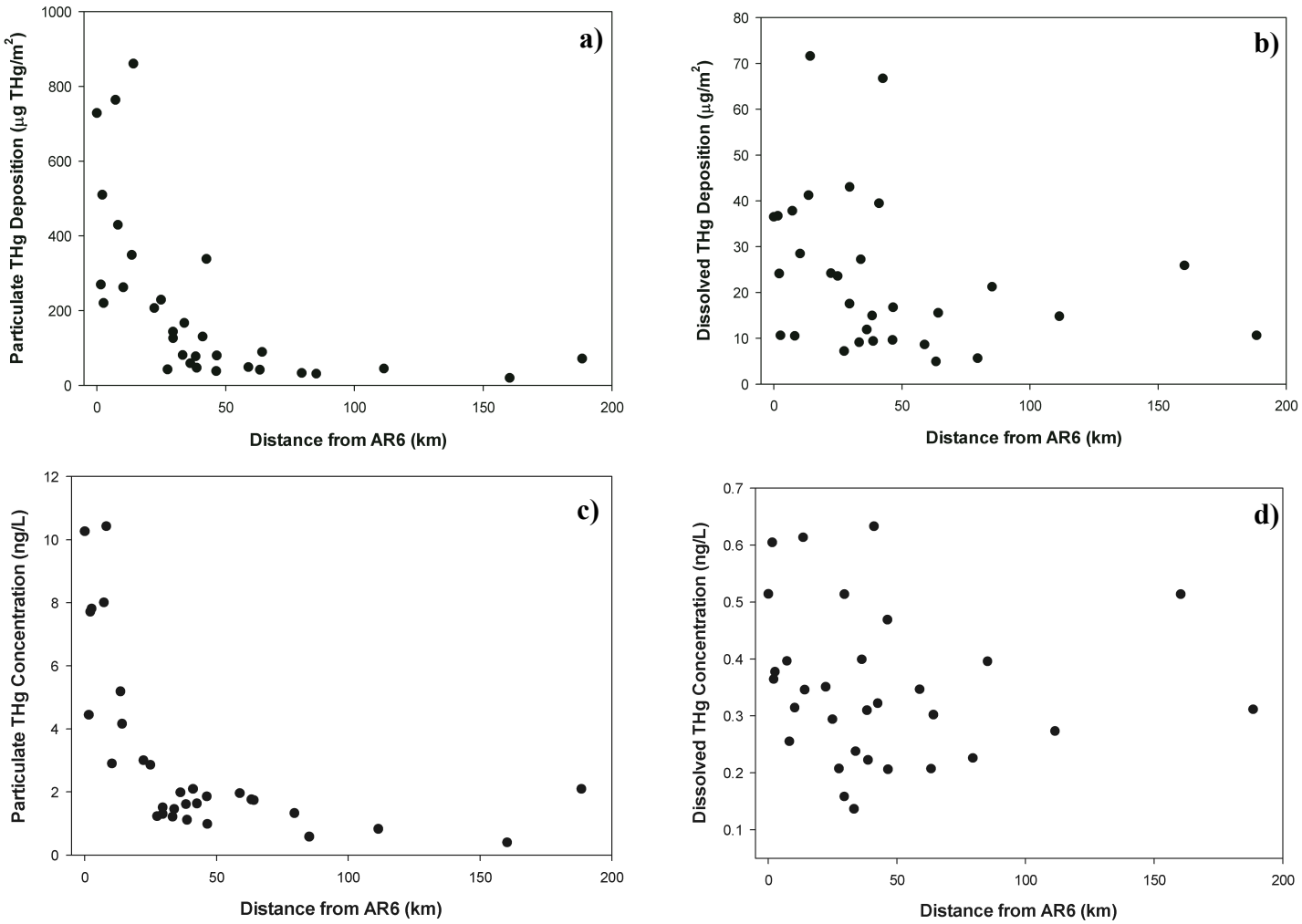

Figure 3.2 Deposition of particulate (a) and dissolved (b) total mercury and concentration of particulate (c) and dissolved (d) total mercury in integrated snowpack samples with increasing distance from upgrading facilities located at site AR6. Deposition is expressed in µg/m^2; concentrations are expressed in ng/L. Adapted from Kelly et al. (2010).

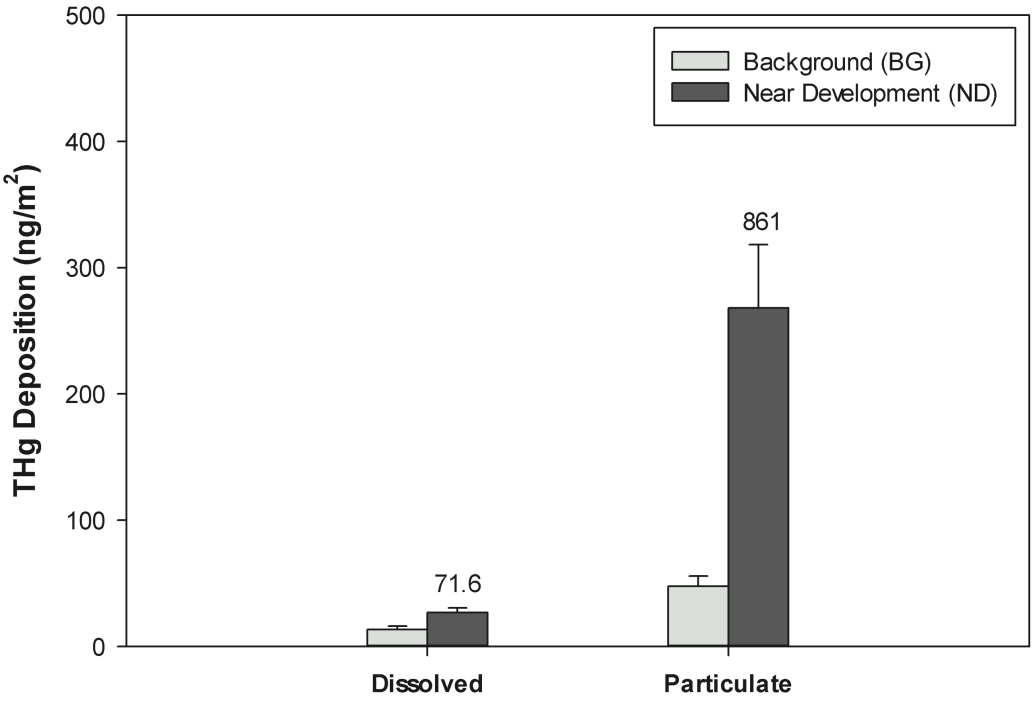

Figure 3.3 Deposition of dissolved and particulate total mercury at sites near oil sands development (ND; within 46 km radius of development) relative to background sites (BG). Data are expressed as mean ± SE. The numbers above the gray bars represent the maximum value near development. Deposition was significantly higher at sites near development (gray bars) relative to background sites (white bars) for particulate ($p < 0.001$, $t = -4.101$, $df = 29$) and dissolved ($p = 0.017$, $t = -2.227$, $df = 29$) mercury.

Table 3.1 Summary statistics of linear regressions between total mercury concentrations* in tissues of willow in summer and white spruce in winter and summer and distance from upgrading facilities located at site AR6.

	Slope	**Intercept**	**p-value**
Spruce winter	0.001	2.232	<0.001
Spruce summer	0.001	-2.175	<0.001
Willow summer	0.001	1.885	<0.001

* Concentrations were $\log_e$ transformed prior to analysis

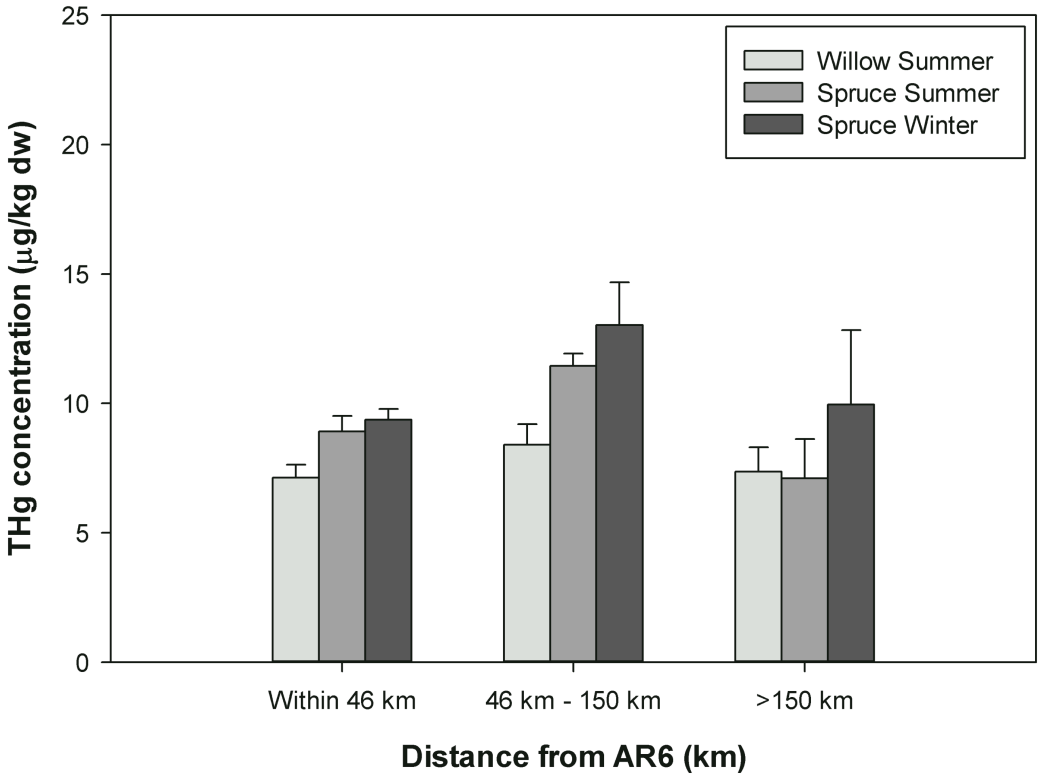

Figure 3.4 Total mercury concentrations in the tissues of willow (*Salix spp.*) in summer and white spruce (*Picea glauca*) in winter and summer with distance from upgrading facilities located at site AR6. Data are presented as mean ± SE. Statistical tests comparing distance were not performed due to low sample size. Total mercury in white spruce was significantly higher than willow (t-test; $p = 0.007$, $t = 2.762$, $df = 80$). Total mercury in white spruce did not differ between winter and summer (t-test; $p = 0.111$, $t = 1.615$, $df = 70$).

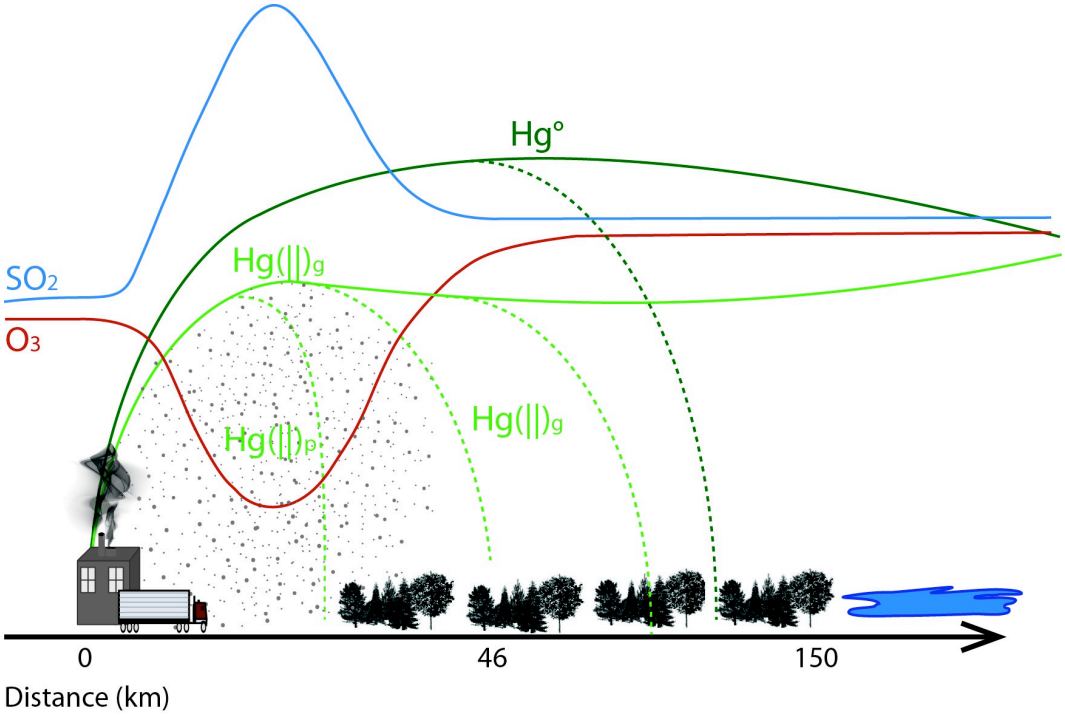

Figure 3.5 Hypothetical model of atmospheric speciation of mercury in the immediate vicinity of and downwind of oil sands development. Downwind of emission sources, ozone is depleted due to chemical scavenging by emitted compounds (ex. No_x) and SO_2 is increased, producing a reducing atmosphere. Emitted Hg(II) is reduced to Hg^0 and transported downwind. Hg(II) that is not reduced adsorbs to particulates and aerosols and is deposited locally as particulate Hg. At moderate distances, ozone concentrations increase and SO_2 concentrations decrease, producing an oxidizing atmosphere. Hg^0 is oxidized to form Hg(II) that is wet and dry deposited.

Table 3.2 Summary statistics of linear regressions between total mercury in Athabasca River water* and the proportion of the McMurray oil sands formation, overall land disturbance, and land disturbance attributable to oil sands development within the catchment of each site in winter and summer.

