Metals Contamination and Chemical Exposures in Canada's "Chemical Valley": Implications for the Aamjiwnaang First Nation

by

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d.w.	dry weight
DDD	Dichlorodiphenyldichloroethane
ppDDE.	p,p'Dichlorodiphenyldichloroethylene
ppDDT	p,p'-Dichlorodiphenyltrichlorothane
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
NPRI	National Pollutant Release Inventory
OCP	Organochlorine Pesticide
ON	Ontario
OMOEE	Ontario Ministry of Environment and Energy
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PFC	Perfluorinated Compounds
PFDA	Perfluorodecanoic acid
PFHxS	Perfluorohexane solfonate
PFNA	Perfluoronanoic acid
PFOA	Perfluorooctanic acid
PFOS	Perfluorosulfonic acid
PFUnA	Perfluoroundecanoic acid
TRI	Toxics Release Inventory

Abstract

The Aamjiwnaang First Nation is an Ojibwe Tribe at the junction of Lake Huron and the St. Clair River, and is surrounded by 58 petrochemical facilities collectively known as Canada's Chemical Valley. To increase understanding of chemical contamination and exposures, this dissertation was conducted in partnership with the Aamjiwnaang First Nation Health and Environment Committee.

Aim One was to study metals contamination of stream ecosystems on-Reserve (n=4), within the surrounding Chemical Valley (n=14), and a reference community (n=4) during three seasons (2010-2011). Aluminum (3-fold), cadmium (20-fold), lead (2-fold), and cobalt (1.5-fold) levels in streams on-Reserve were greater than the reference community (as indicated in brackets). Many sites were above screening levels for aluminum.

Aim Two focused on mercury, motivated by knowledge of existing legacy and active mercury sources in the region. Mercury concentrations of sediments and soils were assessed at stream sites. Levels on-Reserve were higher than the reference community (soil=2.5-fold; sediment=6-fold). One on-Reserve site exceeded screening values in sediment and soil. Human exposures were assessed in 43 mother-child pairs. Mean hair (mothers=242.1±188.9 µg/kg; children=126.7±112.9 µg/kg) and blood levels (1.7±2.0 µg/L; 1.5±1.9 µg/L) were lower than the general public. This is likely due to low

amounts of fish consumption. Urinary mercury (0.8±0.9 µg/L; 0.5±0.9 µg/L) exceeded values seen nationally.

Aim Three was to increase understanding of multiple chemical exposures among Aamjiwnaang mothers and children. Blood, serum, and urine were used as biomarkers of metals (n=9 elements), perfluorinated compound (n=6 congeners), polycyclic aromatic hydrocarbon (n=12), organochlorine pesticide (n=2), polychlorinated biphenyl (n=5), and polybrominated biphenyl ether (n=5) exposures. Distributions of multiple chemicals were elevated in Aamjiwnaang participants.

The outcome of this dissertation significantly increased understanding of multiple chemical exposures for the Aamjiwnaang First Nation. The disproportionate placement of industrialization depicts an environmental justice issue seen among many Tribes. The data will fill gaps in the literature, since First Nations Tribes are under-represented in environmental health research. In identifying key chemicals, future studies can be molded to better serve the community. The data will empower the Aamjiwnaang First Nation in taking public health actions to reduce exposures and improve health.

Chapter 1

Introduction

1.1. Introduction to the Aamjiwnaang First Nation

The Aamjiwnaang First Nation Reserve consists of 2850 acres of land on which 850 residents live and is located on the Southern border of the city of Sarnia, Ontario (ON) within Lambton County. Previously known as the Chippewas of Sarnia, Aamjiwnaang is part of the Chippewa (or Ojibwe) Nation. The Chippewa Nation includes approximately 100,000 members who live mostly in the Great Lakes basin (Michigan, Wisconsin, Minnesota, North Dakota, and Ontario). The Reserve is positioned at the junction of the St. Clair River and Lake Huron, within the Laurentian Great Lakes.

The Aamjiwnaang Reserve is contained within the boundaries of the bi-national St. Clair River '"Area of Concern". Further, within a 25 km radius of Aamjiwnaang lands exists "Chemical Valley", a region with 58 U.S. and Canadian petrochemical, polymer, chemical industrial plants, and power generating stations that collectively released more than 110 million kilograms of pollution in 2009 (Figure 1.1) (Environment Canada, 2010; U.S. EPA, 2011). Despite being surrounded by chemical pollution, the scientific evidence concerning environmental health issues at the Aamjiwnaang First Nation Reserve is disparate and insufficient. Accordingly, the purpose of this introduction is to provide a systematic overview of pertinent environmental health issues

at the Aamjiwnaang First Nation Reserve. This will be achieved by providing a brief historical overview of industry in the region, reviewing previous data pertaining to environmental and ecological concerns in the area, local human exposures, and potential health issues.

1.2. Brief History of "Chemical Valley"

Sarnia (Lambton County, Ontario, Canada) has had a long history of petrochemical and related industry. Petroleum was discovered in the Sarnia region dating back to early 19th century with asphalt production arising because of this (Ford, 2004). Shortly after oil was discovered and wells were established throughout much of Lambton County, came the addition of the railway system making Sarnia one of the first petroleum resources in North America and a desirable location for refinery industry. In addition to oil production facilities, World War II brought about the introduction of petrochemical manufacturers. Industrial growth occurred exponentially, as railways and the deep water port allowed for excellent capacity of import and export of goods, especially located near the Canadian-US border. Oil refinement and other chemical processes attracted facilities which use petrochemical products to create rubber, paints, plastics, fertilizers, textiles, detergents and dyes, among others. Due to the combination of production, refinement, and transport within the region earned the nickname of Canada's "Chemical Valley".

Oil refinement and related production plays a large role in Canada's economic status, especially in Lambton County. Approximately 50% of Lambton County residents have either worked in, or know at least one person who has been or currently is employed by, local industry (CCL, 2010). In 2010, petrochemical industry (e.g. chemical processing) was accountable for $2.4 billion in exports alone (Industry Canada, 2011).

Today, the petrochemical industry extends approximately 25km south of the Sarnia region and is home to 40% of Canada's petrochemical industry (MacDonald and Rang, 2007). In addition to the petrochemical industry the area contains fertilizer manufacturers, coal-fired power plants, as well as other manufacturers on the Canadian side (Environment Canada, 2010). On the U.S. side, there exist paper mills, spices extractions, power plants, and packaging industries (U.S. EPA, 2011). While the day-to-day operation releases of such industry can cause environmental contamination and pose health hazards to nearby residents, these effects are likely to be enhanced by the accidental spills, passage of chemicals through the area, and vehicular transportation of goods. The area has experienced either a spill or explosion almost monthly (at least one incident in 22 of 24 months) while all of Toronto generally experiences only five such incidences per year (OECO, 2006).

1.3. Environmental Exposure and Ecology

1.3.1. Industrial Sources and Air Pollution

Between 1995 and 2009, 66 facilities in or near Sarnia (Figure 1.1) were listed under Environment Canada's National Pollution Release Inventory (NPRI) or the U.S. National Pollutant Release Inventory (NPRI) (Environment Canada, 2010). Of the reporting facilities in 2009, twelve were involved in basic chemical production, seven were involved in electric power generation, and five were involved in each pipeline transportation of natural gas, resin and rubber manufacturing, and industrial vehicular manufacturing (Figure 1.2; Environment Canada, 2011; U.S. EPA, 2011). Since 1995, bi-national onsite releases of chromium, copper, and arsenic near the Aamjiwnaang Reserve have increased, while benzene has decreased (Figure 1.3). Specifically on the Ontario

side, facilities located near Aamjiwnaang have reported decreasing trends of onsite releases of volatile organic compounds (VOCs) and particulate matter smaller than 10 microns (PM_{10}) (Figure 1.4). In total, these facilities released 109,899, 249, and 843 tons of pollution into the air, water, and land, respectively in 2008 (Environment Canada, 2010; U.S. EPA, 2011). With multiple companies emitting many of the same pollutants, it is difficult to track a pollution event to a single source, and little is known of the effects of the interactions of these multiple pollutants.

Air pollution is seen as a common exposure source to all individuals in the community. Among the facilities reported to emit pollutants in the air, Ontario Power Generation and Imperial Oil were the largest sources between the years of 2000 and 2008 (Environment Canada, 2010). The total air pollution released by reporting industries shows a general increasing trend from 1995-2005, but that trend has slightly sloped downward since 2005 (Figure 1.3) (Environment Canada, 2010; U.S. EPA, 2011). Within Sarnia and the Aamjiwnaang Reserve, volatile organic compounds such as benzene, ethylbenzene, toluene, xylene, nitrous oxides, and particulate matter have all been found in measurable concentrations, especially in areas with industry, highways, and high residential counts (Atari and Luginaah, 2009).

1.3.2. Aquatic Pollution

The facilities located near the Sarnia area release multiple pollutants into water bodies, occurring during general production and as waste disposal. The largest polluter directly to water bodies during 2009 was Imperial Oil (Environment Canada, 2010; U.S. EPA, 2011). Liquid wastes from the former Welland Chemical, a facility located that the northern boundary of the Reserve, enters four lagoons which have previously been shown

to contain high surface water concentrations of acetone (16,000 µg/L), a chemical that may be toxic to certain aquatic organisms, and levels of bis (2-ethylhexyl) phthalate and diethylphthalate above the Provincial Water Quality Objectives (PWQO) criteria (Golder Associates Ltd, 2004). The lagoons release into a discharge drain where, in 1999, water discharge exceeded Ontario Ministry of the Environment (OMOEE) surface water criteria for six metals (i.e., cadmium, chromium, lead, copper, mercury, and arsenic), total organic carbon, suspended solids, and conductivity, and have exhibited high levels of chloride. Though it has not yet been formally tested, chemicals from these ponds are not believed to leach into the ground water as the surrounding soil is fairly impermeable clay silt (Mallard, 1999). Approximately 1500 meters south of this site is Talfourd Creek, a direct tributary to the St. Clair River. Tadpoles placed into sites along Talfourd and Marsh, located south of the Reserve, Creeks showed significantly higher DNA damage in erythrocytes than did tadpoles at nearby reference sites, as seen through COMET assays (Ralph and Petras, 1998).