	Winter			Summer		
	Slope	**Intercept**	**p-value**	**Slope**	**Intercept**	**p-value**
McMF	0.356	-0.243	0.453	0.743	1.705	0.286
Overall Disturbance	-0.043	2.232	0.391	-0.077	6.145	0.303
Oil Sands Disturbance	0.786	0.217	0.396	2.166	1.685	0.096

* Concentrations were $\log_e$ transformed prior to analysis

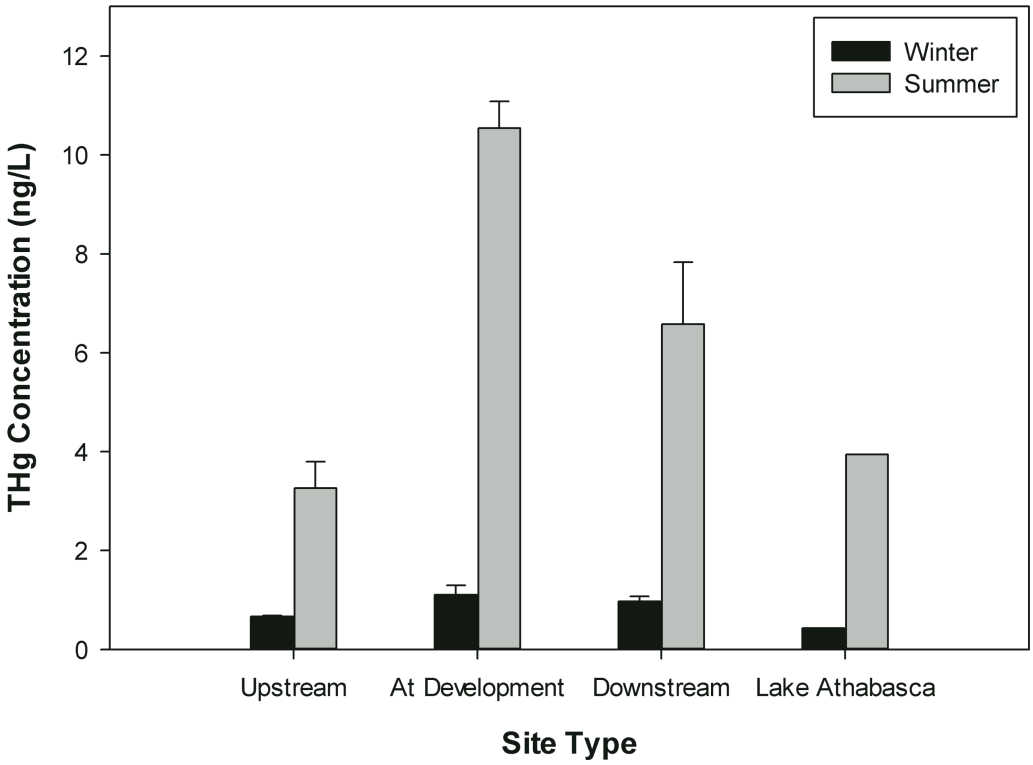

Figure 3.6 Total mercury concentrations in Athabasca River water sampled in February and June of 2008 upstream of oil sands development (n = 3), at/near oil sands development (n = 7), downstream of oil sands development and Athabasca Delta (n = 6), and Lake Athabasca (n = 1). Concentrations are expressed as mean $\pm$ SE. THg concentrations were significantly higher in summer than winter ($p < 0.001$, $F = 198.547$, $df = 31$). In summer, concentrations of THg were significantly higher at development relative to upstream ($p = 0.002$) and remained elevated above upstream sites downstream of development, though not significantly so. Concentrations during winter were not significantly different.

Table 3.3 Summary statistics of linear regressions between total mercury in tributary water* and the proportion of the McMurray oil sands formation, overall land disturbance, and land disturbance attributable to oil sands development within the catchment of each site in winter and summer.

	Winter			Summer		
	Slope	**Intercept**	**p-value**	**Slope**	**Intercept**	**p-value**
McMF	0.002	0.103	0.785	-0.016	1.039	0.217
Overall Disturbance	0.004	-0.021	0.517	0.003	0.811	0.721
Oil Sands Disturbance	0.016	0.065	0.357	0.007	0.879	0.625

* Concentrations were $\log_e$ transformed prior to analysis

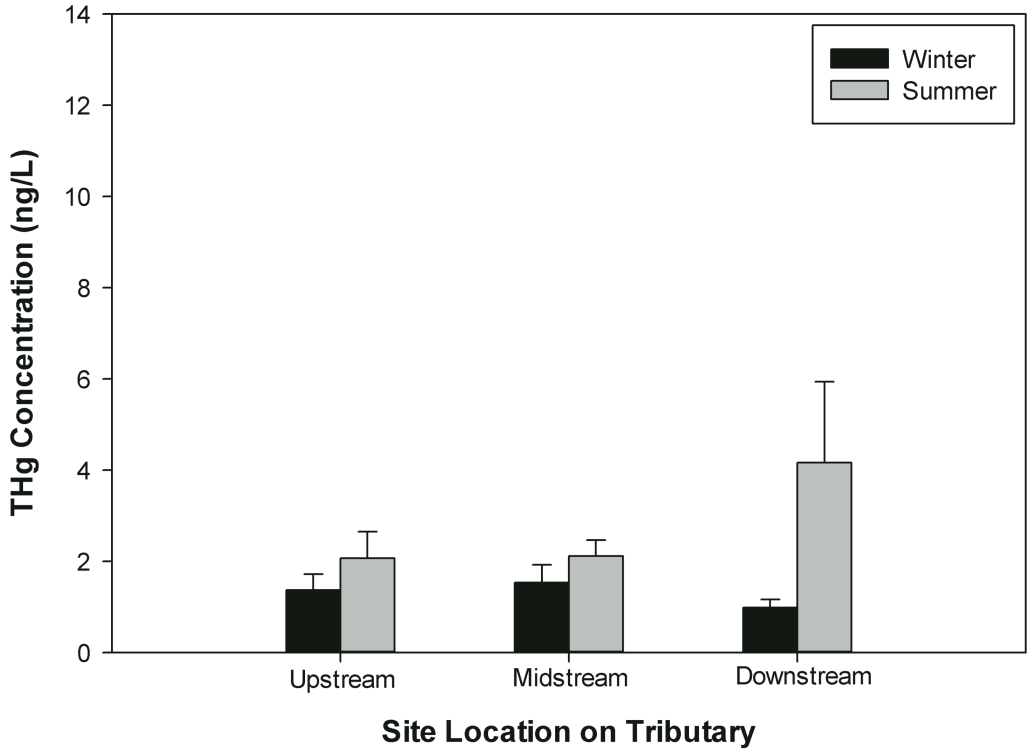

Figure 3.7 Total mercury concentrations in tributary water sampled in February and June of 2008 at sites upstream of the McMurray oil sands formation and oil sands development (n = 6), sites within the McMurray formation but upstream of oil sands development (n = 6), and at sites within the McMurray formation and downstream of oil sands development (n = 6). Concentrations are expressed as mean $\pm$ SE. Concentrations were not significantly different between site locations ($p = 0.867$).

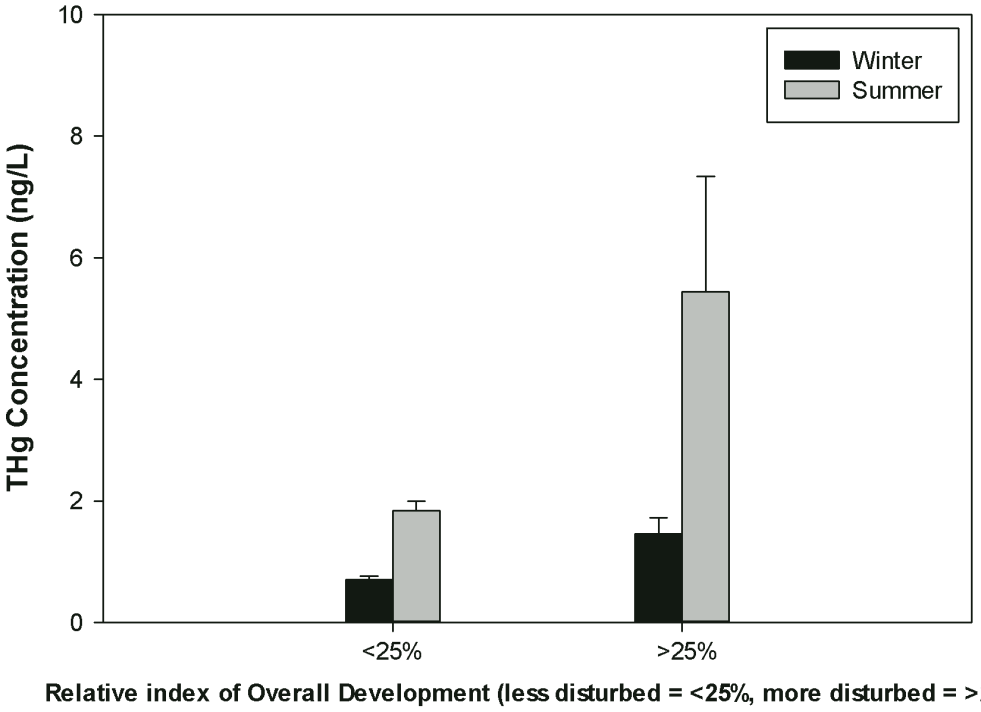

Figure 3.8 Total mercury concentrations in water from midstream and stream mouth tributary sites classified by relative index of overall land disturbance by development: <25%, less disturbed; >25%, more disturbed. Concentrations are expressed as mean $\pm$ SE. Concentrations were significantly higher at midstream and stream mouth sites with >25% overall land disturbance relative to midstream and stream mouth sites with <25% overall land disturbance ($p = 0.038$, $F = 4.719$, $df = 34$).

Chapter 4: Mercury in biota of the Athabasca River

Introduction

The production of crude oil from oil sand in the northeast corner of Alberta has expanded rapidly in the last decade. Much of this development has taken place in close proximity to the Athabasca River, so the potential exists for oil sands operations to contribute significant loadings of contaminants of concern, such as mercury, to the Athabasca watershed. Emissions of mercury from oil sands development more than quadrupled between 2000 and 2010 (NPRI 2012). Mercury concentrations in predatory fish species are known to be high in the Lower Athabasca River and in Lake Athabasca (Donald et al. 1996; Timoney 2007); however, a consumption advisory is only in effect for walleye in the Lower Athabasca River (Government of Alberta 2012). The spatial distribution of mercury concentrations in fishes in the Athabasca River and Lake Athabasca was examined to determine if oil sands development is a significant source of mercury within the Athabasca region. Further, mercury concentrations in fish populations were compared to established consumption guidelines for mercury to assess risk to people within downstream communities.

Mercury may be released to the Athabasca River and its tributaries through leaks, spills, or licensed discharges of process affected water and materials, such as tailings (Price 2008). In addition, mercury released to the air from oil sands facilities and upgraders (NPRI 2012) is deposited directly to the surface of the river or deposited onto vegetation and soils within the watershed (Edgerton et al. 2006). Pools of inorganic mercury sequestered in soils may be

mobilized into tributaries and the Athabasca River through runoff from rain events (Hintelmann et al. 2002), during spring freshet, or through the construction of facilities, land clearing, and the building of roads and pipelines due to increased erosion and sedimentation rates (Kelly et al. 2009; Kelly et al. 2010). Once released into aquatic systems, inorganic mercury is converted into methyl mercury (MeHg) through microbial activity (Jensen and Jernelov 1969) and rapidly enters food webs (Jernelov and Lann 1971). Therefore, increased mercury inputs to aquatic systems can be reflected in fish tissues shortly after being deposited (Harris et al. 2007). Methyl mercury (MeHg) is a neurotoxic form of mercury that bioaccumulates within individuals and biomagnifies within aquatic food webs and is responsible for the majority of human health related fish consumption advisories worldwide (Agah et al. 2010).

Accumulation of MeHg at higher trophic positions is almost entirely due to dietary exposure from ingestion of contaminated prey items rather than from exposure to contaminated water (Hall et al. 1997). The greatest concentration step occurs at the base of the food web, with concentrations of MeHg in primary producers up to ten thousand times greater than concentrations in ambient water (Pickhardt et al. 2007). MeHg from dietary sources is incorporated into tissues and is highly persistent; therefore, concentrations may increase two- to fivefold across each trophic level, resulting in substantially increased concentrations at the highest trophic levels (Ward et al. 2010a).

While concentrations of MeHg in prey items influence MeHg concentrations in higher trophic levels, elevated MeHg concentrations have been

found in fish from systems with low MeHg concentrations in lower trophic levels. This is because the extent to which ingested MeHg is incorporated into tissues is determined by the growth rate or growth efficiency of an individual (Ward et al. 2010a). For a given mass of ingested mercury, an individual with a high growth rate/efficiency will accumulate more body mass per unit of MeHg compared to an individual with a low growth rate/efficiency, a process known as somatic growth dilution (Ward et al. 2010b; Trudel and Rasmussen 2006). Growth dilution may also occur at the base of the food web in productive systems, as higher primary productivity dilutes the amount of bioavailable MeHg in a higher amount of biomass, reducing the concentration of MeHg per unit of prey ingested (Ward et al. 2010a).

The Regional Aquatics Monitoring Program (RAMP) is a multi-stakeholder, industry-funded monitoring program responsible for monitoring the effects of oil sands development within the oil sands region. RAMP has measured mercury levels in various environmental media since its inception in 1997 and consistently concludes that the contribution of industry to mercury concentrations within the Athabasca River is negligible, and that any increases are due to natural erosion of oil sands formations. An independent scientific review highlighted numerous weaknesses in the RAMP program, such as a lack of true baseline data or reference sites, inadequate detection limits, low sampling effort on the Athabasca River, ambiguous descriptions of site locations relative to development, and inconsistent sampling, among others (RAMP 2011). The reviewers concluded that the RAMP study design was not capable of

distinguishing impacts resulting from development from natural variability, and that "it is likely that the current monitoring program is biased towards concluding no effect, even if one is present." (J.R. Post, RAMP 2011).

As a result of the regional monitoring program's shortcomings, the ability of RAMP to properly monitor the effects of oil sands development on the Athabasca watershed has been repeatedly called into question by academics/scientists (Kelly et al. 2009; RAMP 2011), non-profit advocacy groups (Price 2008; Donahue 2011), and citizens. Many people living downstream of oil sands development continue to follow a traditional subsistence lifestyle that includes hunting, trapping, fishing, and drinking water directly from the river. Therefore, individuals within downstream communities experience a high level of exposure to contaminants that bioaccumulate within food webs, such as mercury, due to a higher consumption rate of contaminated food (Wheatley and Paradis 1995). As a result, individuals within the region are at a greater risk for adverse health effects associated with exposure to mercury and other contaminants of concern relative to individuals in the general population. Depending on exposure, the human health effects of MeHg range from decreased ability to concentrate (Grandjean et al. 1997), decreased visual-spatial ability (Harada et al. 2005), impaired motor function and language (Harada et al. 2005), to blindness (Myers and Davidson 2000), deafness (Murata et al. 2004), seizures (Myers and Davidson 2000), paresthesia (Yorifuji et al. 2008), cerebral palsy (Gilbertson 2004), and in the most severe instances, death (Eto et al. 2002). As mercury interferes with the development of neuronal cells, the health effects of mercury are of greater

concern to women of childbearing age (because of exposure to the fetus *in utero*) and children (Clarkson 2003).

Individuals in the downstream community of Fort Chipewyan have raised concerns about a potential link between contaminants derived from oil sands operations and increased incidences of rare cancers within their community. As a result, studies of health risks due to exposure to contaminants as well as disease prevalence has focused almost exclusively on cancer rates and contaminants that are known carcinogens (Chen 2009), while the effects of exposure to mercury on human populations within the region remains unassessed.