Within sediment collected from Talfourd Creek, high levels of polychlorinated biphenyls (PCBs), metals and polycyclic aromatic hydrocarbons (PAHs) were found at various locations (Leadley and Haffner, 1996) (Table 1.1). In 1995, mercury sediment levels at three Talfourd Creek locations exceeded OMOEE lowest effect level guidelines, and copper at six locations were above OMOEE standards. When exposed to organochlorine pesticides (OCPs), dichlorodipheynyltricholorethane (DDT), dichlorodiphenyldichloroethylene (DDE), dichlorodiphyenyldichloroethane (DDD), hexachlorohexane (HCH), chlordane, and nonachlor extracted from sediments taken from Ainkii jig, a pond located on Reserve, human HepG2 cells showed a significant induction

of cytochrome P450 activation (CWAIGG, 2005). The pond sediment also contained levels of eight metals (aluminum, arsenic, cadmium, chromium, copper, manganese, mercury, and nickel) at or near the lowest effect level established by the OMOEE.

When tested for chemicals, largemouth bass and pickerel caught from Ainkii jig contained mercury levels above the restriction benchmark for women of child bearing age but did not show elevated levels for organic contaminants (CWAIGG, 2005). Mercury, PCB, DDT, and hexachlorobenzene (HBC) concentrations in fish tissue collected from the St. Clair River decreased with conservation efforts between 1970 and 1990 but have since stabilized and are still considered to be of concern to the health of both humans and fish-consuming wildlife (Gewurtz *et al.,* 2010). However, PCB, dioxin/furan, and organochlorine pesticide levels in snapping turtles (*Chelydra serpentine)* were not elevated in the St. Clair River in comparison to a reference site in 2002 (de Solla and Fernie, 2004).

1.3.3. Terrestrial Pollution

Soil samples from the St. Clair (Welland) Chemical site were analyzed for VOCs, semi volatile organics (SVOCs), metals, and petroleum hydrocarbons. Four samples showed styrene values above the OMOEE lowest effect levels, two were over these benchmark values for ethylbenzene, and one was over these values for xylene (Golder Associates, Ltd, 2004). In 1999 it was noted that much of the bare soil present was coated with brownish deposits or was a blue/green in color, potentially indicating the direct dumping of chemical onto the soil surface (Mallard, 1999). A soil sample collected in 2005 from a ditch marking the northwestern limit of the Reserve was analyzed for metals, pesticides, phenols, triazines, PAHs, total petroleum hydrocarbons (TPHs), VOCs, and

PCBs by Atkinson Davies (2005). Researchers noted solvent odors being emitted from soil samples. This effort also showed that heavy metal contamination is an issue at this particular site with arsenic values of 5.5 mg/kg and mercury values of 2.58 mg/kg.

On Reserve, north of the St. Clair (Welland) Chemical landfill, forested areas have been dwindling. The Phytotoxicity Branch of the Ontario Ministry of Environment reports foliar damage to the existing vegetation (Vasiloff, 1992). Surrounding the landfill area, the forest composition consisted of oak, hickory, maple, blue beach, cherry trees along with cattails, while directly on the landfill site was bare soil with a number of dead trees to the north. The remaining natural habitat was located to on the southeast corner of the property but wildlife passage was restricted by chain-link fencing. Within the standing water bodies on location, no aquatic wildlife was found and a lack of birds or other wildlife was noted (Mallard, 1999). When analyzed for PCBs and DDT, dear, duck, rabbit, and goose, which are thought to be the most widely consumed game by Tribal members, did not show unsafe levels of contaminants for consumption (CWAIGG, 2005).

1.4. Human Health Considerations

1.4.1 Chemical Exposures

Despite the fact that members of the Aamjiwnaang First Nation have resided beside industry for upwards of two centuries, little is known about their direct exposures to industrial pollutants. Recently, a small sample comprised of three members was surveyed in order to determine body burdens of eleven different classes of chemicals (Environmental Defense, 2007). Polybrominated diphenyl ethers (PBDEs), PCBs, OCPs in blood plasma; perfluorinated compounds (PFCs) in serum; PAHs and

organophosphate insecticide metabolites in urine; and arsenic, cadmium, lead, manganese, and mercury in whole blood were all found to be present within the individuals. When compared to other individuals living in Ontario during the same study, the individuals living on Aamjiwnaang tended to have higher levels of PCBs, OCPs, PFCs, organophosphate insecticide metabolites, arsenic and manganese. Despite interesting results of possible concern, the small sample size and lack of connection of body burden to health adversities in these individuals calls for a need to conduct a larger environmental epidemiology study.

Human, particularly First Nation, exposure to contaminants, including those produced by industry, can be impacted by the lifestyle of the population at hand. Aboriginal Peoples conducting a subsistence way of life, for example, would be heightened in comparison to the average suburban exposure (Harris and Harper, 1997). Thus, environmental exposures to First Nations members are likely to be underestimated. A survey conducted at the Confederated Tribes of Umatilla Indian Reserve, which is similar to the Aamjiwnaang First Nation in that its historical lifestyle is centered around the Columbia River much like the Aamjiwnaang is centered around the St. Clair River, near the U.S. Department of Energy's Hanford Site found that approximately one hour per day is spent in contact with some sort of water source (bathing, fishing, washing foods, etc.). Within this study, major sources of exposure are soil water, air, sweat lodges, and biota. The members of the Umatilla Tribe were shown to ingest about four times the amount of soil, twice as much water, and eight times the amount of fish than their suburban counterparts (Harris and Harper, 1997). According to a survey conducted at the Aamjiwnaang reserve, approximately half of the members of the Aamjiwnaang

community consume food from a local source (CWAIGG, 2005). Nearly 30% of individuals polled engaged in hunting, fishing, or both and approximately one fourth of the individuals ate locally caught fish species. The majority of locally grown produce consumed consists of tomatoes, peppers, and cucumbers. Cedar needles and wood, fungi, and herbs are also collected and consumed by Tribal members (Figure 1.5), representing an exposure source that other nationalities may not encounter. Thus, the Aamjiwnaang may be particularly vulnerable to environmental exposure to contaminants not only due to proximity to industry but also because of traditional activities.

1.4.2. Health outcomes near petrochemical industry

A recent community-based survey on 263 Aamjiwnaang adults was conducted in order to identify health outcomes of concern to community members (AHEC, 2005). Of the 132 women participating in the study, 39% reported at least one miscarriage or stillbirth, more than double that of the U.S. average of 15% (Ventura *et al.*, 1999). Many of the chemicals measured in the environment and in Aamjiwnaang people are endocrine disruptors that have potential to affect reproductive health. A study by researchers and community members documented that the rate of male births has declined from 0.551 during 1989-1993 to 0.348 during 1999-2003 (Mackenzie *et al.*, 2006). It is also noted that a skewed sex ratio was not determined throughout the rest of Lambton County (Greensmith, 2006), and was significantly lower than expected when compared to the Canadian average. Follow-up birth ratio studies have not yet been performed within the Aamjiwnaang First Nation. Studies performed in petrochemically industrialized areas of Taiwan and Iran (Yang *et al.*, 2000), however did not find an altered sex ratio in association with proximity to petrochemical industry, though there exists a body of

literature suggesting that chemical exposures may in fact skew birth gender ratios (Safe, 2005). Other adverse pregnancy outcomes that have been a topic of concern in petrochemically industrialized areas includes preterm birth, spontaneous abortion, and term low birth weight (Lin *et al.,* 2001; Yang *et al.,* 2004; Xu *et al.,* 1998). More local to the Aamjiwnaang First Nation, Lambton County's rates of birth, fertility, infant mortality and full term low birth weight have decreased at a higher rate than has the rest of Ontario between 1990 and 2007, while preterm birth rate has increased over time (Palleschi, 2007a).

Another major concern reported by Aamjiwnaang members was a perceived rise in cancer rates (AHEC, 2005). Lambton's rates of mesothelioma, testicular, colorectal, and prostate cancers in the population and melanoma and breast cancer in women were higher than Ontario rates between 1995 and 2003 (Palleschi, 2007a). Within Lambton County, rates of death due to lung cancer increased between 1986 and 2003, when adjusted for age (Palleschi, 2007b) and the overall occurrence of lung cancer during 1995-2003 rose to levels above those expected for the province. Positive associations among residential proximity and childhood leukemia (Barregard *et al,.* 2009; Yu *et al.,* 2006; Weng *et al.,* 2008, Linos *et al,.* 1991) have been found in other industry centers, however no increase in childhood cancer rate has been found in Lambton County in comparison to Ontario (Palleschi, 2007b). Risk of lung cancer has been found to increase with proximity to petroleum industry in some studies conducted in Taiwan and Louisiana, USA (Yang *et al.* 1999; Yang *et al.* 2000; Gottlieb *et al.* 1982) but not in others conducted in Louisiana, USA (Simonsen *et al.* 2010). Positive associations have

also been made in regards to bladder cancer (Tsai e*t al.* 2009), pancreatic cancer (Pickle, 1980), and breast cancer (Argo, 2010).

The Aamjiwnaang community led survey revealed that 22% of local children self-reported to have asthma, compared to childhood asthma rate of 8.2% in Lambton County (AHEC, 2005) and 8.7% among U.S. children under 17 years of age (Akinbami, 2005). The rates of visits to the emergency room due to asthma-related symptoms were higher in Lambton County than in all of Ontario (Palleschi, 2008). A linkage between living near petrochemical industry and non-cancerous respiratory effects such as asthma and wheezing in children have been made in some studies (Wichmann *et al.,* 2009; Loyo-Berrios *et al.,* 2007; Liao *et al.,* 2009), but not in others (Yang *et al.,* 1998; Bhopol *et al.,* 1998). Of the 79% of residents living in Lambton County who believe that nearby industry may be contributing to health effects, 94% are most concerned with respiratory illness (CCL, 2010).

Of particular concern, the 2005 study revealed that 23% of children living on the Reserve had self-reported learning or behavioral difficulties (AHEC, 2005). This is compared to 3-5% of children in Lambton County and the general U.S. population. Associations between residence near such industrial complexes and neurotoxic outcomes have been identified (Aungudornpukde *et al.,* 2012; Kilburn and Warshaw, 1995). Chemicals released within the "Chemical Valley" region (e.g. heavy metals, PCBs) have previously been shown to cause neurotoxic effects (Hu *et al.*, 2007, Carpenter *et al.*, 2002; Schantz, 1996).

Though a variety of health effects (e.g. asthma, reproductive effects, childhood development, cancers) have been reported to be of concern and although there is

plausible evidence in the literature that living within heavily industrialized areas have been linked to such adversities, little is known about the health impacts on Aamjiwnaang residents. Most toxicity data for these chemicals were acquired via laboratory tests performed with single chemical exposures on animals (ATSDR 1999). Moreover, few studies have documented effects of 'real-world' mixtures in children (Sexton and Adgate, 2001; Hu *et al.,* 2007).

1.5. Significance and Objective

As a Tribe of the Chippewa band, the Aamjiwnaang First Nation is subject to Environmental Justice issues. Race and socioeconomic status are the most significant indicators of the unequal placement of hazardous waste, facilities, coal-fired power plants, chemical plants, refineries and incinerators (Bullard *et al.*, 2007; Mohai and Saha, 2007). In 1827, Aamjiwnaang lands were greatly reduced under the British Crown to a region that would soon after become Canada's "Chemical Valley". The disproportional settlement of industrialization and pollution sources near Tribal lands is well-documented (Schell *et al.,* 2003; Nriagu *et al.,* 2011).

The Aamjiwnaang First Nation (formerly The Chippewas of Sarnia) has been seeking information about chemical contamination and hazardous exposures and the Reserve for nearly four decades:

> *"*Be it resolved that the Chippewas of Sarnia Band request… examine the problem of chemical pollutants falling on the Sarnia Reserve and the potential or existing health hazard to the residents…*"* (Band Council Resolution, 1977).

In addition to potential health adversities in the region, knowledge of pollution has limited culturally important activities such as fishing, hunting, and medicine gathering. Such changes in lifestyle have been documented in Tribes across North

America and have been detrimental to culture, spirituality, economy, and diets of Native Peoples (Kroll-Smith and Couch, 1991; Smith, 2006). Pollution's impact on the cultural framework of a highly susceptible group of peoples is sentinel of our society's failure to protect the environmental rights of indigenous groups.

The people of the Aamjiwnaang First Nation are surrounded by a substantial amount of pollution-releasing industries which may give rise to local fears of contamination, explosion, and tax-payer burden (Mallard, 1999). The demand for the community to be educated in regards to human and ecological health is growing among tribal members. Much work is needed to identify health hazards and initiate ecological restoration. The objective of the study was to perform an unbiased characterization of metals contamination in stream ecosystems, human exposures to multiple chemicals, and an overview of health concerns. The findings of this dissertation will likely serve as the first step in identifying chemical hazards and will refine future research interests in the region.

1.6. Specific Aims

Aim 1. To assess levels of multiple metals in stream water on and off the Reserve. *Hypothesis 1A.* Contamination of stream water by metals will be higher on Reserve in correspondence to such levels in communities off Reserve. *Hypothesis 1B.* Metal concentrations on Reserve will exceed regulatory benchmarks. *Hypothesis 1C* . Metals concentrations will differ according to season. *Hypothesis 1D.* Stream sites with drainage tubes will have higher concentrations of metals downstream than upstream of the tube.

Aim 2. To determine levels of mercury in the ecosystem and in biomarkers of Aamjiwnaang First Nation members and non-members living on and near the Reserve. *Hypothesis 2A.* Mercury contamination in stream sediment and soils will be higher on

Reserve than surrounding communities. *Hypothesis 2B.* Mercury in sediment and soils may be higher than benchmark levels. *Hypothesis 2C.* Exposures to multiple chemicals may be similar on and off-Reserve. *Hypothesis 2D.* Mercury exposures may be higher in "Chemical Valley" than the general population.

Aim 3. To assess exposures to multiple chemical stressors in participants living in "Chemical Valley". *Hypothesis 3A.* Exposures of individuals living on-Reserve to multiple chemicals will span ranges above those seen in the general population. *Hypothesis 3B.* Metals exposures on-Reserve may be similar to exposures of off-Reserve participants.

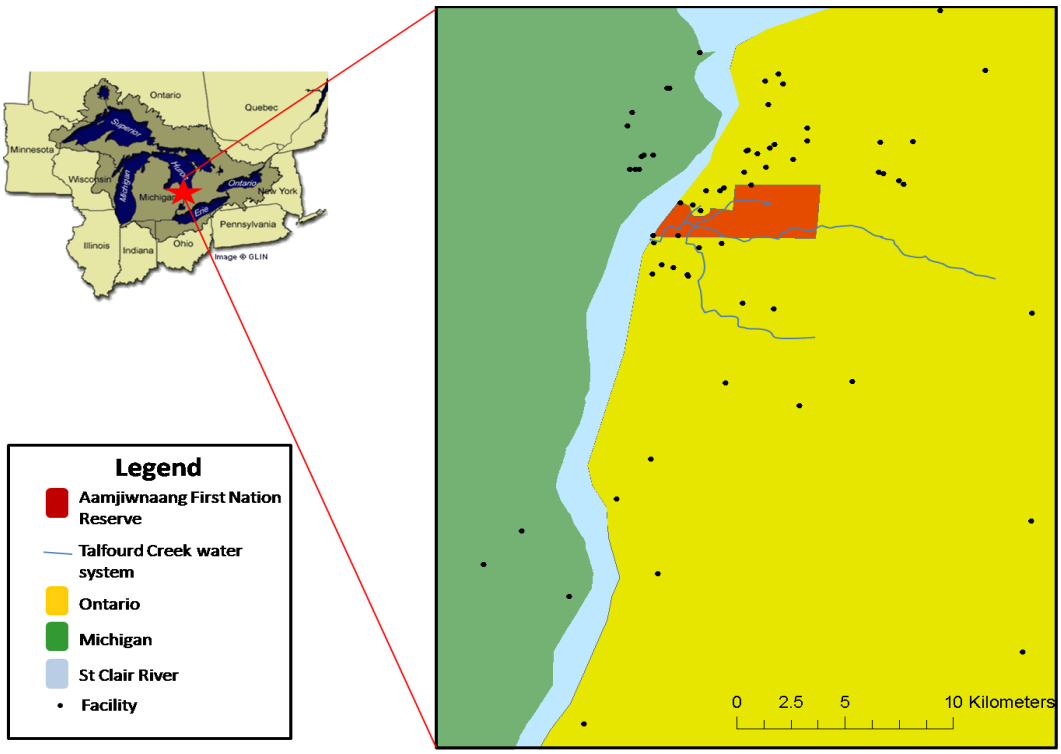

Figure 1.1 Map of the Aamjiwnaang First Nation Reserve and surrounding area. Talfourd Creek and its tributaries flow through the Reserve and surrounding area. Facilities reporting to the National Pollutant Release Inventory (Environment Canada, 2011) or the Toxics Release Inventory (U.S. EPA, 2010) are represented by black dots.

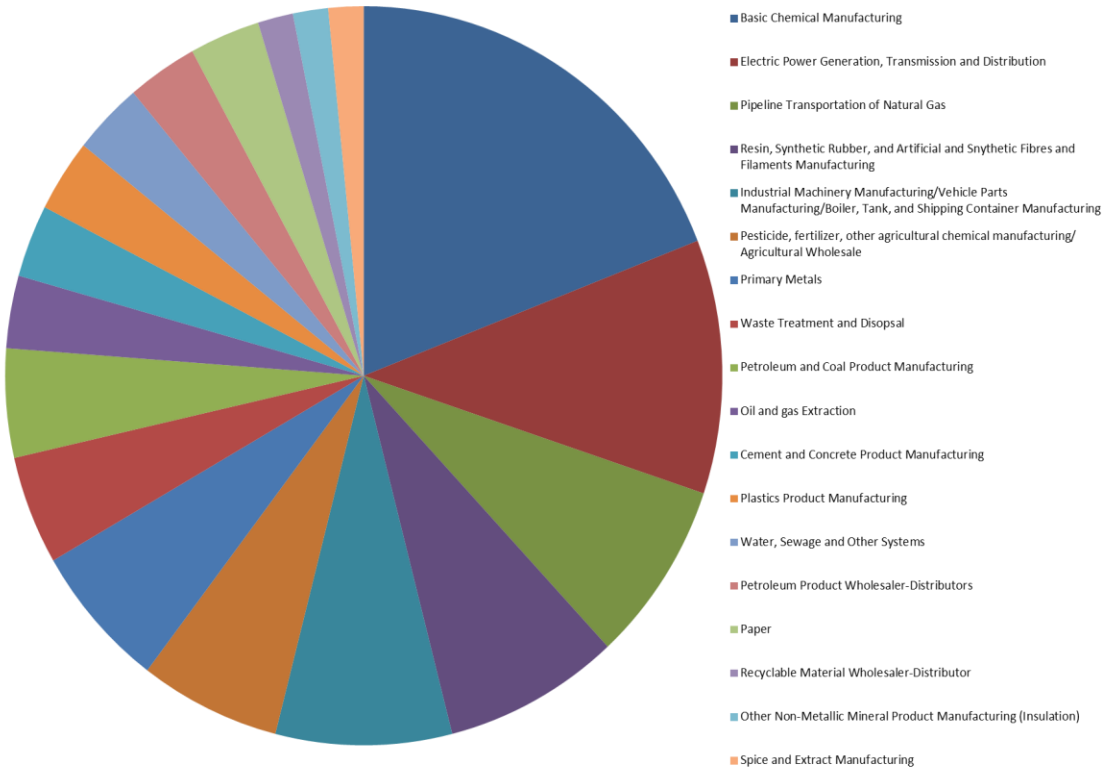

Figure 1.2 Industry sectors represented by facilities within the “Chemical Valley” region during 2009.