At the time this study was conducted, accurate and independent assessments of the contribution of oil sands development to mercury concentrations in the Athabasca watershed did not exist. Further, a regional assessment of the impact of oil sands development on aquatic ecosystems within the oil sands region had not been conducted, as environmental impacts are assessed on a project-by-project basis. The primary objective of this study is to conduct an independent assessment of the geographic distribution of mercury within aquatic biota of the Athabasca watershed to determine if oil sands development and processing is a significant source of mercury to the Athabasca River and its tributaries.

Rivers and streams have a high connectivity to their watersheds, so they are highly responsive to changes in their watersheds such as land disturbance and atmospheric deposition of contaminants (Brigham et al. 2009; Chasar et al. 2009). Therefore, Hg concentrations of discrete sediment and water samples in lotic

systems are transient and highly variable as they are influenced by seasonality, precipitation events, local physical land disturbance, and variation in flow, discharge, runoff, and water chemistry (Chasar et al. 2009). For this reason, it is often difficult to relate concentrations of mercury in discrete water and sediment samples to tissue concentrations of aquatic biota (Hornberger et al. 2009). Furthermore, highly motile organisms, such as fishes, integrate variability over larger spatial scales and may move into and out of methylation "hotspots" (Ward et al. 2010a) that differ in Hg availability, prey contamination, and food web complexity (Fowlie et al. 2008).

Benthic macroinvertebrates are the most commonly utilized organisms in ecological monitoring of freshwater systems (Bailey et al. 2004). They are particularly useful in bioassessments of the distribution of contaminants of concern within lotic systems for various reasons. The small body size of benthic macroinvertebrates restricts the size of their range, so their contaminant body burdens reflect localized concentrations. Lastly, most freshwater benthic invertebrates have 1-2 year life cycles, so their body burdens represent relatively recent contaminant concentrations. Benthic macroinvertebrates were sampled to assess the spatial distribution of mercury within benthic communities of the Athabasca River, and to assess dietary exposure for fish species that utilize benthic macroinvertebrates as prey items.

The spatial distribution of mercury concentration in fishes was compared within and among species. Mercury concentrations in fishes from this study and data from Health Canada were used to derive mercury exposure ratios to assess

risk to people living within downstream communities. Mercury concentrations in fishes were compared to established fish mercury consumption guidelines to facilitate comparisons of the findings of this study with other assessments of fish mercury conducted within the region.

Materials and Methods

Field Sampling

In July and August of 2008, ten sites on the Athabasca River were sampled for fish. Sample sites on the Athabasca River were located upstream of oil sands development (n = 1; AR3, Figure 3.1), at oil sands development (n = 3; AR5, AR6, AR8, Figure 3.1), downstream of oil sands development (n = 2; AR9, AR10, Figure 3.1), and in the Athabasca delta (n = 4; AR11, AR18, AR12, AR14, Figure 3.1). The study sites covered a large geographical area, ranging from 33 km south of Fort McMurray north to Fort Chipewyan. For a map of the study area and sampling locations, refer to chapter three.

Fishes were collected using 100 yd single mesh size (4.5”) gillnets. Fishes were identified and measured for total length, fork length, and wet mass. Fishes were dissected while in the field. Using clean sampling protocols, a sample of dorsal muscle tissue for Hg analyses, and ageing structures were collected from each fish and frozen immediately on dry ice. Saggital otoliths were removed and preserved in 50% ethanol and scales and fin rays were collected and kept on dry ice.

Benthic macroinvertebrates colonized bricks that were attached to polyethylene membrane devices (PMDs) that had been deployed one month

earlier as part of a concurrent study (Kelly et al. 2009). As invertebrates were not included in the original sampling protocol and collected opportunistically (when present in sufficient numbers on sampler bricks), they were only collected from ten sites (upstream n = 1, at development n = 3, downstream n = 2, delta n = 3, lake n = 1). Individuals were visually sorted to order and frozen in ambient river water in sterile Whirl-Paks over dry ice. Individuals were not depurated prior to being frozen.

Sample Preparation and Analysis

Benthic macroinvertebrates were identified to the lowest taxonomic resolution possible, typically genus, using a stereomicroscope (Clifford 1991; Wiggins 1996). Surface particulate matter was removed by rinsing individuals in ultra-pure de-ionized water. Only Trichoptera (Caddisfly larvae) were collected at sufficient biomass from multiple sites to allow for mercury analysis. Individual Trichoptera larvae from the same site were pooled in order to obtain a sufficient mass for Hg analysis. Dorsal muscle tissue from individual fish and composite whole body Trichoptera samples were freeze-dried for 48 hours. Dried samples were homogenized using a sterile glass mortar and pestle. Subsamples of the resultant powder were analyzed for total mercury (THg) concentration. In fish, the majority of total mercury present in tissues (90-100%) is in the form of methylmercury. Therefore, total mercury was used as a less expensive proxy for measuring methylmercury concentrations.

Fish tissue samples were analyzed for total mercury at the Universite du Quebec a Rimouski Laboratoire de Chimie Marine et Spectrometrie de Masse, Institut des Sciences de la Mer de Rimouski. Approximately 100 mg of freeze-dried fish tissue was microwave digested in 4 mL of trace metal grade nitric acid and 3 mL high purity grade hydrogen fluoride at 800 W, 200°C, and 800 psi for 20 minutes. Samples were transferred to a Teflon beaker and residual hydrogen fluoride was removed by allowing the samples to dry for 2 hours at 200°C. The remaining liquid was diluted to 50 mL with ultrapure water and 2% nitric acid in a clean volumetric flask. Total mercury in aqueous solution was analyzed by ICP/quadrupole MS (Agilent 7500c) with a microflow nebulizer and Chemstation software (revision C). Total mercury was quantified in normal mode with a seven-point calibration plot over a concentration range of 0.65-200 ng mL-1. Certified reference material (National Research Council of Canada) and procedural blanks were analyzed to assess instrument performance. Fishes were aged by Environment Canada. Fish ages were determined by counting otolith rings under a dissecting microscope.

Benthic macroinvertebrate samples were analyzed for total mercury at the University of Alberta Low-Level Mercury Analytical Laboratory. A subset of fish tissue samples was also analyzed to facilitate inter-lab comparison of total mercury measurements. Subsamples of homogenized freeze-dried fish and invertebrate tissue were weighed into Teflon bombs (to the nearest 0.00001 g) and 7 mL of a 7:3 trace metal grade HNO_3 and H_2SO_4 mixture was added. Bombs were wrench-tightened and baked for 2 hours in a 130°C oven. After cooling to

room temperature, 19 mL of MilliQ water and 1 mL of BrCl was added to each bomb. Total mercury was measured using BrCl oxidation, $SnCl_2$ reduction, purge and trap, and cold vapour atomic fluorescence spectrometry (CVAFS) (modified (USEPA 1996, Olson et al. 1997)). The detection limit was 0.02 ng/L. Sample blanks, spike recoveries, standard reference materials (National Research Council of Canada), and duplicates were included for all mercury analyses. The relative percent difference between duplicates was 10% or less.

Statistical Analyses

The distribution of all fish and invertebrate data sets was examined using Shapiro-Wilk and Kolmogorov-Smirnov tests, in addition to visual inspection of histograms (Zar 1999). Fish and invertebrate THg data pooled across all sites deviated from a normal distribution and were natural log transformed to satisfy the normality assumption of parametric statistics (Zar 1999).

Trichoptera from three genera (*Hydropsyche*, *Brachycentrus*, and *Neureclipsis*) were collected from a total of ten sites. As part of a concurrent study, samples were analyzed for a suite of metals. A sufficient mass for both metals and total mercury analysis was only collected from eight sites (at development n = 3, downstream n = 2, delta = 2, lake n = 1); therefore, no data from sites upstream of oil sands development are presented for Trichoptera.

A one-way ANOVA was used to compare THg concentrations in Trichoptera at sites near or at development, downstream of development, and in

the delta. As only one site was sampled in Lake Athabasca, it was excluded from statistical analysis (n = 1).

Four species of fish were collected from the Athabasca River, walleye (*Sander vitreus*), northern pike (*Esox lucius*), goldeye (*Hiodon alosoides*), and lake whitefish (*Coregonus clupeaformis*).

Linear regression was used to examine the relationship between THg and variables that influence fish mercury concentration (age, mass, and total length). Of the variables that determine fish-mercury relationships, the most linear relationship existed between fish mercury concentration and age (Table 4.2). Therefore, age was used to correct fish THg concentrations for increases related to fish size.

Spatial trends of total mercury within fish species were assessed by using linear regression to correct for the effect of age on Hg concentrations, followed by performing a one-way ANOVA on the age corrected data. A post hoc Tukey's test was performed to identify significant pair-wise differences. The number of walleye collected at some site types was too low for statistical analysis so general trends are presented and described.

Analysis of covariance (ANCOVA) was used to determine if THg concentrations varied between fish species within the Athabasca River. ANCOVA combines regression and ANOVA to remove or adjust for an uncontrolled source of variation, the covariate, from the dependent variable. For example, in this model, age was the covariate, fish species was the factor, and THg concentration

was the dependent variable. A post-hoc Tukey's was performed to determine significant pair-wise differences.

ANCOVA was also used to determine if condition factor (K) and absolute growth rate differed significantly among fish species in the Athabasca River. A post-hoc Tukey's was performed to determine significant pair-wise differences. Linear regression was used to determine if absolute growth rate and condition factor were significantly related to mercury concentrations within species. Absolute growth rate was calculated by dividing age by fish fork length (mm). Condition factor was calculated using the following formula:

$$\text{Condition factor (K)} = \frac{W \times 10^5}{L^3}$$

Where W = weight (g), L = length (mm), and 10^5 is a scaling factor used to bring K closer to 1 (Barnham and Baxter 1998; Nash et al., 2006).

The risk associated with consuming the fish species captured in this study for people living within downstream communities was assessed using Health Canada's Exposure Assessment methods (Health Canada 2013). Human exposure to MeHg in fish was determined by calculating the Probable Daily Intake (PDI) values for 1) the general adult population; 2) pregnant women and women of reproductive age; 3) children between 5 and 11 years of age; and 4) children between 1 and 4 years of age. PDI was determined as follows:

$$\frac{\text{PDI (µg/kg bw/day)} = \text{fish muscle intake (g/day)} \times [\text{MeHg µg/g}]}{\text{average body weight (kg)}}$$

Once the PDI value is calculated it must be compared to the provisional tolerable daily intake (pTDI) of MeHg for the age group in question. The ratio of PDI and pTDI is determined and expressed as a percentage (PDI/pTDI x 100). Values exceeding or approaching 100% indicate exposure scenarios where the toxicological reference value may be exceeded and that must be evaluated further.

% pTDI values were calculated using the average body weights and fish muscle intakes of the general Canadian population for each population group, as these are the values used by Health Canada. However, many people living within the region live a subsistence lifestyle and likely consume significantly higher amounts of fish than the rest of the Canadian population. In order to assess the risk associated with higher consumption rates of the fish captured in this study, % pTDI values were calculated using daily fish intake data from a report by the First Nations and Inuit Health Branch of Health Canada (FNIHB) in the Lesser Slave Lake Area, as these values are likely a more accurate representation of fish consumption rates for subsistence populations. However, daily fish intake values were only reported for adults. To enable the calculation of % pTDI values for children, it was assumed that relative serving sizes were consistent across Canadian populations. Daily fish intake values for children were then calculated by determining the percent difference between adult and children daily intakes for the Canadian population (daily intake values were 36% lower than adult intake values for children age 5-11 and 55% lower for children age 1-4), and were applied to the daily intake values contained within the FNIHB report (for example, adult intake = 273 g/day, so intake for children age 5-11 = 273 g/day x

0.64 = 175 g/day). To obtain a more conservative risk estimate, 100% of the mercury in fish samples was considered to be in the form of MeHg.

The mean mercury concentrations in fish species captured in this study were also compared to Health Canada fish consumption guidelines that are no longer used (Health Canada 2008). This was done to facilitate comparison of the findings of this study to those of others from the same year, such as the RAMP program. Fish mercury concentrations were compared to the frequent or subsistence consumption guideline (0.2 µg/g) and to the commercial consumption guideline (0.5 µg/g) previously utilized by Health Canada (RAMP 2009).

Results

Spatial Trends of Total Mercury in Trichoptera

Mean THg concentrations in Trichoptera differed significantly between sites (ANOVA, $F = 19.433$, $p < 0.001$, $df = 2, 11$). Post hoc testing indicated that the mean THg concentration in Trichoptera was significantly higher downstream of oil sands development (64.04 µg/g) compared to at or near oil sands development (49.02 µg/g; Tukey's $p = 0.016$; Figure 4.1) and the Athabasca delta (37.53 µg/g; Tukey's $p < 0.001$; Figure 4.1). Post hoc testing also indicated that the mean THg concentration in Trichoptera was significantly higher at or near development relative to Trichoptera in the Athabasca Delta (Tukey's $p = 0.013$; Figure 4.1).

While not assessed statistically due to low sample sizes (Lake Athabasca n = 1), mean THg concentrations in Trichoptera near development, downstream of

development, and in the Athabasca Delta were 1.6, 2.1, and 1.2 times higher, respectively, than at the Lake Athabasca site (29.74 µg/g).

Spatial Trends of Total Mercury Within Fish Species

The mean THg concentration in goldeye was 0.20 µg/g at upstream sites, 0.21 µg/g at sites near development, 0.28 µg/g at downstream sites, and 0.27 µg/g at sites within the Athabasca Delta. The mean THg concentration in walleye was 0.24 µg/g at upstream sites, 0.24 µg/g at sites near development, 0.33 µg/g at sites downstream of development, and 0.34 µg/g at sites within the Athabasca Delta. The mean THg concentration in northern pike was 0.22 µg/g at sites near development, 0.31 µg/g at sites near development, and 0.24 µg/g at sites within the Athabasca Delta. The mean THg concentration in lake whitefish was 0.08 µg/g at sites near development, 0.06 µg/g at downstream sites, and 0.08 µg/g at sites within the Athabasca Delta.

Mean THg concentrations differed significantly between sites in northern pike (ANOVA, $F = 6.102$, $p = 0.01$, $df = 2,19$) and goldeye (ANOVA, $F = 3.213$, $p = 0.033$, $df = 3,43$). THg concentrations in northern pike were significantly elevated downstream of development compared to sites located near development (Tukey's $p = 0.015$, Figure 4.2) and sites located within the Athabasca Delta (Tukey's $p = 0.031$, Figure 4.2). The overall ANOVA performed on the goldeye data was significant; however, subsequent multiple comparisons were not, likely due to low power (Zar 1999). Mean THg concentrations in lake whitefish did not display a significant spatial trend (Figure 4.2).

THg concentrations in walleye were not investigated statistically; however, concentrations exhibited the same spatial trend as for goldeye, with elevated concentrations downstream of development and in the delta relative to upstream sites and sites near development (Figure 4.2).

Comparisons Among Fish Species

Mean THg concentration in fish species ranged from 0.08 µg/g to 0.35 µg/g (walleye = 0.35 µg/g; northern pike = 0.30 µg/g; goldeye = 0.27 µg/g; lake whitefish = 0.08 µg/g). Mean THg concentration varied significantly among fish species (ANCOVA, $F = 12.55$, $p<0.0001$, $df = 3, 105$; Figure 4.3). Post-hoc testing revealed that northern pike and walleye had significantly higher THg concentrations than goldeye and lake whitefish (Tukey's $p<0.05$). Northern pike and walleye were not significantly different from one another (Tukey's $p>0.05$). Goldeye and lake whitefish were not significantly different from one another (Tukey's $p>0.05$) (Figure 4.3).

Condition factor was not significantly related to fish mercury concentrations (Table 4.1). Growth rate was significantly related to fish mercury concentration in all species except northern pike (Table 4.1). Condition factor varied significantly among species (ANCOVA, $F = 12.15$, $p<0.01$, $df = 3,104$; Figure 4.4). A post-hoc Tukey's revealed that the condition factor of lake whitefish was significantly higher than all other species (Tukey's, $p<0.05$) and the condition factor of walleye was significantly higher than northern pike (Tukey's, $p<0.05$). Growth rates differed significantly among species (ANCOVA, F =

29.001, $p<0.01$, df = 3,104). Post-hoc testing indicated that the growth rate of goldeye was significantly higher than all other species (Tukey's, $p<0.05$). The growth rate of walleye and lake whitefish did not differ significantly, but were significantly higher than the growth rate of northern pike (Tukey's, $p<0.05$).

Human Health Risk Assessment

The weekly fish intake of the general Canadian population was 154 g/week, 98 g/week, and 70 g/week for adults, children aged 5-11, and children aged 1-4, respectively. The corresponding PDI:pTDI ratios were as follows: **1) walleye:** adults = 27, women = 63, children age 5-11 = 91.86, and children age 1-4 = 120.29; **2) northern pike** = adults = 23, women = 54, children age 5-11 = 78, and children age 1-4 = 103; **3) goldeye:** adults = 21, women = 50, children age 5-11 = 73, and children age 1-4 = 95; and **4) lake whitefish:** adult = 21, women = 50; children age 5-11 = 73, and children age 1-4 = 95.

For a subsistence consumer population with a "high" weekly fish intake (>100 g/day; 5% of surveyed population, n = 125), the weekly intakes were 1911 g/week for adults, 1223 g/week for children age 5-11, and 860 g/week for children age 1-4. The corresponding PDI:pTDI ratios were as follows: **1) walleye:** adults = 335, women = 788, children age 5-11 = 1148, and children age 1-4 = 1480; **2) northern pike:** adults = 286, women = 673, children age 5-11 = 980.85, and children age 1-4 = 1264; **3) goldeye:** adults = 266, women = 626, children age 5-11 = 911, and children age 1-4 = 1174 and **4) lake whitefish:** adults = 80.44, women = 189, children age 5-11 = 275, and children age 1-4 = 355.

For a subsistence consumer population with a "medium" weekly fish intake (30-99 g/day; 14% of surveyed population, n = 125), the weekly intakes were 322 g/week for adults, 206 g/week for children age 5-11, and 145 g/week for children age 1-4. The corresponding PDI:pTDI ratios were as follows: **1) walleye:** adults = 57, women = 133, children age 5-11 = 190, and children age 1-4 = 253; **2) northern pike:** adults = 48, women = 113, children age 5-11 = 163, and children age 1-4 = 216; **3) goldeye:** adults = 45, women = 105, children age 5-11 = 151, and children age 1-4 = 201; **4) lake whitefish:** adults = 14, women = 32, children age 5-11 = 46, and children age 1-4 = 61.

For a subsistence consumer population with a "low" weekly fish intake (5-29 g/day; 38% of surveyed population, n = 125), the weekly intakes were 91 g/week for adults, 58 g/week for children age 5-11, and 41 g/week for children age 1-4. The corresponding PDI/pTDI ratios were as follows: **1) walleye:** adults = 16, women = 38, children age 5-11 = 52, and children age 1-4 = 72; **2) northern pike:** adults = 14, women = 32, children age 5-11 = 45, and children age 1-4 = 62; **3) goldeye:** adults = 13, women = 30, children age 5-11 = 42, and children age 1-4; **4) lake whitefish:** adults = 4, women = 9, children age 5-11 = 13, and children age 1-4 = 17.

For a subsistence consumer population with a "very low" weekly fish intake (<4 g/day; 43% of surveyed population, n = 125), the weekly intakes were 11.2 g/week for adults, 7 g/week for children age 5-11, 5 g/week for children age 1-4. The corresponding PDI/pTDI ratios were as follows: **1) walleye:** adults = 1.97, women = 4.62, children age 5-11 = 6.69, and children age 1-4 = 8.66; **2)**

northern pike: adults = 1.68, women = 3.95, children age 5-11 = 5.72, and children age 1-4 = 7.4; **3) goldeye:** adults = 1.56, women = 3.67, children age 5-11 = 5.31, and children age 1-4 = 6.87; **4) lake whitefish:** adults = 0.47, women = 1.11, children age 5-11 = 1.61, and children age 1-4 = 2.08.

Comparison to Consumption Guidelines

The Health Canada mercury consumption guideline for commercial fish consumption is 0.5 μg/g. Of the fish captured in this study, 4% of goldeye, 20% of northern pike, and 20% of walleye exceeded this guideline (Figure 4.5). The Health Canada mercury consumption guideline for frequent fish consumption is 0.2 μg/g. Of the fish captured in this study, 72% of goldeye, 75% of northern pike, and 80% of walleye exceeded this guideline (Figure 4.5). The only fish species that did not exhibit any guideline exceedances was lake whitefish (Figure 4.5).

At all site types, mean THg concentrations in all fish species except lake whitefish approached or exceeded the Health Canada mercury consumption guideline for frequent fish consumption (Figure 4.6). Exceedances were greater downstream of development and within the Athabasca Delta relative to sites upstream of development or near development (Figure 4.6). The average concentration in walleye in the Athabasca Delta approached the Health Canada mercury consumption guideline for commercial fish consumption (Figure 4.6).

Discussion

Spatial Trends of Total Mercury in Biota of the Athabasca River

The spatial distribution of THg in Trichoptera, northern pike, goldeye, and walleye suggests that oil sands development is a significant source of mercury within the oil sands region (Figure 4.1, 4.2). The spatial distribution of THg in Trichoptera, northern pike, goldeye, and walleye is consistent with the distribution of THg in vegetation on the adjacent landscape (Figure 3.4, chapter three). This suggests a potential link between deposition of mercury emitted by oil sands development within the Athabasca watershed and increased concentrations of mercury in biota of the Athabasca River.

The elevated concentrations in biota downstream of development and in the Athabasca Delta relative to sites near development are likely the result of increased deposition of particulate-bound mercury caused by upstream land disturbance within the development area (Evans and Talbot 2012). Land disturbance associated with oil sands development mobilizes sequestered mercury, other contaminants of concern, and dissolved organic carbon (DOC) to the Athabasca River (Gueguen et al. 2011, Timoney and Lee 2011). Oil sands development has been shown to increase loadings of dissolved organic matter (DOM) up to 8-fold at sites near development relative to upstream sites (Gueguen et al. 2011). Mercury and other contaminants of concern form complexes with DOM, mediating their transport through watersheds. Recent large-scale studies indicate that in-channel production of MeHg in sediments of lotic systems is generally low due to a lack of suitable methylation sites, so the predominant source of MeHg to stream ecosystems is runoff containing mercury methylated within watersheds and connected wetlands (Brigham et al. 2009; Marvin-

Dipasquale et al. 2009). Therefore, it is likely that the majority of bioavailable mercury within the Athabasca River is derived almost entirely from the Athabasca watershed and that land disturbance associated with oil sands development increases loadings downstream of the development area, increasing the exposure of biota inhabiting these habitats.

Evidence from the Experimental Lakes Area indicates that a very small proportion of newly deposited mercury in terrestrial and wetland ecosystems is mobilized by subsequent precipitation events while the remainder becomes sequestered in vegetation and immobilized in soils (Hintelmann et al. 2002). However, numerous studies have concluded that historical mercury sequestered in soils is a significant source of mercury to aquatic systems. Given over 40 years of substantial mercury deposition to the Athabasca watershed from oil sands emissions (Barrie and Kovalick 1980; Murray 1981) and evidence of increased deposition of mercury to lakes northeast of upgrading facilities within the last 20 years (Curtis et al. 2010), it is likely that a massive store of mercury exists in soils of the region. This pool of mercury may be periodically mobilized by natural processes such as forest fires (Kelly et al. 2006), or by anthropogenic land disturbance and represents a long-term source of mercury within the region.

Comparisons of Mercury Among Fish Species

Mercury concentrations in northern pike and walleye were significantly higher than concentrations in goldeye and lake whitefish. While not examined in the present study, differences in mercury concentrations likely reflect differences

in dietary items utilized and differences in trophic position, as mercury concentrations are highly associated with trophic level (Cabana and Rasmussen 1994; Kidd et al. 1995). Lake whitefish have a varied diet, but they mainly consume aquatic insects, zooplankton, and molluscs, but have been reported to occasionally feed on small fish (Nelson and Paetz 1992). Within lotic systems with low densities of zooplankton, they are mainly bottom feeders and consume aquatic insects. A study of feeding ecology and diet of goldeye in the Athabasca River found that adult goldeye primarily consumed Corixids and other aquatic insects as well as small fish (Donald and Kooyman 1977). Both walleye and northern pike are primarily piscivores as adults (Nelson and Paetz 1992). Among species differences in mercury concentrations observed in the current study are consistent with these trophic positions. Of the four species examined, northern pike and walleye occupy the highest trophic positions and exhibited significantly higher mean mercury concentrations than lake whitefish and goldeye that occupy lower trophic levels (Figure 4.3). Lake whitefish occupy the lowest trophic level and exhibited the lowest mean mercury concentration (Figure 4.3). Goldeye occupy an intermediate trophic level relative to the other three species examined and exhibited an intermediate mean mercury concentration (Figure 4.3).

Within species, condition factor was not significantly related to mercury concentration (Table 4.1). Pollutant effects on condition factor are often masked in wild populations due to other factors that affect fish condition factor, such as competition and food availability, that interact synergistically to cause declines in fish health (Schlenk et al. 2008). A study of health of brown trout (*Salmo trutta*)

in a mining-impacted river in Montana concluded that individuals from contaminated sites were likely physiologically impaired as a result of metals exposure as indicated by increased products of lipid peroxidation, Cu inclusions, and metallothionein concentrations; however, fish from reference sites displayed larger variation in condition factor relative to fish from contaminated sites (Farag et al. 1995). While not statistically significant, condition factor among fish species in the current study was highest in lake whitefish, the species with the lowest mean mercury concentration, and condition factor was lowest in northern pike, a species with a comparatively high mean mercury concentration (Figure 4.4). While other factors that may influence fish condition factor were not examined in the current study, these results agree with the findings of a study of yellow perch (*Perca flavescens*) in Ontario lakes that found that higher liver metal concentrations were associated with lower relative condition factor compared to fish of a similar age from less contaminated lakes (Eastwood and Couture 2001).

The growth rate of goldeye, lake whitefish, and walleye was negatively related to mercury concentration (Table 4.1), suggestive of somatic growth dilution (Trudel and Rasmussen 2006; Ward et al. 2010). Northern pike displayed lower growth rates relative to the other species examined and growth rate was not significantly related to mercury concentrations (Table 4.1). Northern pike are a slow-growing species after reaching sexual maturity (Diana 1983). Biomagnification factors of northern pike over prey in a southern Alberta reservoir were 2.4 in 2-year old pike compared to 5.8 in 5-6 year old pike (Brinkmann and Rasmussen 2010). The average age of northern pike in the

current study was 8.6 years old; therefore, low growth rate and condition factor could reflect lower somatic growth dilution of ingested mercury relative to the other species examined.

Human Health Risk Assessment

The estimated % pTDI values obtained using fish intake values from the general Canadian population indicate that children may be at risk from consuming walleye, northern pike, and goldeye within the region, while consumption of lake whitefish at these intake levels likely do not pose a significant health risk (Tables 4.4 and 4.5). At similar consumption levels to the rest of the Canadian population, adults and women within the region are likely not at risk from consumption of the species captured in this study (Tables 4.2 and 4.3).

Estimated % pTDI values based on the very low (< 4 g/day) and low (5-29 g/day) intake values for subsistence consumers in Lesser Slave Lake are well below 100 for adults, women, and children for the fish species examined, suggesting minimal health risks from exposure to MeHg under this consumption scenario (Tables 4.2, 4.3, 4.4, and 4.5). However, communities within the Athabasca region are much more isolated than Lesser Slave Lake. As a result, it is likely that people living within the region consume much higher amounts of fish, as alternate food items are much more expensive (personal observation). Therefore, the very low and low intake values likely underestimate the exposure of people within the region to MeHg in their diet. It is likely that the medium (30-99 g/day) to high (>100 g/day) fish intake values for the Lesser Slave Lake

population better approximate fish consumption habits of people within the Athabasca region.

The % pTDI values obtained for high fish intake were much greater than 100 for walleye, northern pike, goldeye, and lake whitefish for women and children (Tables 4.3, 4.4, and 4.5). For the adult population, % pTDI values were greater than 100 for walleye, northern pike, and goldeye (Table 4.2). This indicates that mercury exposure at these consumption levels likely exceeds toxicological reference values and may pose significant health risks associated with exposure to MeHg. Consumption of lake whitefish by adults at this intake rate was the only scenario that did not present potential health risks associated with fish consumption (Table 4.2). Under the medium fish intake scenario, women and children % pTDI values exceeded 100 for walleye, northern pike, and goldeye, while values did not exceed 100 for lake whitefish (Table 4.3, 4.4, and 4.5). % pTDI values did not exceed 100 for the adult subpopulation, indicating minimal health risks under this intake scenario (Table 4.2).

The % pTDI values calculated for walleye, northern pike, and lake whitefish for adults and women in this study are similar to % pTDI values obtained by RAMP (2009). However, the % pTDI values obtained for goldeye in this study are similar to those for walleye and northern pike and are much higher than those obtained by RAMP (2009). The RAMP human health risk assessment (2009) suggests restricted intake of walleye in the region for the Lower Athabasca River, but not northern pike or goldeye. However, our findings suggest that

consumption of goldeye and northern pike from the Lower Athabasca River may pose similar health risks as consumption of walleye.