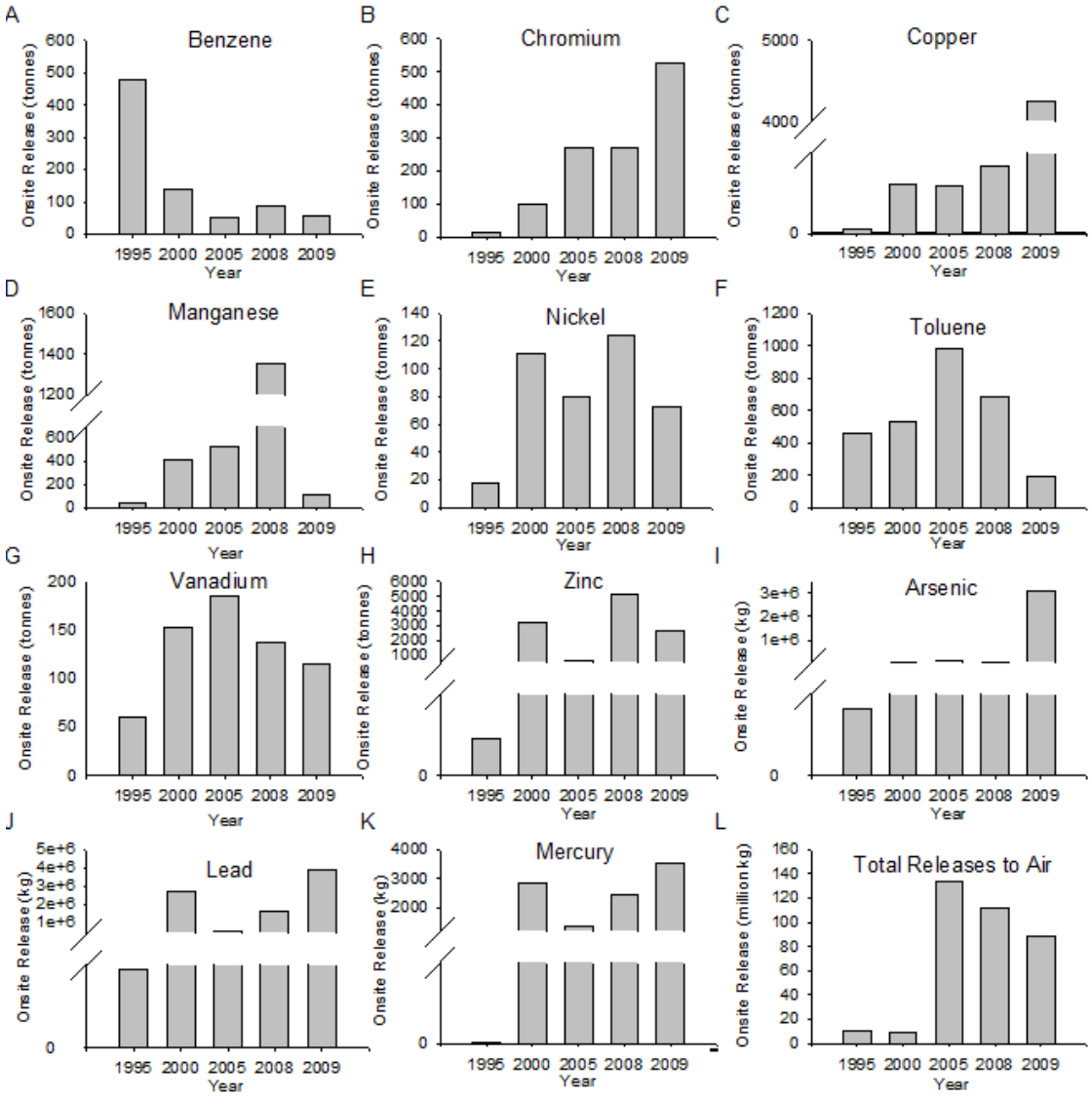

Figure 1.3 Onsite release of multiple chemicals within "Chemical Valley" between 1995 and 2009. Releases of benzene (A), chromium (B), copper (C), manganese (D), nickel (E), toluene (F), vanadium (G), zinc (H), lead (J), and mercury (K) to all environmental media, and total onsite air releases (L) during the years 1995, 2000, 2005, and 2009 by facilities within a 25 km radius of the Aamjiwnaang First Nation Reserve. Data are self-reported to the National Pollutant Release Inventory (Environmental Canada, 2011) or the Toxics Release Inventory (U.S. EPA, 2010).

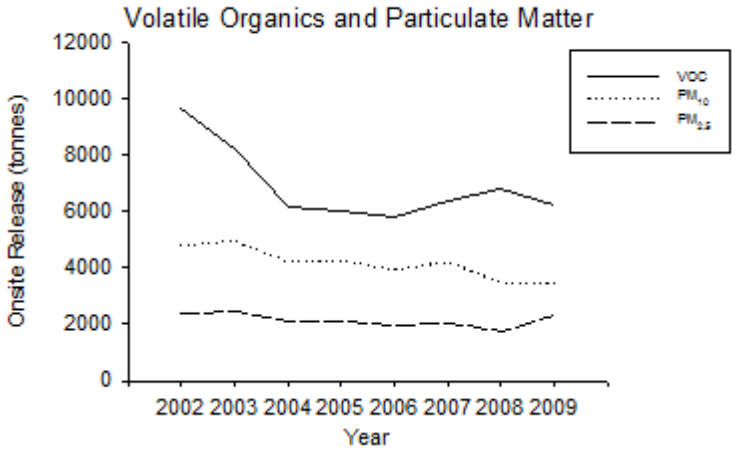

Figure 1.4 Total volatile organic compounds and particulate matter released by facilities located in Ontario with 25 km of the Aamjiwnaang First Nation Reserve. Data is self-reported to National Pollutant Release Inventory (Environment Canada, 2011).

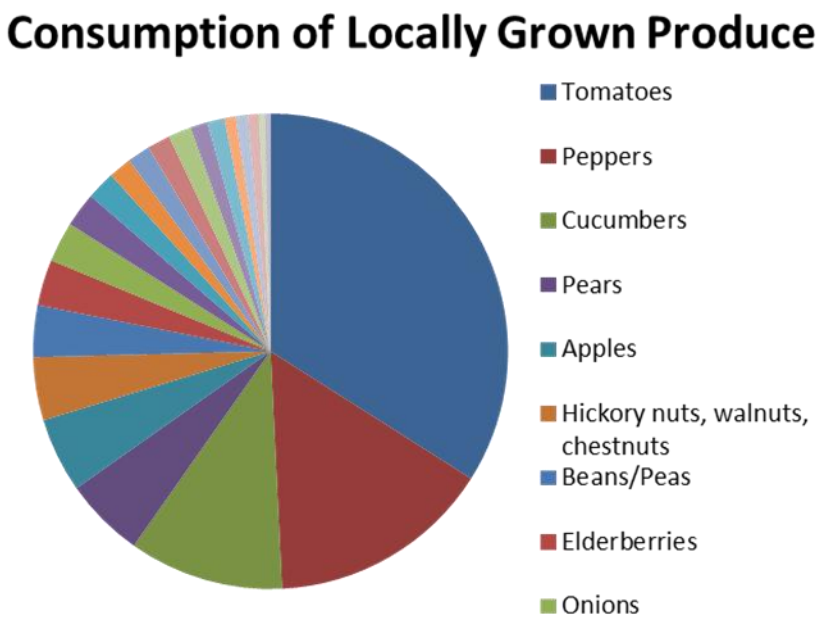

Figure 1.5 Variety of locally grown produce consumed by Aamjiwnaang members (CWAIGG, 2005).

Table 1.1 Summary of community-based efforts showing elevated levels of chemicals in Aamjiwnaang sediments.

POLLUTANT	ATSDR PRIORITY RANK[1]	MEASURED VALUE (ppm)	EPA LEL[2]	MAX-FOLD ABOVE EPA LEL
Aluminum	182	11700-12,200[5]	n/a	n/a
Arsenic	1	4.8-10.2[4,6]	6[3]	1.7 x
Cadmium	7	0.5-3.3[6]	0.6[3]	5.5 x
Chromium	77	29.6[4]	26[3]	1.1 x
Copper	128	13-35[4,6]	16[3]	2.2 x
Lead	2	5-282[6]	31[3]	9.1 x
Manganese	117	488-626[4,5]	460[3]	1.4 x
Mercury	3	0.1-2.6[4,6]	0.2[3]	13 x
Nickel	53	17-49[4]	16[3]	3.1 x
Zinc	74	60-650[6]	120[3]	5.4 x
PAH	8	0.1-24.9[4]	4[7]	6.2x
PCB	5	.01-.4[4,5,6]	.07[7]	5.7x

[1]ATSDR, 2007; [2] EPA LEL = U.S. Environmental Protection Agency's Lowest Effect Level; [3] values from Buchman, 2008; [4]Leadley and Haffner, 1996; [5]Wren and Associates, 2004a; [6]Atkinson Davies, 2005
[7]Persaud, 2008

1.7. References

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Chapter 2

Stream Metal Contamination in Canada's "Chemical Valley": Implications for the Aamjiwnaang First Nation

2.1. Introduction

It has been well established that oil refining and petrochemical industry are sources of multiple environmental contaminants such as polycyclic aromatic hydrocarbons (PAHs) and halogenated hydrocarbons (Mehlman, 1991). Much less is known about metals released from such petrochemical epicenters, even though they may be directly discharged into the local and regional atmosphere, land or stream waters (U.S. EPA, 2011). Metals are naturally occurring elements, are persistent in the environment, may build up in the tissues of exposed organisms, and may potentially have toxic effects at high levels. While trace metals such as manganese and zinc are required for metabolic processes, elevated exposures can cause adverse effects in wildlife and humans (Fosmire, 1990; Rainbow, 2007; Crossgrove and Zheng, 2004). Other metals, such as lead, and cadmium have no known biological function (ATSDR, 2007a; 2007b). A number of metals, notably arsenic, lead, and mercury are the top three of the 2011 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (ATSDR, 2011).