The % pTDI values found in this study were obtained using methods and data that have many assumptions and uncertainties. However, the high % pTDI values found under exposure scenarios likely approximating those of people within the Athabasca region illustrate the need for detailed risk assessments of the health risks of mercury exposure within the region. It is imperative that consumption habits within the region be assessed (determination of accurate average local daily intake values, determination of intake values for different fish species, etc.), as the application of data from a population other than the population under study may under or over estimate exposure risk.

Comparison to Mercury Consumption Guidelines

The Regional Aquatics Monitoring Program measures mercury in fish tissues in the oil sands region. However, inconsistency in sampling locations, species sampled and inconsistent sampling of locations and species over time makes it virtually impossible to compare spatial trends from the RAMP program to the results of the current study. Concentrations of mercury in walleye and lake whitefish were assessed at a single site downstream of oil sands development; concentrations in goldeye and northern pike were not assessed (RAMP 2009). At the single Athabasca River main stem site sampled by RAMP in 2008, 0% of lake whitefish exceeded subsistence or commercial consumption guidelines, 62% (n =

16) of walleye exceeded the subsistence consumption guideline, and of that 62%, 3% exceeded the commercial consumption guideline (RAMP 2009).

In the current study, mercury concentrations in lake whitefish (n = 27) did not exceed either consumption guideline, likely due to the low trophic position of this species. Across all sites on the main stem of the Athabasca River, Athabasca Delta, and Lake Athabasca, 80% of walleye (n = 20) exceeded frequent consumption guidelines and 20% exceeded commercial guidelines, 75% of northern pike (n = 20) exceeded frequent consumption guidelines and 20% exceeded commercial guidelines, and 72% of goldeye (n = 47) exceeded frequent consumption guidelines and 4% exceeded commercial guidelines (Figure 4.5). Upstream of oil sands development, one walleye exceeded frequent consumption guidelines, the remaining exceedances occurred at sites at oil sands development and downstream of oil sands development (Figure 4.6).

The range of mercury concentrations found in fish species in this study is similar to those found in other assessments of the same species within the region (RAMP 2009; Evans and Talbot 2012); however, a greater proportion of individuals captured in this study exceeded consumption guidelines for subsistence or frequent consumers (Figure 4.5). While other assessments maintain that mercury in fish species is not increasing over time, an assessment of mercury egg burdens in water birds nesting on Lake Athabasca found that mercury burdens in eggs had increased by 40% between 1977 and 2009 (Hebert et al. 2011). The authors concluded that the cause for the increase was not due to differences in trophic level, but was likely a result of increased mercury inputs from upstream

sites (Hebert et al. 2011). It is highly unlikely that mercury concentrations in bird populations are increasing without a corresponding increase in their prey; therefore, the trends found by Evans and Talbot (2012) likely result from the limitations of their data set (variation in analytical techniques, sampling techniques, small sample sizes in some years at some sites, etc.). Accurate, long-term assessments of mercury within biota of the region are crucial to determine if concentrations are increasing over time and if these increases pose a risk to people living within downstream communities.

Literature Cited

Agah, H., M. Leermakers, Y. Gao, S.M.R. Fatemi, M.M. Katal, W. Baeyens, and M. Elskens. 2010. Mercury accumulation in fish species from the Persian Gulf and in human hair from fishermen. Environmental Monitoring and Assessment **169**:203-216.

Bailey, R.C., R.H. Norris and T.B. Reynoldson. 2004. Bioassessment of freshwater ecosystems using the reference condition approach. Kluwer Academic Publishers, Boston. 184 p.

Barnham, C., and A. Baxter. 1998. Condition factor, K, for salmonid fish. Fisheries Notes **0005**:1-3.

Barrie, L.A., and J. Kovalick. 1980. A wintertime investigation of the deposition of pollutants around an isolated power plant in Northern Alberta. Prepared for the Alberta Oil Sands Environmental Research Program by Atmospheric Environment Service. AOSERP Report 90. 115 p.

Brigham, M.E., D.A. Wentz, G.R. Aiken, and D. P. Krabbenhoft. 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. Environmental Science and Technology **43**:2720-2725.

Brinkmann, L., and J.B. Rasmussen. 2010. High levels of mercury in biota of a new prairie irrigation reservoir with a simplified food web in Southern Alberta, Canada. Hydrobiologia **641**:11-21.

Cabana, G. and J.B. Rasmussen. 1994. Modelling food chain structure and contaminant bioaccumulation using stable nitrogen isotopes. Nature **372**:255-257.

Chasar, L.C., B.C. Scudder, A.R. Stewart, A.H. Bell, and G.R. Aiken. 2009. Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation. Environmental Science and Technology **43**:2733-2739.

Chen, Y. 2009. Cancer incidence in Fort Chipewyan, Alberta 1995-2006. Alberta Cancer Board, Division of Population Health and Information Surveillance, Alberta Health and Wellness, Government of Alberta.

Clarkson, T.W., L. Magos, and G.J. Myers. 2003. The toxicology of mercury - current exposures and clinical manifestations. The New England Journal of Medicine **349**:1731-7.

Clifford, J.S. 1991. Aquatic invertebrates of Alberta. University of Alberta Press, Edmonton, Alberta.

Diana, J.S. 1983. An energy budget for northern pike (*Esox lucius*). Canadian Journal of Zoology **61**:1968-1975.

Donald, D.B., and A.H. Kooyman. 1977. Food, feeding habits, and growth of goldeye, *Hiodon alosoides* (Rafinesque), in waters of the Peace-Athabasca Delta. Canadian Journal of fisheries and Aquatic Sciences **55**:1038-1047.

Donald, D.B., H.L. Craig, J. Syrgiannis. 1996. Contaminants in environmental samples: mercury in the Peace, Athabasca and Slave River basins. Northern River Basins Study project report no. 105. Edmonton, Alberta.

Eastwood, S., and P. Couture. 2002. Seasonal variations in condition and liver metal concentrations of yellow perch (*Perca flavescens*) from a metal-contaminated environment. Aquatic Toxicology **58**:43-56.

Eto, K., H. Tokunaga, K. Nagashima, and T. Takeuchi. 2002. An autopsy case of Minamata Disease (methylmercury poisoning) - pathological viewpoints of peripheral nerves. Toxicological Pathology **30**:714-722.

Farag, A.M., M.A. Stansbury, C. Hogstrand, E. MacConnell, and H.L. Bergman. 1995. The physiological impairment of free-ranging brown trout exposed to metals in the Clark Fork River, Montana. Canadian Journal of Fisheries and Aquatic Sciences **52**:2038-2050.

Fowlie, A.R., P.V. Hodson, and M.B.C. Hickey. 2008. Spatial and seasonal patterns of mercury concentrations in fish from the St. Lawrence River at Cornwall, Ontario: Implications for monitoring. Journal of Great Lakes Research **34**:72-85.

Gilbertson, M. 2004. Male cerebral palsy hospitalization as a potential indicator of neurological effects of methylmercury exposure in Great Lakes communities. Environmental Research **95**:375-384.

Government of Alberta. 2012. Alberta guide to sportfishing regulations.

Grandjean, P., K. Murata, E. Budtz-Jorgensen, and P. Wiehe. 2004. Cardiac autonomic activity in methylmercury neurotoxicity: 14-year follow-up of a Faroese birth cohort. Journal of Pediatrics **144**:169-176.

Gueguen, C., O. Clarisse, A. Perroud, and A. McDonald. 2011. Chemical speciation and partitioning of trace metals (Cd, Co, Cu, Ni, Pb) in the lower Athabasca river and its tributaries (Alberta, Canada). Journal of Environmental Monitoring **13**:2865-2872.

Hall, B.D., R.A. Bodaly, R.J.P. Fudge, J.W.M. Rudd, and D.M. Rosenberg. 1997. Food as the dominant pathway of methylmercury uptake by fish. Water, Air, and Soil Pollution **100**:13-24.

Harada, M., T. Fujino, T. Oorui, S. Nakachi, T. Nou, T. Kizaki, Y. Hitomi, N. Nakano, and H. Ohno. 2005. Followup study of mercury pollution in indigenous tribe reservations in the province of Ontario, Canada, 1975-2002. Bulletin of Environmental Contamination and Toxicology **74**:689-697.

Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott, and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology **36**:5034-5040.

Hornberger, M.I., S.M. Luoma, M.L. Johnson, and M. Holyoak. 2009. Influence of remediation in a mine-impacted river: metal trends over large spatial and temporal scales. Ecological Applications **19**:1522-1535.

Jensen, S. and A. Jernelov. 1969. Biological methylation of mercury in aquatic organisms. Nature **223**:753-754.

Jernelov, A. and H. Lann. 1971. Mercury accumulation in food chains. Oikos **22**:403-406.

Kelly, E.N., D.W. Schindler, V.L. St. Louis, D.B. Donald, and K.E. Vladicka. 2006. Forest fire increases mercury accumulation by fishes via food web restructuring and increased mercury inputs. Proceedings of the National Academy of Sciences **103**:19380-19385.

Kelly, E.N., J.W. Short, D.W. Schindler, P.V. Hodson, M. Ma, A.K. Kwan, and B.L. Fortin. 2009. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. Proceedings of the National Academy of Sciences USA 106:22346-22351.

Kidd, K.A., D.W. Schindler, R.H. Hesslein, and D.C.G. Muir. 1995. Correlation between stable nitrogen isotope ratios and concentrations of organochlorines in biota from a freshwater food web. The Science of the Total Environment **160/161**: 381-390.

Marvin-Dipasquale, M., M.A. Lutz, M.E. Brigham, D.P. Krabbenhoft, G.R. Aiken, W.H. Orem, and B.D. Hall. 2009. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and bed sediment-pore water partitioning. Environmental Science and Technology **43**:2726-2732.

Murata, K., M. Sakamoto, K. Nakai, P. Weihe, M. Dakeishi, T. Iwata, X. Liu, T. Ohno, T. Kurosawa, K. Kamiya, and H. Satoh. Effects of methylmercury on neurodevelopment in Japanese children in relation to the Madeiran study. International Archives of Occupational Health **77**:571-579.

Murray, W.A. 1981. The 1981 snowpack survey in the AOSERP study area. Prepared for the Alberta Oil Sands Environmental Research Program by Atmospheric Environment Service. AOSERP Report 125. 137 p.

Myers, G.J., and P.W. Davidson. 2000. Does methylmercury have a role in causing developmental disabilities in children? Environmental Health Perspectives **108**:413-420.

Nash, R.D.M., A.H. Valencia, and A.J. Geffen. 2006. The origin of Fulton's condition factor - setting the record straight. Fisheries **31**: 236-238.

National Pollutant Release Inventory (NPRI). 2012. www.ec.gc.ca/inrp-npri/. Accessed March 13, 2012.

Nelson, J.S., and M.J. Paetz. 1992. The fishes of Alberta. The University of Alberta Press, Edmonton, Alberta.

Olson, M.L., L.B. Cleckner, J.P. Hurley, D.P. Krabbenhoft, and T.W. Heelan. 1997. Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades. Fresenius Journal of Analytical Chemistry **358**:392-396.

Pickhardt, P.C., and N.S. Fisher. 2007. Accumulation of inorganic and methylmercury by freshwater phytoplankton in two contrasting water bodies. Environmental Science and Technology **41**:125-131.

Price, M. 2008. 11 Million Litres a Day: The Tar Sands' Leaking Legacy. Environmental Defence, Toronto.

Regional Aquatics Monitoring Program. 2009. Final 2008 Technical Report. Hatfield Consultants, Stantec Consulting Ltd., Klohn Crippen Berger Ltd., and Western Resource Solutions.

Regional Aquatics Monitoring Program. 2011. 2010 regional aquatics monitoring (RAMP) scientific review. Integrated Water Management Program. Alberta Innovates - Technology Futures, Calgary, Alberta. 160 pp.

Schlenk, D., R. Handy, S. Steinert, M.H. Depledge, and W. Benson. 2008. Pages 683-733 *in* R.T. Di Giulio and D.E. Hinton, editor. Toxicology of Fishes. CRC Press, Boca Raton, Florida.

Timoney, K. 2007. A study of water quality as related to public health issues, Fort Chipewyan, Alberta. Treeline Ecological Research, Edmonton, Alberta.

Timoney, K.P., and P. Lee. 2011. Polycyclic aromatic hydrocarbons increase in Athabasca River Delta sediment: temporal trends and environmental correlates. Environmental Science and Technology **45**:4278-4284.

Trudel, M., and J.B. Rasmussen. 2006. Bioenergetics and mercury dynamics in fish: a modelling perspective. Canadian Journal of Fisheries and Aquatic Sciences **63**:1890-1902.

U.S. Environmental Protection Agency, 1996, Draft Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry: EPA 821-R-96-012, Office of Water, 32 p.

Ward, D.M., K.H. Nislow, and C.L. Folt. 2010a. Bioaccumulation syndrome: identifying factors that make some stream food webs prone to elevated mercury bioaccumulation. Annals of the New York Academy of Science **1195**:62-83.

Ward, D.M., K.H. Nislow, C.Y. Chen, and C.L. Folt. 2010b. Rapid, efficient growth reduces mercury concentrations in sream-dwelling Atlantic Salmon. Transactions of the American Fisheries Society **139**:1-10.

Wheatley, B., and S. Paradis. 1995. Exposure of Canadian Aboriginal peoples to methylmercury. Water, Air and Soil Pollution **80**:3-11.

Wiggins, G.B. 1996. Larvae of the North American caddisfly genera (Trichoptera). University of Toronto Press, Toronto, Ontario.

Yorifuji, T., T. Tsuda, S. Takao, and M. Harada. 2008. Long-term exposure to methylmercury and neurologic signs in Minamata and neighboring communities. Epidemiology **19**:3-9.

Zar, J.H. 1999. Biostatistical Analysis. 4th edition. Prentice Hall, Upper Saddle River, New Jersey. pp 210-214.

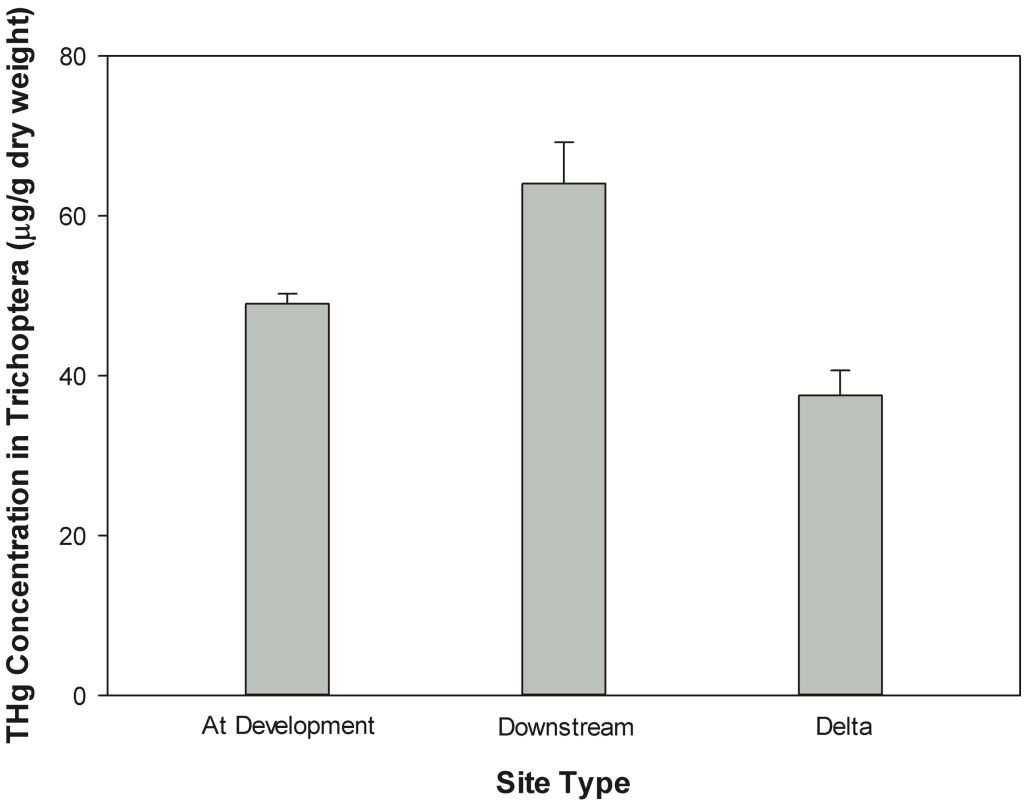

Figure 4.1 Total mercury concentrations (mean ± SE) in Trichoptera by sample site type. THg varied significantly with site type (ANOVA, $F = 19.433$, $p < 0.001$, $df = 2,11$). THg was significantly higher at sites near oil sands development relative to sites in the Athabasca delta (Tukey's, $p = 0.013$). THg was significantly higher at sites downstream of oil sands development relative to sites near oil sands development (Tukey's, $p = 0.016$) and in the Athabasca delta (Tukey's, $p < 0.001$). Due to an insufficient sample mass obtained at upstream sites and low sample size in Lake Athabasca ($n = 1$), only sites near development, downstream of development, and in the Athabasca delta could be compared statistically.

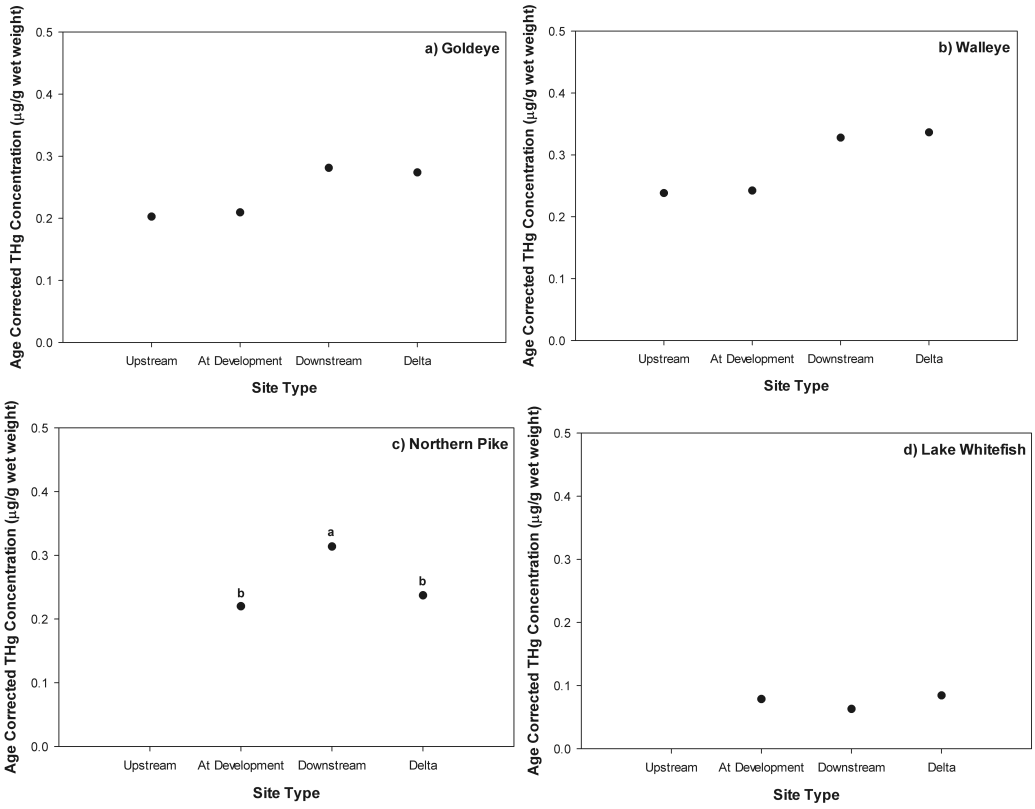

Figure 4.2 Least squared mean THg concentration in fishes from the Athabasca River by sample site type. THg varied significantly with site type in goldeye (n = 47; ANOVA, F = 3.213, p = 0.033, df = 3,43) and northern pike (n = 20; ANOVA, F = 6.102, p = 0.010, df = 2,19) populations. Lake whitefish (n = 27) did not display a significant spatial trend. THg concentrations in goldeye were significantly higher at delta sites relative to sites upstream of and near development (Tukey's, $p<0.05$). THg concentrations in northern pike were significantly elevated downstream of oil sands development relative to concentrations near development (Tukey's, p = 0.015) and in the Athabasca delta (Tukey's, p = 0.031). Significant pair wise differences are indicated by letters. Sample sizes obtained for walleye (n = 20) at some site types were too low (at development n = 2) to permit statistical analysis of spatial trends in THg; however, the distribution of mean THg concentrations across site types is similar to goldeye.

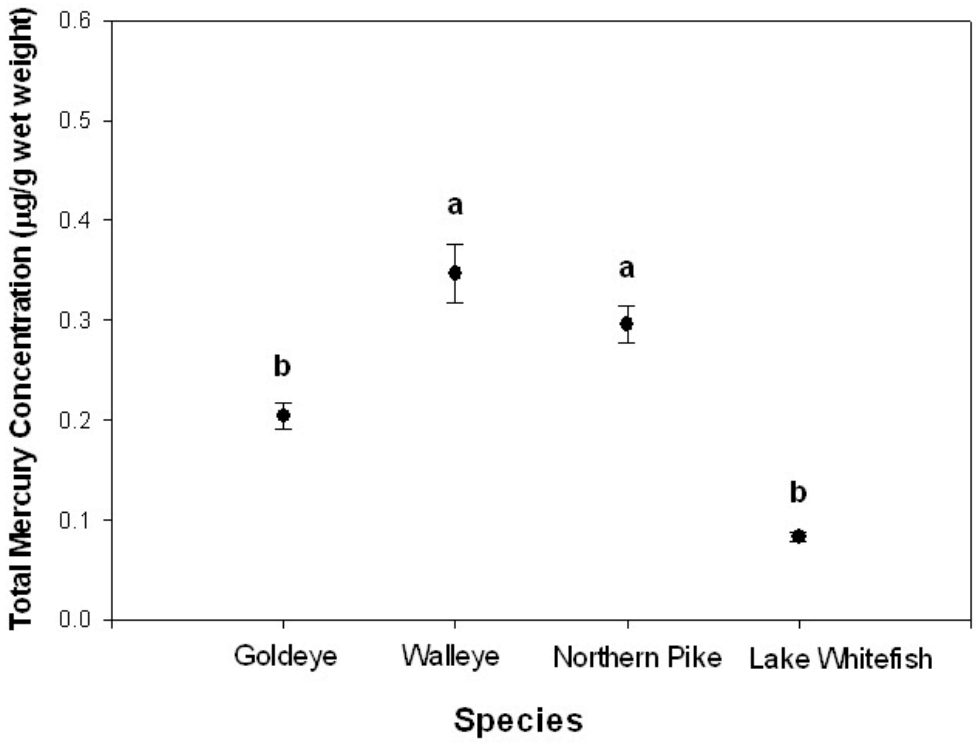

Figure 4.3 Mean total Hg concentration ± SE (age corrected, dorsal muscle tissue) among fish species within the Athabasca River and Athabasca delta. Walleye exhibited the highest THg concentrations. THg concentrations in walleye (n=20) and northern pike (n=20) were significantly higher than goldeye (n=47) and lake whitefish (n=27) (Tukey's test $p<0.001$). Letters indicate significant pair-wise differences.

Table 4.1 Results of simple linear regressions between mercury in fish from the Athabasca River and Athabasca delta and factors that influence mercury concentrations in fishes. The direction of the relationship (+ or -) is reported for significant relationships only.

Fish Species	Explanatory Variable	+/-	F-Ratio	Slope	p-value	r^2
Goldeye	Total Length	+	20.961	0.011	<0.01	0.333
(n = 44)	Age	+	38.358	0.077	<0.01	0.477
	Mass	+	6.374	0.001	0.015	0.132
	Growth Rate	-	32.436	29.390	<0.01	0.436
	Condition Factor		0.168	0.134	0.684	0.004
Walleye	Total Length	+	6.680	<0.00	0.019	0.271
(n = 20)	Age	+	14.005	0.085	<0.01	0.438
	Mass		3.054	<0.00	0.098	0.145
	Growth Rate	-	7.739	30.522	0.012	0.301
	Condition Factor		0.585	0.142	0.454	0.032
Northern Pike	Total Length	+	21.107	0.002	<0.01	0.540
(n = 20)	Age	+	68.172	0.159	<0.01	0.791
	Mass	+	22.745	<0.00	<0.01	0.556
	Growth Rate		1.183	26.432	0.291	0.062
	Condition Factor		0.130	-0.016	0.722	0.007
Lake Whitefish	Total Length	+	10.685	0.004	0.003	0.308
(n = 26)	Age	+	7.928	0.059	0.010	0.498
	Mass	+	9.696	<0.00	<0.01	0.288
	Growth Rate	-	5.312	24.380	0.030	0.181
	Condition Factor		0.822	0.110	0.374	0.033

Table 4.2 Exposure ratios to mercury in fish (expressed as % pTDI values) for adults in the Athabasca region under various weekly fish intake scenarios. A % pTDI value approaching or above 100 identifies exposure scenarios where the toxicological reference value is exceeded. "General" refers to the average weekly fish intake of the Canadian population. "Very low to high" refers to weekly fish intake classifications of a subsistence population in Slave Lake, AB. Very low < 4g/day, low = 5-29 g/day, medium = 30-99 g/day, and high > 100 g/day. The pTDI for adults = 0.47 µg/kg bw/day.

Fish Species	Mean THg (µg/g)	% pTDI				
		General	Very Low	Low	Medium	High
Walleye	0.35	27	1.97	16	57	335
Northern Pike	0.30	23	1.68	14	48	286
Goldeye	0.28	21	1.56	13	45	266
Lake Whitefish	0.08	6	0.47	4	14	80

Table 4.3 Exposure ratios to mercury in fish (expressed as % pTDI values) for women of childbearing age and pregnant women in the Athabasca region under various weekly fish intake scenarios. A % pTDI value approaching or above 100 identifies exposure scenarios where the toxicological reference value is exceeded. "General" refers to the average weekly fish intake of the Canadian population. "Very low to high" refers to weekly fish intake classifications of a subsistence population in Slave Lake, AB. Very low < 4g/day, low = 5-29 g/day, medium = 30-99 g/day, and high > 100 g/day. The pTDI for women of childbearing age and pregnant women = 0.2 µg/kg bw/day.

Fish Species	Mean THg (µg/g)	% pTDI				
		General	Very Low	Low	Medium	High
Walleye	0.35	64	4.62	38	133	788
Northern Pike	0.30	54	3.95	32	113	673
Goldeye	0.28	50	3.67	30	105	626
Lake Whitefish	0.08	15	1.11	9	32	189

Table 4.4 Exposure ratios to mercury in fish (expressed as % pTDI values) for children between the ages of 5 and 11 in the Athabasca region under various weekly fish intake scenarios. A % pTDI value approaching or above 100 identifies exposure scenarios where the toxicological reference value is exceeded. "General" refers to the average weekly fish intake of the Canadian population. "Very low to high" refers to weekly fish intake classifications of a subsistence population in Slave Lake, AB. Very low < 4g/day, low = 5-29 g/day, medium = 30-99 g/day, and high > 100 g/day. The pTDI for children age 5-11 = 0.2 µg/kg bw/day.

Fish Species	Mean THg (µg/g)	% pTDI				
		General	Very Low	Low	Medium	High
Walleye	0.35	92	6.69	52	190	1148
Northern Pike	0.30	78	5.72	45	163	981
Goldeye	0.28	73	5.31	42	151	911
Lake Whitefish	0.08	22	1.61	13	46	275

Table 4.5 Exposure ratios to mercury in fish (expressed as % pTDI values) for children between the ages of 1 and 4 in the Athabasca region under various weekly fish intake scenarios. A % pTDI value approaching or above 100 identifies exposure scenarios where the toxicological reference value is exceeded. "General" refers to the average weekly fish intake of the Canadian population. "Very low to high" refers to weekly fish intake classifications of a subsistence population in Slave Lake, AB. Very low < 4g/day, low = 5-29 g/day, medium = 30-99 g/day, and high > 100 g/day. The pTDI for children age 1-4 = 0.2 µg/kg bw/day.