The Aamjiwnaang First Nation Reserve consists of 2850 acres of land on which 850 residents live. The Reserve is located on the Southern border of the city of Sarnia,

ON within Lambton County (Figure 2.1). The Reserve is positioned at the junction of the St. Clair River and Lake Huron, within the Laurentian Great Lakes. The Aamjiwnaang Reserve is contained within the boundaries of the bi-national St. Clair River "Area of Concern".

Sarnia has been home to petroleum industry since the early 19th century (Ford, 2000). Further, within a 25 km radius of Aamjiwnaang lands exists "Chemical Valley", a region with 58 U.S. and Canadian petrochemical, polymer, and chemical industrial plants that collectively released more than 110 million kilograms of pollution in 2009 (Environment Canada, 2010; US EPA, 2011). This region accounted for 60% of all of Ontario's air pollution and is home to nearly half of all petrochemical industry in all of Canada (Environment Canada, 2010; MacDonald and Rang, 2007). In addition to the petrochemical industry the area contains paper mills, fertilizer manufacturers, coal-fired power plants, spices extractions, and packaging industries on both sides of the border (Environment Canada, 2010; US EPA, 2011). In total, these facilities collectively released over 80,000, 493,000, and 42,500 kilograms of arsenic, lead, and mercury, respectively in 2010 (Table 2.1; US EPA 2011, Environment Canada, 2011).

There is some evidence of metals contamination at Aamjiwnaang. Levels of contaminants, including metals, in the sediment of Talfourd Creek, which runs through the Reserve and is a direct tributary to the St. Clair River, have been present at levels posing threat to aquatic organisms (Table 2.2; Mallard, 1999; Leadley and Haffner, 1996). Genotoxicity studies performed on tadpoles have proven that Talfourd Creek may not be conducive for wildlife health (Ralph and Petras, 1998). A former industrial site was shown to contain surface waters with elevated levels of six metals (arsenic,

cadmium, copper, chromium, lead, and mercury) in 1999 (Mallard, 1999). Sediments collected from Ainkii jig, a local pond, contained elevated levels of eight metals (CWAIGG, 2005). Collectively these studies raise some concern about the presence of metals in the region, though these studies were small scale, funded by the Aamjiwnaang, did not include samples from the areas outside of "Chemical Valley" for comparison, and were not replicated over time. Thus, there is a need for additional work in the region. The community has been actively engaged in bringing attention to the environmental justice issue at hand via hosting documentaries and initiating studies (Mackenzie *et al.*, 2005; Luginaah *et al.*, 2010). As such, the current study was conducted to help fill this knowledge gap. The first goal of this study was to characterize levels of aluminum, arsenic, cadmium, cobalt, lead, manganese, and zinc in stream waters from around the region. The second goal was to determine if the stream metal levels are higher on Reserve than off Reserve, and if sites in "Chemical Valley" are higher than reference sites. Finally, we aimed to identify streams with metal levels that exceed benchmark values.

2.2. Methods

2.2.1. Sample Collection

All samples were collected from stream sites on the Aamjiwnaang First Nation Reserve (n=4 on Reserve) and off the Reserve (n= 19; Cryderman *et al.*, Chapter 3). Sites were grouped into communities in each direction of the Reserve (Figure 2.1): Aamjiwnaang First Nation Reserve (sites 1-4; AAMJ), Port Huron, Michigan (sites 5-9; W), northern Port Huron, Michigan (sites 10-12; NW), eastern Sarnia, Ontario (sites 13-15; E), northern Sarnia, Ontario (sites 16-17; N), and Corunna, Ontario (sites 18-19; S). Kettle Point, Ontario (sites 20-23; Ctrl) serves as the reference community as it is over 40

kilometers to the northeast of the affected area and upstream waters go through a nature preserve. Locations and site descriptions are further outlined in chapter 3 (Table 3.1). Drainage tubes, dumping waste waters directly into streams, were present at 4 sites (2, 14, 15, and 16). Here, samples were collected from both upstream and downstream of the point source and values for subsamples collected downstream of the source have been designated with the site number followed by the letter "a". Collections were replicated during Fall 2010, Spring 2011, and Summer 2011 in order to identify any seasonal variability.

Water samples were collected from all sites. At each site, three separate samples were collected, one at the entry point, and two subsequent samples each at 10 meters up stream of the previous location (n=3 per site). All water was collected as near the middle of the stream as possible, using the EPA's 'Clean Hands' method, into acid-washed 15mL Corning tubes. Each water sample was acidified to pH <2 using Optima Nitric Acid (Fisher) on site and placed on ice until arrival to the lab. Samples were frozen until analysis. For sites with drainage tubs, three sub-samples each upstream and downstream of the source were collected (n=3 upstream, n=3 downstream). During each day for all collection seasons field blanks were created by the addition of milliQ water and nitric acid.

2.2.2. Analysis- Metals in Stream Water

Water samples were analyzed for aluminum, arsenic, cadmium, cobalt, copper, lead, manganese, nickel and zinc. Metals were detected using an Inductively Coupled Plasma Mass Spectrometer (ICPMS; Agilent 7500c, Agilent Technologies, Palo Alto,

CA) equipped with a quadrupole analyzer and octopole collision/reaction cell pressurized with either a hydrogen or helium reaction gas.

All samples were batch processed according to sample type. ICPMS conditions included 0.4mL/min sample uptake via peristaltic pump. 1.2 L/min carrier Ar gas was added. The combination then passed through a Babbinton-style nebulizer and Peltier-cooled double-pass spay chamber. Another 1.0 and 12.0 L/min auxiliary and plasma gas Ar were added. Samples then passed through a series of two nickel cones for a sampling depth of 8.5mm. Resolution and sensitivity were tuned under manufacturer's recommendations of 10ppb Li, Y, Ce, Tl, and Co (Agilent internal standard mix). A ratio of <2.0% doubly charged ions and oxides were established by optimizing plasma conditions.

Accuracy and precision were measured by use of certified reference materials, including NIST 1640 for metals in water. In addition, each batch run contained procedural blanks and replicate runs. For each particular element, the analytical detection limit was calculated as 3 times the standard deviation of the mean blank value (Table 2.4). Samples for which a contaminant was detected but the concentration was below the theoretical method detection limit (TMDL) were assigned their measured values. These samples are reported in the results section. For all seasonal analyses, recovery rates ranged from 73.6 to 86.1% for aluminum, 86.8 to 85.1% for arsenic, 88.4 to 94.5% for cadmium, 70.1 to 88.1% for cobalt, 85.2 to 96.5% for lead, 76.9 to 88.8% for manganese, and 97.0 to 121.8% for zinc (Table 2.4). Results were not adjusted for these recovery rates.

2.2.3 Statistics

For all sites, the three subsamples were averaged together to determine an overall site value. This was performed for aluminum, arsenic, cadmium, cobalt, manganese, lead, and zinc in stream water. Statistics were performed using the overall site averages, keeping the sites separated into the communities described above. All statistics were performed in SPSS statistical package. As stream data did not fit the normality assumption, differences between communities and between seasons were found using Kruskal-Wallis and further investigated using Mann-Whitney tests. For sites containing a point source, Mann-Whitney tests were used to identify differences between concentrations upstream and downstream of the source. Significant comparisons are reported without correction for multiple comparisons.

In addition to the previously described comparisons, metal concentrations among stream sites will be compared to acute and chronic screening values for freshwater invertebrates as outlined by the National Oceanic and Atmospheric Administration (Table 2.3; Buchman *et al.,* 2008).

2.3. Results

All metals except for Ni and Se were measured at above the analytical detection limit. The four sites containing a point source showed no significant differences between subsamples collected upstream and downstream of the point source.

2.3.1 Physiochemical Conditions

Temperature ranged from 4.1 °C to 9.9 °C in streams during fall, 7.8 °C to 20.8 °C during the spring, and 16.3 °C to 29.0 °C during the summer (Table 2.5). As expected, temperatures during each collection season were statistically different

(p=0.001). Ranges of pH, dissolved oxygen, and conductivity in the fall, spring, and summer were also statistically different (p <0.001 for each comparison).

2.3.2 Aluminum

All water samples collected were above the respective TMDL for aluminum (Table 2.4). Samples from nearly all sites (88.5%) were above the NOAA screening value for chronic freshwater exposures (Figure 2.2; 2.3). Sites on Aamjiwnaang First Nation Reserve were among the highest in the area. Sites on the reference area showed some of the lowest levels of aluminum, and were approximately 2-fold lower than those found on the Reserve. In general, aluminum concentrations in water samples collected in the fall were higher than samples collected during spring and summer. While levels of aluminum were variable both within and between communities, significant differences were found among community groups (p=0.008). Notably, the Aamjiwnaang Reserve was significantly higher than the reference community (p= 0.001) and Port Huron (p= 0.002; Figure 2.4).

2.3.3 Arsenic

All water samples collected were above the TMDL for arsenic (Table 2.4). Arsenic was also variable between stream sites. Samples collected in the summer were consistently higher than samples collected in fall or spring. Contamination is not a likely factor as field blanks for the summer collections were not higher than other seasons. All of the sites tested were below benchmark levels for freshwater invertebrate health (Buchman, 2008). The distribution of arsenic across communities was significantly different (p= 0.027) with the Reserve being statistically lower than Northern Sarnia (p=

0.046). Though not significant, arsenic distribution on Aamjiwnaang was higher than that of the reference community.

2.3.4 Cadmium

Cadmium was found at levels above the detection limit (Table 2.4) in 67% of the sites during the fall 2010 collection, two sites during the spring 2011 collection, and 4 sites during the summer collection. For all collections, all sites within the reference community were below detection limits. No water samples were above screening values for cadmium. Fall samples were the highest for all sites, and sites in Port Huron were among the highest of all sites. Cadmium concentrations on Aamjiwnaang were higher than those of Kettle Point ($p=0.002$).

2.3.5 Cobalt

One sampling site during the fall (in the reference community) and summer (Corunna) collections were below detection limit (Table 2.4) for cobalt. Sites 10 and 11 in northern Port Huron, MI were highest during the fall collection. Sites on Aamjiwnaang were found to contain higher concentrations of cobalt ($p=0.031$) than sites in Port Huron or Kettle Point ($p=0.031$). When comparing the different collection time points, we found that the fall collection was significantly higher than the spring and summer ($p=0.006$). Overall, no sites were above screening levels set for freshwater invertebrates (Buchman, 2008).

2.3.6 Lead

During the fall collection, two sites in the reference community were found to be below the detection limit while seven sites across multiple communities were below

detection in the summer. Two sites (16, 19) were measured to have an average lead concentration above NOAAs screening level for freshwater invertebrates (Buchman, 2008). Also of note, one seasonal subsample within sites 1 and 3 were measured above this level, though these site averages fell below the benchmark. Interestingly, all of the aforementioned sites except site 1 were located at a drainage tube. All of the measurements exceeding the NOAA benchmark were from the fall 2010 collection. The fall collection was significantly higher than summer ($p=0.034$) but not spring. Average lead levels across communities were statistically different ($p=0.005$). Notably, lead levels on Reserve were significantly higher than in the reference community ($p=0.032$), but below those seen in northern Sarnia ($p= 0.025$).

2.3.7 Manganese

All samples were above the detection limit for manganese. Multiple sites exceeded the NOAA benchmark level for manganese (Figure 2.2; 2.3). There was no overall difference in levels of manganese across communities. Across all communities, samples collected during spring 2011 were found to be significantly lower than those collected during summer 2011 ($p<0.001$).

2.3.8 Zinc

Two samples collected from Port Huron during summer 2011 were below TMDL. No sites exceeded NOAAs chronic freshwater screening level during any of the collection times. Highest concentrations occurred during the fall sampling session, which was significantly higher than both the spring and summer collection ($p=0.003$, $p=0.003$). There were no significant differences between communities for zinc. The Reserve was

found to contain levels below northern Sarnia (p= 0.007) and Corunna (p=0.035). Though not statistically significant, the Reserve was higher than Kettle Point.

2.4 Discussion

This study has identified locations of heavy metal contamination within Canada's "Chemical Valley". When compared to surrounding regions within "Chemical Valley", the Aamjiwnaang First Nation Reserve contained some of the highest concentrations of multiple metals in stream water. Likewise, the reference community, Kettle Point, Ontario showed some of the lowest concentrations. Stream water concentrations on-Reserve were significantly higher than the reference community for aluminum, cadmium, cobalt, and lead but not for arsenic, manganese, or zinc. Each metal investigated has been released within "Chemical Valley" during 2010, and thus are of continued concern for environmental contamination (Table 2.1; Environment Canada, 2012; U.S. EPA, 2012). Our findings for lead contamination in water are in agreement with results found in Spain where a petrochemical region had higher soil levels, though not significantly, than an unpolluted area (Nadal *et al.*, 2004). However, the aforementioned study did not find any significant differences in arsenic concentrations in soils between industrial and unpolluted regions, though those were both higher than a residential area.

Few comparisons of metals concentrations in stream water among seasons have been previously reported. Here, seasonal variability within each site was high. Zinc was significantly higher in the fall than the spring and summer, which is similar to findings reported by Nimick *et al.* (2005) in which ranges of zinc in stream water were higher during the winter months than spring or summer. Arsenic was significantly higher during the summer collection than both spring and fall for all sites. This trend has also been seen

for arsenic in ground water (Nadavakaren *et al.*, 1984). The opposing trends between arsenic and zinc, cobalt, and lead suggest that changes may likely be tied to geochemical influences as other processes such as run-off or groundwater inflow would likely have similar effects on all metals rather than differing effects on cations and anions (Nimick *et al.*, 2005). Another explanation for this variability is higher source releases of arsenic into the environment during the time leading up to summer sampling. However, this is unlikely since all sites across all communities had higher arsenic levels during this time, regardless of location.

While this study has addressed metals concentrations in stream water during three different seasons, it has only captured a cross-sectional view of each of those timeframes. Identification of sites exceeding benchmark levels may require more extensive sampling such as daily or hourly monitoring, as diel cycles have shown to account for large portions of differences among metal concentrations in sites (Nimick *at al.*, 2005). Nonetheless, aluminum in nearly all sites, and manganese in at least one site from each community were above NOAAs screening (Buchman, 2008). Therefore, considerable attention should be paid to these locations in order to address stream water quality in the region.

Our results show that streams closer to the "Chemical Valley" region have higher concentrations than streams in a reference community and that within this region multiple sites exceed screening concentrations. Along with metal contamination, regions laden with petrochemical facilities may be at risk of high levels of polyaromatic hydrocarbons, volatile organic compounds, polychlorinated biphenyls, and dioxin-like compounds (Nadal *et al.*, 2011; Kaisarevic *et al.*, 2007; Gariazzo *et al.*, 2005). Air concentrations of

VOCs has already been investigated in Sarnia, showing that concentrations nearer to the facility complex, and therefore closer to the Aamjiwnaang First Nation Reserve, was higher than in the northern area of Sarnia (Miller and Luginaah, 2009). Our findings, along with others show that the area closest to the petrochemical epicenter in Sarnia, Ontario may be disproportionately exposed to contaminants (Atari and Luginaah, 2008; Miller and Luginaah, 2009).

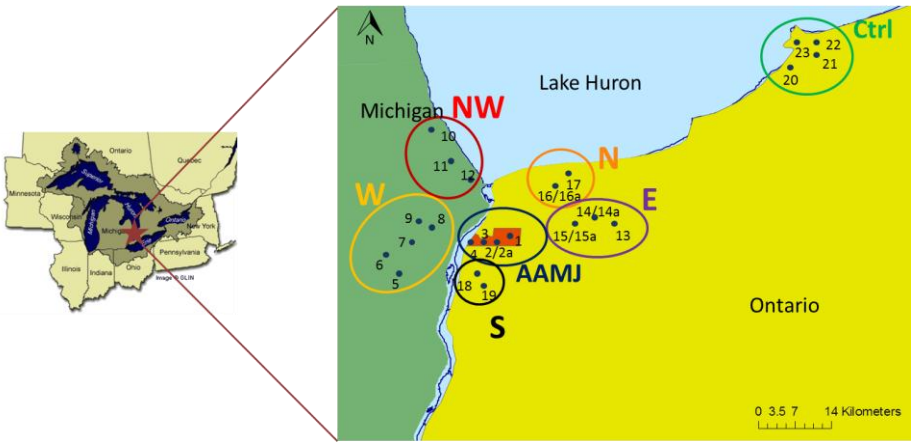

Figure 2.1Map of stream sampling communities. The Aamjiwnaang First Nation Reserve is highlighted in red. Maps and layer data provided by Geography Network Canada, Michigan Center for Geographic Information, and Great Lakes Information Network

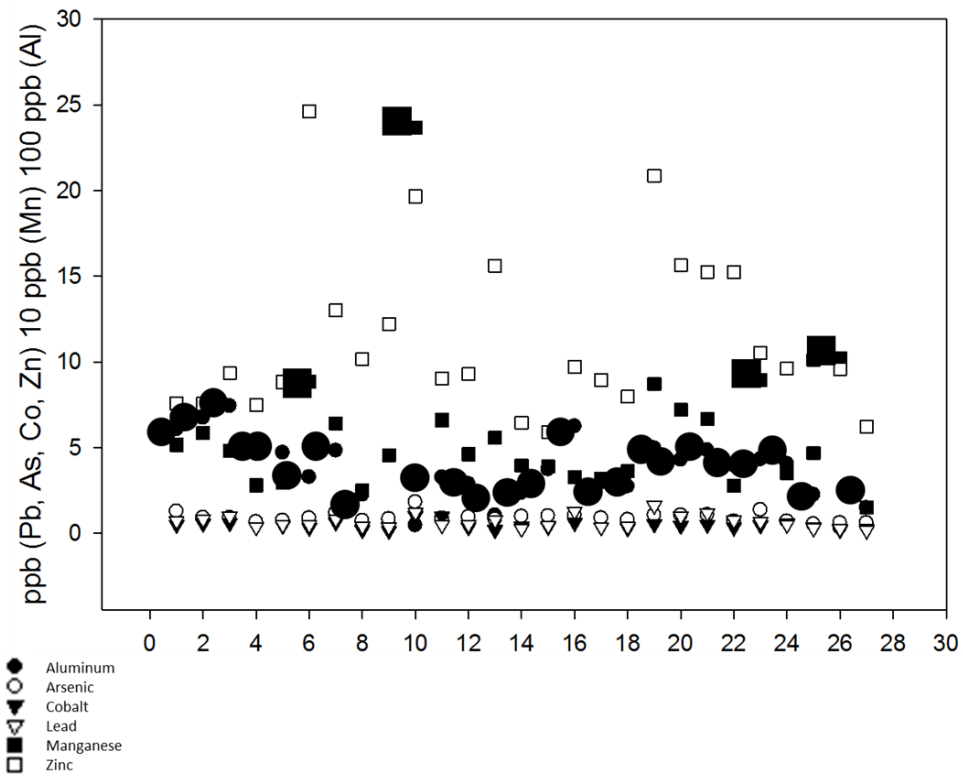

Figure 2.2 Levels of aluminum, arsenic, cobalt, lead, manganese, and zinc at each site. Enlarged symbols represent as site that exceeds NOAAs screening level for that particular metal. Note: arsenic, cobalt, lead, and zinc are reported in ppb, manganese is reported in 10 ppb, and aluminum is reported in 100 ppb.