Fish Species	Mean THg (µg/g)	% pTDI				
		General	Very Low	Low	Medium	High
Walleye	0.35	120	8.66	72	253	1480
Northern Pike	0.30	103	7.40	62	216	1264
Goldeye	0.28	95	6.87	57	201	1174
Lake Whitefish	0.08	29	2.08	17	61	355

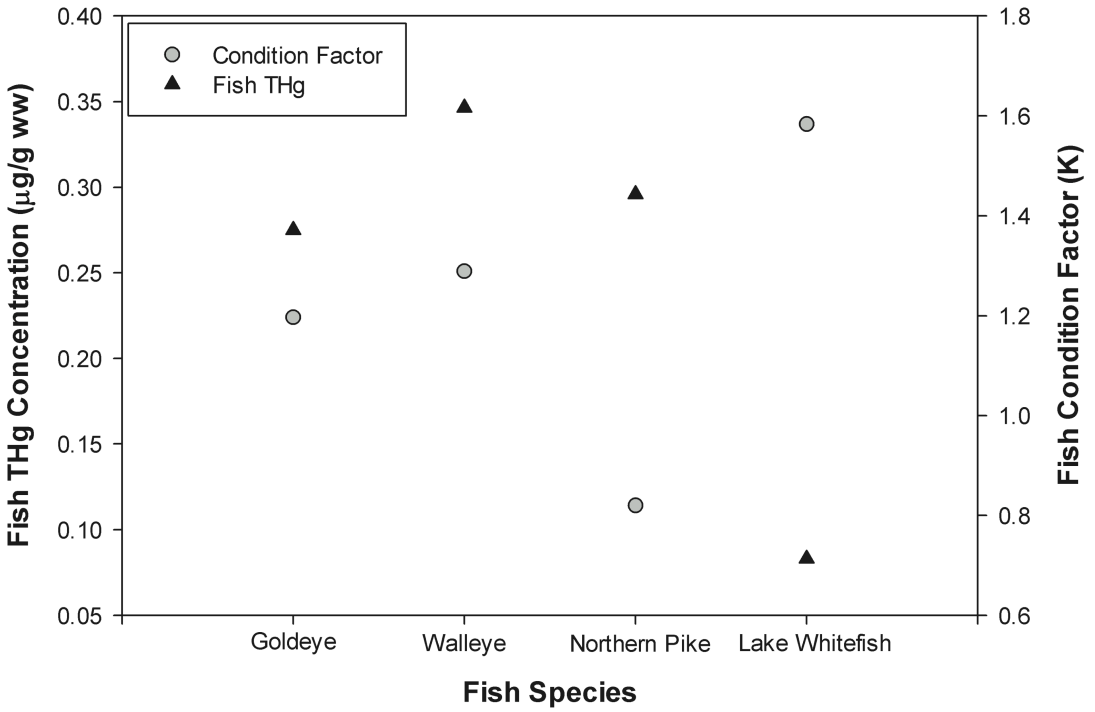

Figure 4.4 Fish condition factor (K) and fish THg concentrations in tissues of fish collected from the Athabasca River and Athabasca Delta.

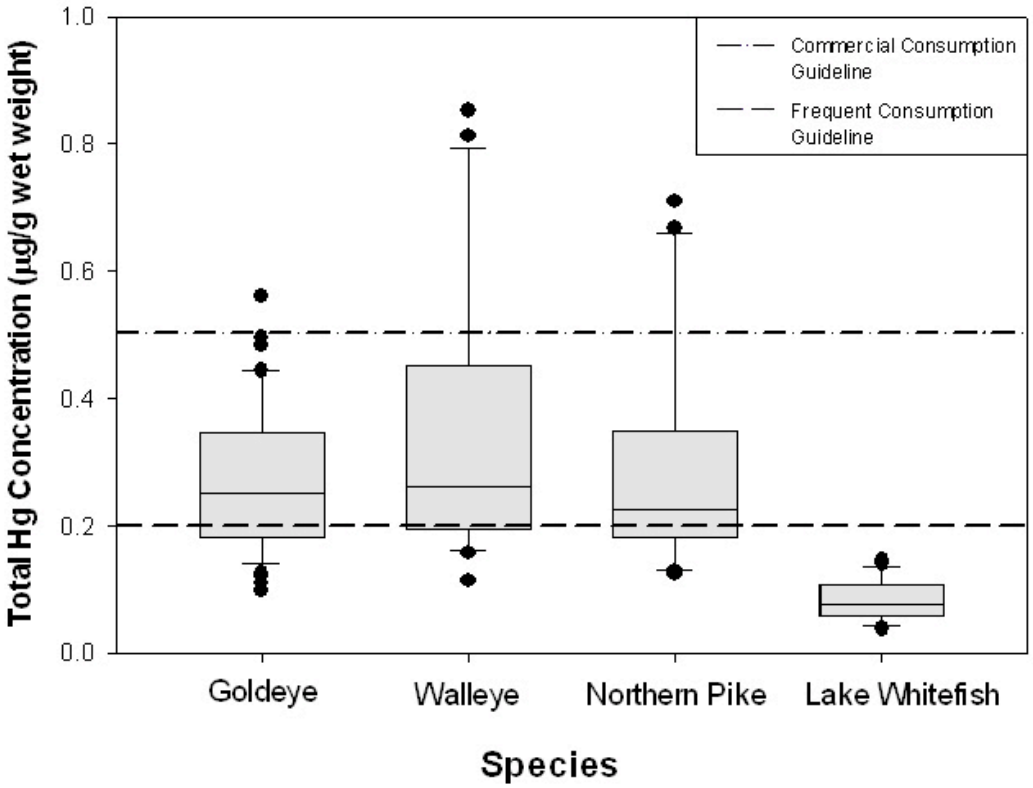

Figure 4.5 Comparison of THg concentrations in fish species within the Athabasca River and Athabasca delta to Health Canada mercury consumption guidelines. 72%, 80%, 75%, and 0% of goldeye (n = 47), walleye (n = 20), northern pike (n = 20), and lake whitefish (n = 27), respectively, exceeded the frequent consumption guideline of 0.2 µg/g (dashed line). 4%, 20%, 20%, and 0% of goldeye, walleye, northern pike, and lake whitefish, respectively, exceeded the commercial consumption guideline of 0.5 µg/g (dashed and dotted line).

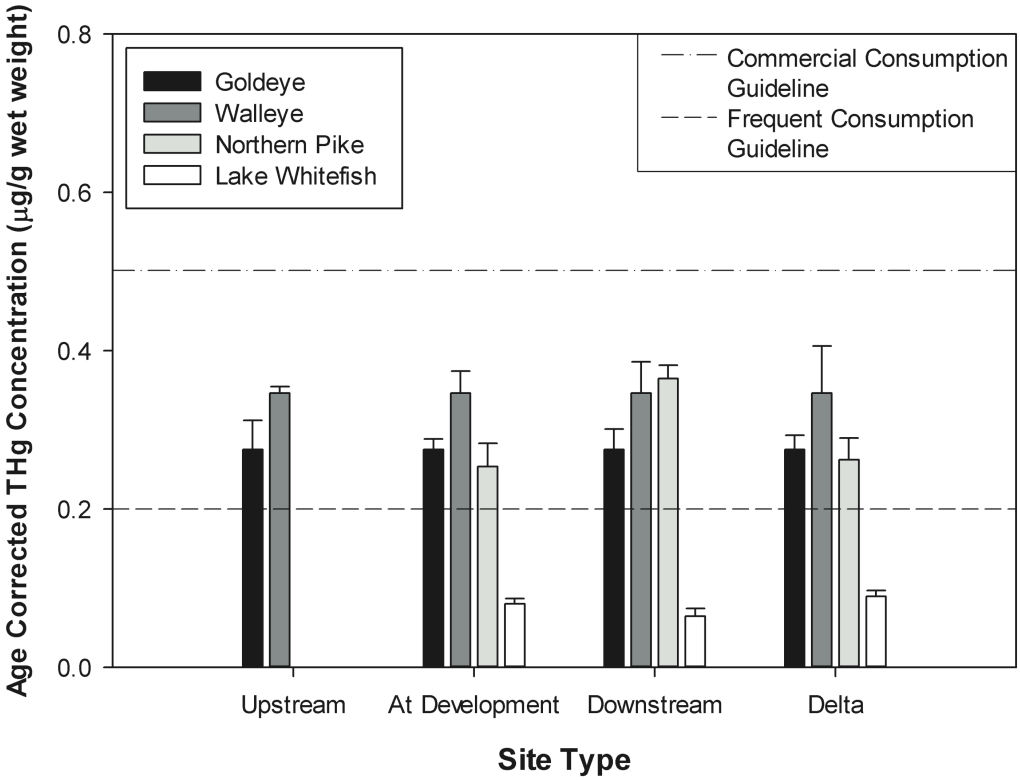

Figure 4.6 Comparison of THg concentrations in fish species of the Athabasca River and Athabasca Delta to Health Canada mercury guidelines by site type (mean ± SE). At all site types, mean THg concentrations in all species except lake whitefish approached or exceeded Health Canada's frequent consumption guideline of 0.2 µg/g. Mean THg concentrations in walleye in the Athabasca Delta approached Health Canada's commercial consumption guideline of 0.5 µg/g. Goldeye n = 47, walleye n = 20, northern pike n = 20, and lake whitefish n = 27.

Chapter 5: General Conclusions

Mercury concentrations in deposition and in vegetation were within the range obtained at sites elsewhere in Canada that have no significant local sources of mercury (Graydon et al. 2006; MDN 2013). Despite these low values, the results of this study indicate that oil sands development increases mercury loadings by 5.6 times at sites near development relative to background sites. This indicates that oil sands upgraders are a significant source of airborne mercury within the oil sands region. Furthermore, given the projected increase in oil sands production within the next decade, it is likely that a corresponding increase in mercury emissions will occur within the region. Given 40 years of historic mercury deposition to the watershed and increasing mercury emissions in the future, it is likely that a massive store of mercury has and will continue to build up within the watershed of the Athabasca River as a result of oil sands development.

The results of this study also indicate that, in addition to substantially elevating mercury concentrations within the development area, oil sands is a significant source of mercury to regions at much greater distances from the immediate vicinity of development. The estimated integrated annual deposition of mercury within a 46 km radius of upgrading facilities was 96% lower than reported mercury emissions within the region for 2008 (NPRI 2012). This indicates that the majority of mercury emitted by oil sands development is deposited outside of the area immediately surrounding development. This finding is consistent with the known long-range transport of mercury within the atmosphere (Schroeder and Munthe, 1998). This finding is further corroborated

by the distribution of mercury in terrestrial vegetation, as concentrations are higher between 50 and 150 km downwind of oil sands development relative to vegetation concentrations within 50 km of upgrading facilities. The distribution of mercury within vegetation may also be driven by differences in atmospheric composition between the development area and moderate distances from development that influence the speciation of mercury within the atmosphere, resulting in higher deposition of emitted mercury to the landscape at moderate distances downwind from the source relative to within the immediate vicinity of the source (Edgerton et al. 2006; Lohman et al. 2006; Vijayaraghavan et al. 2008).

Similarities in the spatial distribution of mercury concentrations in winter snowpack and Athabasca River water indicate emissions of airborne mercury by oil sands developments contribute significant loadings of mercury to the Athabasca River and its watershed. In addition to atmospheric sources, it was found that mercury was higher at sites with a greater proportion of watershed disturbance compared to less disturbed watersheds, likely due to mobilization of soil-bound mercury.

Similarities between the spatial distribution of mercury within vegetation in the watershed of the Athabasca River and biota in the Athabasca River (Trichoptera and some fish species) suggests that mercury deposited to the landscape may enter the river through runoff and litterfall and subsequently enter food webs, linking atmospheric mercury emissions from oil sands development to mercury concentrations within biota. Elevated mercury concentrations in biota at sites downstream of development may also result from increased inputs of

mercury-contaminated particles at upstream sites near development that are deposited to downstream sediments (Vannote 1980).

Mercury concentrations were significantly higher in northern pike and walleye relative to goldeye and lake whitefish. These differences are likely attributable to differences in trophic position between species.

The mean concentration of mercury in walleye within Alberta water bodies ranges from 0.52 µg/g to 0.79 µg/g, mercury in northern pike ranges from 0.04 µg/g to 0.59 µg/g, and concentrations in lake whitefish range from 0.02 µg/g to 0.14 µg/g (RAMP 2009). The mean mercury concentrations obtained for the species captured in this study fall within these ranges and within the range for water bodies elsewhere in North America (RAMP 2009). While mean mercury concentrations in fishes in this study are not particularly high relative to other regions, they are likely high enough to pose health risks for people living within the region due to higher fish consumption rates relative to the general population of North America. High % pTDI values for walleye, northern pike, goldeye, and lake whitefish at medium to high consumption rates indicate that women and children in the region may be at risk for adverse health effects from mercury exposure, while adults may only be at risk if walleye, northern pike, and goldeye are consumed.

A high percentage of the walleye, northern pike, and goldeye captured in this study exceeded Health Canada fish mercury consumption guidelines for frequent consumers; in some species, up to 20% of the individuals captured exceeded the consumption guideline for commercial consumption. The frequency

of guideline exceedances was higher near and downstream of oil sands development relative to upstream of development; suggesting oil sands development may be a source of mercury to downstream food webs within the Athabasca River.

Regular and comprehensive monitoring of contaminant distributions on the landscape and within the Athabasca River is crucial in determining the impact of oil sands development within the oil sands region. In addition, monitoring of contaminants within plant and wildlife species regularly consumed by individuals within the region is essential in evaluating exposure and potential health risks for communities downstream of oil sands development.

Literature Cited

Edgerton, E.S., B.E. Hartsell, and J.J. Jansen. 2006. Mercury speciation in coal-fired power plant plumes observed at three surface sites in the southeastern U.S. Environmental Science and Technology **40**:4563-4570.

Lohman, K., C. Seigneur, E. Edgerton, and J. Jansen. 2006. Modeling mercury in power plant plumes. Environmental Science and Technology **40**:3848-3854.

National Pollutant Release Inventory (NPRI). 2012. www.ec.gc.ca/inrp-npri/. Accessed March 13, 2012.

Schroeder, W.M., and J. Munthe. 1998. Atmospheric mercury - an overview. Atmospheric Environment **32**:809-822.

Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell, and C.E. Cushing. 1980. River continuum concept. Canadian Journal of Fisheries and Aquatic Sciences **37**:130-137.

Vijayaraghavan, K., P. Karamchandani, C. Seigneur, R. Balmori, and S. Chen. 2008. Plume-in-grid modeling of atmospheric mercury. Journal of Geophysical Research **113**:D24305.

Appendix 1: Athabasca Project mercury in snow data. Site code refers to the site location. SWE = snow weight estimate. Dist_AR6km = distance of site from site AR6 in kilometers. Hg_C_T = Total Hg concentration (ng/L). Hg_C_D = dissolved Hg concentration (ng/L). Hg_C_P = particulate Hg concentration (ng/L).