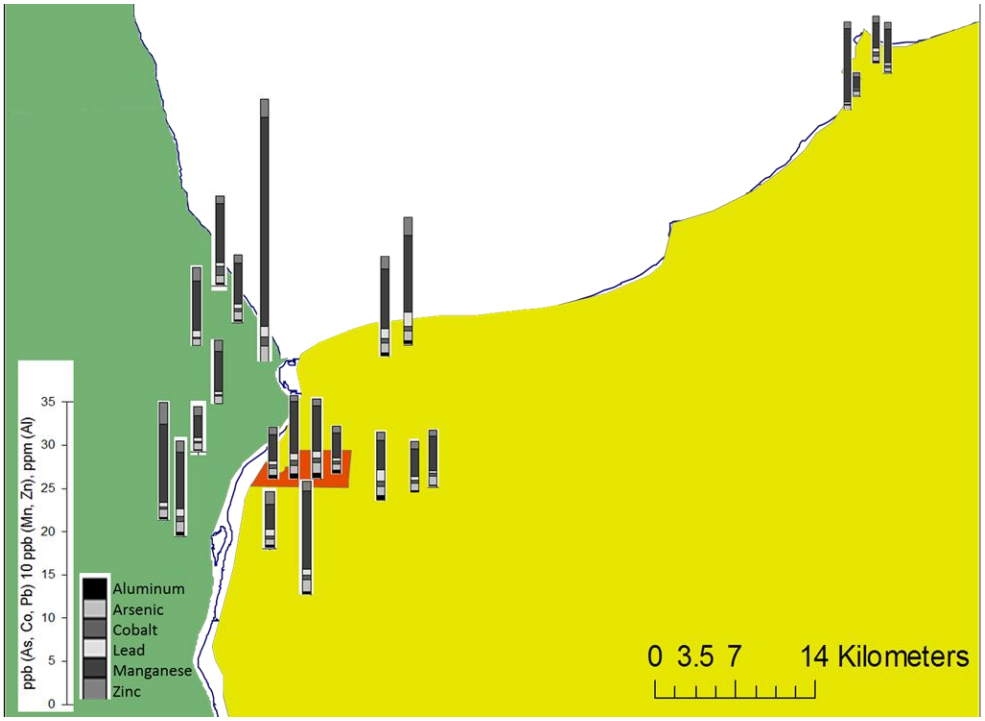

Figure 2.3 Map of metal concentrations in stream water. Aluminum, arsenic, cobalt, lead, and zinc concentrations in stream water at each site are represented by bar graph. Fall 2010, spring 2011, and summer 2011 collections were averaged

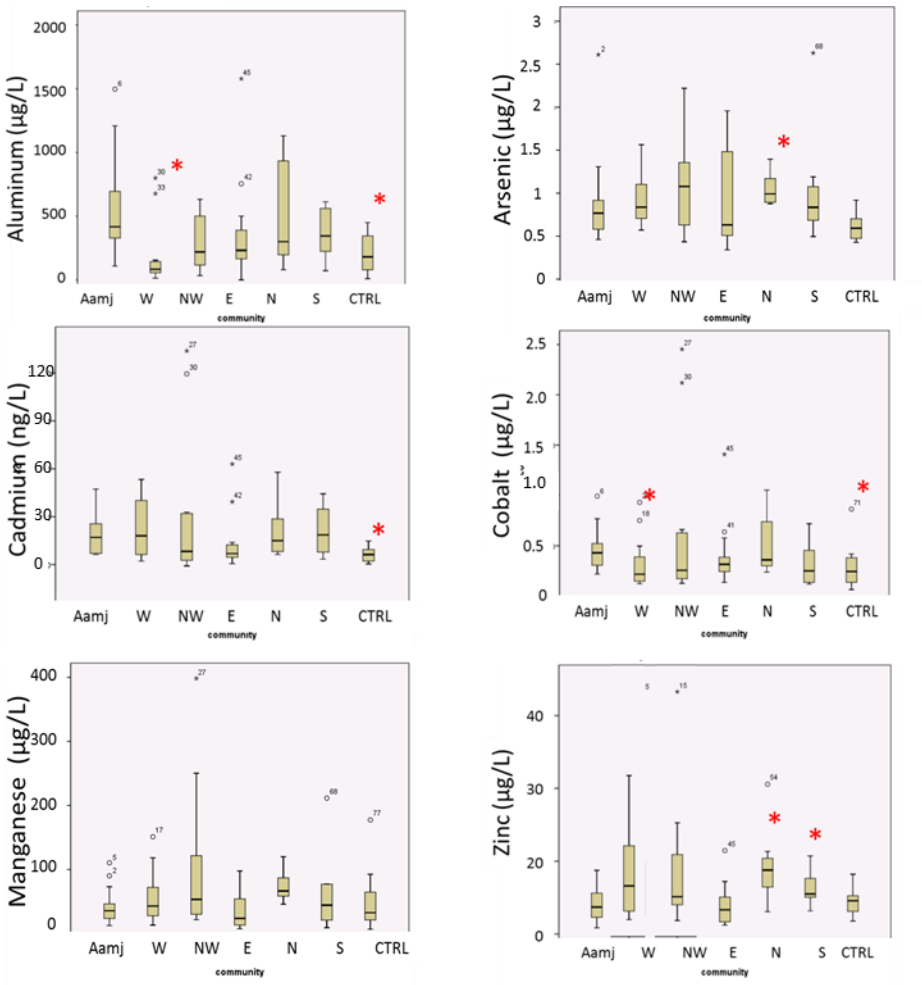

Figure 2.4 Box plots of metals concentrations across communities. Concentrations (µg/L for all elements unless otherwise specified) of aluminum (A), arsenic (B), cadmium (ng/L; C), cobalt (D), manganese (E), and zinc (F). Box and whisker plot of each metal by community. The horizontal line represents the median, the bar represents first through third quartiles, and the whiskers/error bars represent the minimum and maximum values within 1.5 times the length of the first to third quartiles. Asterisks (*) represent communities for which concentrations are significantly different than Aamjiwnaang.

Table 2.1 2010 metal releases within the “Chemical Valley” region (kg) as reported to the U.S. EPA Toxic Release Inventory and Environmental Canada’s National Pollutant Release Inventory (U.S. EPA, 2012; Environment Canada, 2012). Values shown are total onsite releases and disposals

	Releases in 'Chemical Valley' (kg)	% of Total Releases in U.S.
Aluminum	35,000	0.69
Arsenic	80,774	0.08
Cadmium	131,801	10.92
Copper	62,751	0.10
Lead	493,267	0.20
Manganese	120,722	0.16
Zinc	1,034,998	0.36

Table 2.2 Findings of previous studies conducted on metal contamination in sediment on the Aamjiwnaang First Nation Reserve. Arsenic, cadmium, copper, manganese, nickel, lead, and zinc all ranged above lowest effect level established for aquatic invertebrate health (Buchman, 2008).

Metal	Found in Aamjiwnaang Sediment (mg/kg d.w.)	LEL (mg/kg d.w.)[1]
Aluminum	7307-13073	NA
Arsenic	1.78 - 6.73	6
Cadmium	0.12 - 0.80	0.6
Cobalt	6.94 - 15.72	50
Copper	6.71 - 35.00	16
Manganese	111-448	460
Nickel	6.71 - 48.77	16
Lead	<5.00 - 31.56	31
Zinc	22.36 - 650	120

Table 2.3 Screening values established by the National Oceanic and Atmospheric Administration for freshwater invertebrate health (Buchman, 2008).

	Screening Value (µg/L)	
Metal	Acute	Chronic
Aluminum	750	87
Arsenic (total)	340	150
Cadmium	2	0.25
Cobalt	1500	3
Lead	65	2.5
Manganese	2300	80
Zinc	120	120

Table 2.4 Accuracy and detection limits for metals during each sampling season. Recovery rates of aluminum, arsenic, cadmium, cobalt, lead, manganese, and zinc for given standard references materials (NIST 1640, 1640a) during fall 2010, Spring 2011, and Summer 2011 sample analyses.

		Al	As	Cd	Co	Pb	Mn	Zn
	Average Recovery (%)	78.68	85.11	88.69	75.04	90.08	82.08	107.51
Fall 2010	Average TMDL (µg/L)	2.38	0.19	0.02	0.05	1.15	0.27	0.06
	Average Recovery (%)	69.95	71.71	84.94	80.89	84.80	81.48	102.40
Spring 2011	Average TMDL (µg/L)	1.48	0.04	0.04	0.02	1.40	0.32	0.03
	Average Recovery (%)	82.19	78.63	91.98	79.09	90.86	83.75	119.36
Summer 2011	Average TMDL (µg/L)	3.13	0.05	0.02	0.10	1.15	0.06	0.05

Table 2.5 Water quality parameters. Seasonal averages, minimum, and maximum temperature, dissolved oxygen content, pH, and conductivity of stream waters. All sites were averaged for each collection time. All metals reported showed significant differences between seasons.