Site Code	SWE (cm)	Dist_AR6km	Hg_C_T	Hg_C_D	Hg_C_P
AR6	7.104	0	10.778	0.514	10.263
ST3	6.074	1	5.049	0.605	4.444
AR4	6.616	2	8.081	0.365	7.716
AR7	2.820	3	8.192	0.378	7.814
ST2	9.544	7	8.403	0.397	8.007
AR16	4.121	8	10.685	0.255	10.430
BE2	9.062	10	3.212	0.314	2.897
BE3	6.724	14	5.802	0.614	5.188
MU3	20.688	14	4.508	0.346	4.162
AR8	6.887	22	3.356	0.351	3.005
ST1	8.026	25	3.153	0.294	2.858
BE1	3.471	27	1.438	0.208	1.231
EL2	11.062	29	1.458	0.159	1.300
AR2	8.378	30	2.023	0.514	1.509
AR1	6.670	33	1.354	0.137	1.217
EL3	11.442	34	1.697	0.238	1.459
TR3	2.983	36	2.387	0.399	1.988
TR2	4.826	38	1.923	0.310	1.613
EL1	4.230	39	1.337	0.223	1.115
MU2	6.236	41	2.727	0.633	2.094
MU1	20.702	42	1.956	0.322	1.633
AR15	2.061	46	2.329	0.469	1.860
JOC1	8.134	46	1.189	0.206	0.983
FR1	2.494	59	2.307	0.347	1.961
TR1	2.386	63	1.966	0.207	1.759
FR2	5.152	64	2.043	0.302	1.741
FR3	2.496	79	1.554	0.226	1.328
AR9	5.369	85	0.977	0.396	0.581
AR10	5.423	111	1.101	0.273	0.828
AR18	5.043	160	0.914	0.514	0.400
AR12	3.416	188	2.410	0.312	2.098

Appendix 2: Athabasca Project mercury in vegetation data. Site code refers to site location. Dist_AR6_km = distance of site from site AR6 in kilometers. WS_Winter = THg in white spruce in winter (µg/kg dry weight). WS_Summer = THg in white spruce in summer (µg/kg dry weight). WI_Summer = THg in willow in summer (µg/kg dry weight).

Site Code	Dist_AR6_km	WS_Winter	WS_Summer	WI_Summer
AR6	0	9.43	8.8	4.63
AR5	1	9.08	10.5	5.64
ST3	1	11.22	13.92	8.51
AR7	3	13.5	7.87	14.11
ST2	7	9.98	9.53	6.16
AR16	8	8.3	9.58	5.71
BE2	10	8.18	6.63	12.33
BE3	14	9.8	8.78	5.71
MU3	14	7.4	5.97	7.625
AR8	22	8.73	9.89	4.7
ST1	25	12.79	17.35	4.38
BE1	27	6.68	5.78	5.05
EL2	29	15.09	7.97	10.44
AR2	30	7.03	7.41	5.78
AR1	33	7.91	7.96	3.46
EL3	34	7.78	13.98	10.87
TR3	36	9.2	5.87	11.41
TR2	38	8.42	4.58	6.51
EL1	39	8.69	6.96	4.61
MU2	41	10.38	5.83	4.195
MU1	42	11.18	5.07	7.97
AR15	46	7.68	9.34	5.05
FR1	59	10.57	20.53	7.76
TR1	63	7.81	4.95	10.12
FR2	64	16.51	12.43	9.33
FR3	79	8.64	10.41	9.36
AR9	85	12.89	10.84	6.04
AR10	111	14.1	12.11	8.85
AR18	160	12.84	9.09	9.21
AR12	188	7.07	4.13	6.12

Appendix 3: Athabasca Project mercury in water of the mainstem of the Athabasca River. Site code refers to site location. Site type refers to site designation. Hg_Feb = THg concentration in water in winter (ng/L). Hg_June = THg concentration in water in summer (ng/L).

Site Code	Site Type	Hg_Feb	Hg_June
AR3	Upstream	0.71	3.34
AR2	Upstream	0.65	2.30
AR17	Upstream	0.65	4.15
AR16	At Development	0.68	9.66
AR15	At Development	1.44	10.51
AR6	At Development	0.80	9.88
AR5	At Development	0.88	13.45
AR4	At Development	0.65	10.56
AR8	At Development	2.00	8.90
AR7	At Development	1.30	10.82
AR14	Downstream	1.02	6.83
AR11	Downstream	0.69	2.10
AR12	Downstream	1.36	5.39
AR9	Downstream	0.75	6.26
AR10	Downstream	1.17	7.35
AR18	Downstream	0.85	11.56
AR13	Lake Athabasca	0.43	3.94

Appendix 4: Athabasca Project mercury in tributary water data. Site code refers to site location. Site 2 </> = midstream site, greater or less than 25% disturbance designation. Site 3 </> = stream mouth site, greater or less than 25% disturbance designation. Hg_Feb = THg concentration in tributary water in February (ng/L). Hg_Jun = THg concentration in tributary water in June (ng/L).

Site Code	Site 2 </>	Site 3 </>	Hg_Feb	Hg_Jun
AR17DN		less		2.36
AR17UP		less		1.71
BE1			1.03	4.65
BE2	greater		1.39	2.26
BE3		greater	1.57	3.91
Cal		greater		1.87
Clarke		greater		2.12
EL1			1.36	2.69
EL2	greater		0.86	3.61
EL3		greater	1.07	4.44
Eymund		greater		30.99
Fort		greater		2.53
FR3		less	0.74	1.29
FR2	less		0.64	2.15
FR1			2.89	1.18
JOC1			2.23	
MacKay		greater		3.63
McLean		greater		2.45
MU3		greater	0.55	1.02
MU2	greater		2.56	1.00
MU1			1.69	0.80
PopD				1.70
PopU		greater		1.31
ST3		less	0.58	1.81
ST2	less		0.85	1.75
ST1			0.46	1.72
TR1			0.77	1.38
TR2	greater		2.89	1.93
TR3		greater	1.41	12.55
HOR3		greater	0.82	11.49

Appendix 5: Athabasca project mercury concentrations in Trichoptera data. Site code refers to site location. Site type refers to site designation. Trichoptera were identified to the lowest practical taxonomic resolution but were grouped at order for analyses. Hg_Trichoptera = THg in Trichoptera (µg/kg dry weight).

Site Code	Site Type	Genus	Hg_Trichoptera
AR6	At Development	Brachycentrus	53.11
AR6	At Development	Hydropsyche	45.84
AR7	At Development	Brachycentrus	45.71
AR7	At Development	Hydropsyche	51.37
AR8	At Development	Hydropsyche	48.26
AR8	At Development	Brachycentrus	49.85
AR9	Downstream	Brachycentrus	72.11
AR9	Downstream	Hydropsyche	65.6
AR10	Downstream	Hydropsyche	54.41
AR14	Athabasca Delta	Neureclipsis	35.46
AR14	Athabasca Delta	Hydropsyche	43.7
AR12	Athabasca Delta	Neureclipsis	33.44
AR13	Athabasca Delta	Neureclipsis	29.74

Appendix 6: Athabasca Project mercury in goldeye (*Hiodon alosoides*) data. Site code refers to site location. Site type refers to site designation. TL = total fish length in millimeters. FL = fork fish length in millimeters. Hg_Goldeye = THg concentration in goldeye dorsal muscle tissue (µg/g wet weight).

Site Code	Site Type	TL (mm)	FL (mm)	Age	Mass (mg)	Sex	Hg_Goldeye
AR3	Upstream	394	364	9	605	female	0.125
AR3	Upstream	386	354	7	547	female	0.098
AR3	Upstream	429	397	13	765	male	0.348
AR3	Upstream	404	368	17	604	male	0.265
AR5	At Development	415	384	12	624	female	0.181
AR5	At Development	425	390	16	754	female	0.289
AR5	At Development	387	354	7	625	female	0.121
AR5	At Development	425	395	14	693	female	0.204
AR6	At Development	403	370	10	579	female	0.159
AR8	At Development	449	410	12	860	female	0.160
AR8	At Development	386	352	14	550	male	0.251
AR8	At Development	435	404	13	750	female	0.327
AR8	At Development	399	372	11	593	male	0.202
AR8	At Development	456	420	11	928	female	0.160
AR9/AR15	Downstream	404	374	12	625	male	0.247
AR9/AR15	Downstream	471	431	21	994	female	0.356
AR9/AR15	Downstream	463	425	23	804	female	0.444
AR9/AR15	Downstream	441	404	19	1099	female	0.424
AR9/AR15	Downstream	464	426	15	782	female	0.561
AR9/AR15	Downstream	438	397	13	733	female	0.382
AR9/AR15	Downstream	399	371	10	580	female	0.226
AR10	Downstream	425	385	12	671	female	0.281
AR10	Downstream	392	360	8	584	female	0.158
AR10	Downstream	410	376	13	599	female	0.300

AR10	Downstream	420	384	11	589	female	0.281
AR11	Athabasca Delta	361	376	7	458	female	0.110
AR11	Athabasca Delta	415	411	11	603	female	0.290
AR11	Athabasca Delta	424	379	12	686	female	0.200
AR18	Athabasca Delta	415	391	13	599	female	0.443
AR18	Athabasca Delta	448	383	12	837	female	0.496
AR18	Athabasca Delta	410	330	11	658	female	0.244
AR18	Athabasca Delta	416	378	12	663	female	0.317
AR18	Athabasca Delta	415	386	9	605	female	0.393
AR12	Athabasca Delta	396	399	11	559	female	0.213
AR12	Athabasca Delta	415	375	14	694	female	0.245
AR12	Athabasca Delta	414	363	20	614	female	0.483
AR12	Athabasca Delta	387	385	7	563	female	0.164
AR12	Athabasca Delta	408	395	12	697	female	0.180
AR14	Athabasca Delta	432	378	13	768	female	0.338
AR14	Athabasca Delta	411	364	14	674	female	0.250
AR14	Athabasca Delta	394	381	21	489	female	0.432
AR14	Athabasca Delta	420	381	11	617	male	0.186
AR14	Athabasca Delta	432	356	19	709	male	0.319
AR14	Athabasca Delta	407	375	12	525	male	0.249

Appendix 7: Athabasca Project mercury in walleye (*Sander vitreus*) data. Site code refers to site location. Site type refers to site designation. TL = total fish length in millimeters. FL = fork fish length in millimeters. Hg_Walleye = THg concentration in walleye dorsal muscle tissue (µg/g wet weight).

Site Code	Site Type	TL (mm)	FL (mm)	Age	Mass	Sex	Hg_Walleye
AR3	Upstream	515	492	8	1256	female	0.211334272
AR3	Upstream	213	199	2	71	immature	0.113063968
AR3	Upstream	485	463	6	1342	male	0.157857456
AR3	Upstream	566	547	8	1628	male	0.194227974
AR3	Upstream	536	502	8	1410	male	0.188733251
AR8	At Development	446	424	7	766	male	0.200142972
AR8	At Development	510	499	9	1327	male	0.185297666
AR9/AR15	Downstream	464	338	8	810	male	0.293025347
AR9/AR15	Downstream	487	462	15	1021	female	0.325633074
AR10	Downstream	481	454	10	996	male	0.350402915
AR11	Athabasca Delta	482	436	8	1009	female	0.261528725
AR11	Athabasca Delta	505	482	22	1133	male	0.263000618
AR11	Athabasca Delta	522	442	15	1251	male	0.546407647
AR18	Athabasca Delta	459	632	9	848	female	0.617244116
AR18	Athabasca Delta	508	652	15	1146	female	0.812557105
AR18	Athabasca Delta	466	456	12	964	male	0.261966808
AR18	Athabasca Delta	652	477	16	3700	male	0.459482251
AR18	Athabasca Delta	663	500	18	2999	male	0.852270116
AR12	Athabasca Delta	549	530	9	2500	female	0.210611789
AR12	Athabasca Delta	548	532	20	1752	male	0.424056108

Appendix 8: Athabasca Project mercury in northern pike (*Esox lucius*) data. Site code refers to site location. Site type refers to site designation. TL = total fish length in millimeters. FL = fork fish length in millimeters. Hg_Pike = THg concentration in northern pike dorsal muscle tissue (µg/g wet weight).

Site Code	Site Type	TL (mm)	FL (mm)	Age	Mass	Sex	Hg_Pike
AR8	At Development	749	710	7	3800	female	0.12400145
AR8	At Development	740	696	8	3100	male	0.242290926
AR8	At Development	698	660	9	2700	female	0.222881042
AR8	At Development	741	705	9	2700	male	0.241224951
AR8	At Development	1050	1010	15	7700	male	0.710614196
AR9/AR15	Downstream	688	658	6	1962	male	0.175528146
AR9/AR15	Downstream	575	560	6	1187	male	0.164729786
AR9/AR15	Downstream	665	637	5	1846	male	0.196739263
AR9/AR15	Downstream	1120	1080	13	10200	male	0.66760661
AR9/AR15	Downstream	660	625	8	1709	male	0.350017012
AR10	Downstream	770	735	13	2700	male	0.582410134
AR10	Downstream	962	919	11	8200	male	0.516866913
AR11	Athabasca Delta	710	670	7	3100	male	0.210016664
AR11	Athabasca Delta	730	722	7	1938	male	0.236960575
AR11	Athabasca Delta	805	770	13	3800	male	0.347024303
AR11	Athabasca Delta	667	608	7	2550	male	0.204760029
AR12	Athabasca Delta	622	591	7	1726	male	0.152629936
AR12	Athabasca Delta	668	628	7	1813	female	0.227870303
AR12	Athabasca Delta	517	487	5	849	male	0.129087693
AR12	Athabasca Delta	304	291	9	3300	female	0.215453499

Appendix 9: Athabasca Project mercury in lake whitefish (*Coregonus clupeaformis*) data. Site code refers to site location. Site type refers to site designation. TL = total fish length in millimeters. FL = fork fish length in millimeters. Hg_WF = THg concentration in lake whitefish dorsal muscle tissue (µg/g wet weight).

Site Code	Site Type	TL (mm)	FL (mm)	Age	Mass (mg)	Sex	Hg_WF
AR5	At Development	480	443	9	1401	female	0.108763503
AR5	At Development	476	421	6	1130	female	0.086383218
AR5	At Development	454	414	7	1032	male	0.105190095
AR8	At Development	394	353	5	726	male	0.078361157
AR8	At Development	470	411	7	1158	female	0.057525412
AR8	At Development	469	423	5	1104	male	0.070975236
AR8	At Development	449	404	5	1027	female	0.0491727
AR9/AR15	Downstream	508	458	13	1342	male	0.086779914
AR9/AR15	Downstream	419	373	3	697	male	0.075111558
AR10	Downstream	395	356	6	657	female	0.058182387
AR10	Downstream	399	362	4	715	female	0.03938212
AR11	Athabasca Delta	389	404	3	628	female	0.070992437
AR11	Athabasca Delta	391	351	3	623	female	0.074903962
AR11	Athabasca Delta	405	350	5	712	male	0.037704647
AR11	Athabasca Delta	392	363	8	619	male	0.096502185
AR11	Athabasca Delta	397	359	7	691	female	0.044784448
AR18	Athabasca Delta	451	357	4	1171	male	0.134862698
AR12	Athabasca Delta	539	516	16	2400	male	0.140958877
AR12	Athabasca Delta	374	431	4	575	male	0.071341038
AR12	Athabasca Delta	495	465	5	1497	female	0.087129267
AR12	Athabasca Delta	506	443	11	1130	male	0.145518194
AR14	Athabasca Delta	558	416	10	1835	male	0.1348969
AR14	Athabasca Delta	438	494	5	1195	female	0.059432543
AR14	Athabasca Delta	511	336	7	1501	male	0.07694261

AR14	Athabasca Delta	489	456	4	1304	female	0.058548978
AR14	Athabasca Delta	450	469	4	1035	female	0.109993531