	Fall 2010			Spring 2011			Summer 2011			p-value
	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	
Temperature °C	6.1	4.1	9.9	11	7.8	16.4	21	16.3	29	0.001
pH	8.3	6.4	9.9	8.4	7.8	8.7	8.1	6.9	10	<0.001
Conductivity (S/cm)	0.4	0.1	0.7	0.5	0.1	8.1	1.6	0.4	6.9	<0.001

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Chapter 3

An Epidemiological and Environmental Investigation of Mercury Contamination at the Aamjiwnaang First Nation

3.1. Introduction

The Aamjiwnaang First Nation is an Ojibwe Tribe and the Reserve consists of 2850 acres of land on which 850 members live. It is located on the southern border of the city of Sarnia, Ontario within Lambton County (Figure 3.1). The reserve is situated along the St. Clair River, and is located within Canada's "Chemical Valley", a region that has been home to dozens of industries since the early 19th century (Ford, 2000). Nowadays, within a 25 km radius of Aamjiwnaang exist 58 U.S. and Canadian petrochemical, polymer, and coal-fired power plants that collectively release 131 million kilograms of pollutants into the air (MacDonald and Rang, 2007).

Though many chemicals are released in the Aamjiwnaang region, mercury remains of particular concern. As early as the 1940s, the St. Clair waterway was known to be a hotspot for mercury contamination (UGLCCS, 1988). The "Mercury Crisis of 1970" was spurred by the discovery of substantial mercury discharges directly into the St. Clair River by a chlor-alkali plant in Sarnia (USEPA, 2009). Discharges averaged 30 pounds released per day for upwards of two decades and in 1969 as much as 75 pounds per day was estimated to be released (OME, 1975). Reports of mercury contamination in fish showed muscle levels in excess of five ppm during the 1970s (note, the Health

Canada standard is 0.5 ppm in fish). At that time, owing to the presence of mercury, commercial fishing was banned resulting in the potential loss of over $1-2 million per year. Since the 1970, mercury concentrations in predatory species (e.g. walleye) have fallen to levels generally below 0.5 ppm, though larger fish may still exceed consumption guidelines for children and women of child bearing age (Gewurtz *et al.*, 2010; Richman and Milani, 2010). In addition to fish tissue residues, there exist some studies to show elevated levels of mercury in the region's sediment. For example, sediment mercury concentrations near Sarnia in 1985 were 4-fold higher than the U.S. EPA's current severe effect level for fresh water invertebrates, and in a study from 2006-2008 sediment concentrations remained elevated above this threshold (Murdoch and Hill, 1989; Richman and Milani, 2010).

Indigenous groups worldwide (including Native American and First Nations populations) are particularly susceptible to mercury exposure given their reliance on country foods such fish and seafood, which are well-documented to contain mercury (Nriagu *et al.*, 2012). Despite the long history of mercury pollution in the Aamjiwnaang region, there is no information on mercury exposure among area residents and little is known about mercury in the region's broader environment. Accordingly, this study was conducted at the request of the Aamjiwnaang Health and Environment Committee to increase understanding of mercury exposure and potential risks in the area. The aims of the current study were to: 1) assess the releases of mercury from facilities within the "Chemical Valley" region; 2) characterize mercury levels in stream sediment and soil from the region; 3) determine if mothers and children living on Reserve were more highly exposed to mercury than those living off the Reserve; and 4) explore predictors of

mercury exposure. In terms of characterizing human mercury exposure, detailed surveys and biomarkers (hair, urine, blood) were used that provided information on exposure to both organic mercury and inorganic mercury.

3.2 Materials and Methods

3.2.1 Source Investigation

Canada's National Pollutant Release Inventory (NPRI) and the U.S. Toxics Release Inventory (TRI) were queried to investigate the releases of mercury from industry within the "Chemical Valley" area for the year 2010, similar to the analysis performed with 2005 data by MacDonald and Rang (2007). The NPRI and the TRI are government programs which provide publicly accessible databases regarding industrial uses and releases of specified chemicals. Each program has specific reporting requirements. Canadian businesses which have a specified number of employees, or release, produce, process, or otherwise use a specific threshold of any one of 346 chemicals are required to self-report all chemical releases from that facility each year to the NPRI (Environment Canada, 2012b). The TRI is a similar reporting system for businesses in the United States (U.S. EPA, 2011). Facilities must report for all chemicals if: the business operates under specified sectors, has ten or more full-time employees, produces greater than 25,000 lbs., or uses greater than 10,000 lbs. of any one of 650 designated chemicals. Reported information includes on-site releases to air, water, and land, on- and off-site recycling and off-site transfers. The current study addresses total on-site releases, disposals, and recycling for each facility, excluding off-site disposal and recycling since locations for these are not provided. For this report, only those facilities located within the greater Sarnia area (postal codes N7T 7H9, N7T 7N4, N7T 7H8, N7T 2l3, N7T 7H3, N7T 8H8,

N7T 7MS, N7T 7J2, N7T 7M2, N7T 8A3, N7T 7J3, N7T 7K2, N7T 7W1, N7S 5N5, N7S 5N2, N7S 5M4, N7H 8H1, NON 1G0, NON 1B0, NON 1MO, and NON 1H0) and the U. S. zip codes of 48060, 48061, 48054, and 48079 were investigated.

3.2.2 Ecological Study

3.2.2.1 Sample Collection

Stream sediment and stream bank soil were collected from sites on the Aamjiwnaang First Nation Reserve (n=4 sites) and off the Reserve (n= 20) (Table 3.1). For ease of geographical comparison, sites were grouped into communities in both Ontario (ON) and Michigan (MI; Figure 3.2). Community 1 is The Aamjiwnaang First Nation Reserve (ON), Community 2 is located in Marysville (MI), Community 3 is Port Huron (MI), Community 4 is eastern Sarnia (ON), Community 5 is northern Sarnia (ON), and Community 6 is Corunna, (ON). Community 7 is in Kettle Point (ON) and serves as the reference community as it is over 40km to the northeast of the Aamjiwnaang Reserve and its upstream waters go through a nature preserve. In three of the sites, drainage tubes were present and thus samples were collected from both upstream and downstream of the point source (Table 3.1). To address seasonal variability samples were collected from all sites during Fall 2010 (November 18-21), Spring 2011 (May 2-4), and Summer 2011 (August 31 – September 3).

For sediment, a ~10 gram grab sample was collected into a fresh Wirlpack at the point of entry as well as at two 10 meter intervals upstream of the entry point thus resulting in n=3 sediment samples per site. Water quality measures (temperature, pH, and conductivity) were recorded at each stream site using a YSI 556MPS probe (Yellow Springs, OH) and GPS coordinates were recorded using a Garmin Oregon 450 (Olathe,

KS; Table 3.1). For soil, a site was identified approximately 5 meters from the stream bank and from that site five subsamples of soil were collected from the middle and four corners of an approximate 12x12" square Sediment and soil samples were shipped to the University of Michigan and frozen until analysis.

3.2.2.2 Total Mercury Analysis

Approximately 5 grams of sediment or soil was dried at 60°C for 72 hours. Approximately 0.1 grams of sample was analysed for total mercury content using a Direct Mercury Analyzer 80 (DMA80; Milestone, Shelton, CT) using EPA Method 7473 as we have previously outlined (Basu et al., 2010; Nam and Basu, 2011). All samples were batch processed and analyzed in triplicate, after each seasonal collection.

Accuracy (within 20% of expected values; mean recovery: 107.03%) and precision (within 7% relative standard deviation; mean RSD was 1.99%) were measured using standard reference materials including National Institute of Standards and Technology San Joaquin Soil (NIST 2709), Trace Elements in Soil (NIST 2586), and National Research Council Canada Dogfish Liver (NRC DOLT-4). The theoretical method detection limit (TMDL; 3 times the standard deviation of the mean blank value) ranged from 0.01 to 0.67ng mercury. Samples for which concentrations were below limit of detection are noted in the results section with the measured value being retained.

3.2.2.3 Ecological Statistical Analysis

For all sites, the three sediment subsamples were averaged together to determine an overall site value. Statistics were performed using the overall site averages for sediment and the individual site values for soil mercury concentration, keeping the sites separated into the communities described above. Stream data did not fit the normality

assumption. Differences among communities and among seasons were evaluated using Kruskal-Wallis and further investigated using Mann-Whitney tests. Correlations between soil and sediment mercury concentrations with water quality measures were performed using Spearman correlations. For water quality parameters and mercury concentrations, comparisons of interest focused primarily on differences between communities within the "Chemical Valley" region and between the Aamjiwnaang First Nation and the reference community. Each stream site is compared to benchmark values as addressed in the text. All statistics were performed in SPSS (Version 19.0; Armonk, New York).

3.2.3 Human Exposure Study

3.2.3.1 Human Subjects Interactions

Institutional Review Board (IRB) approval was obtained from the University of Michigan (HUM00029363), and permission was obtained from the Aamjiwnaang Band Council via a Band Council Resolution (2008/2009-28). Mother-child pairs (n=43) were recruited from the Reserve and surrounding areas. Written informed consent was obtained from each mother for her and her child's participation, along with the child's assent. Participants were met either in their home or at the Aamjiwnaang First Nation Health Center.

3.2.3.2 Surveys and Biological Samples

A written survey was filled out by each mother to capture diet, self-reported health, activity, and household information. Mothers were asked to provide the same information for their children. Fish consumption, by species, over the most recent six months was addressed along with consumption of local produce and game. Participant recollection was reinforced by a 24-hour recall survey.

From both mothers and children, biological samples were collected for mercury analysis. Participants were instructed to give a mid-stream urine sample into acid-washed 120 mL BD Vacutainer urine cups (urine reflects exposure to inorganic mercury). Approximately 30-50 strands of hair were cut from the occipital region of the head, as close to the scalp as possible and placed on tape so that approximately 3cm of hair from the cut end was hanging over the edge of the tape (hair reflects exposure to organic mercury). The taped hair was placed into a plastic bag. Intravenous blood samples were collected following sterile procedures by a licensed phlebotomist from the antecubital fossa into BD Vacutainer trace metals tubes (blood main reflects exposure to organic mercury). A portion of mother (n=12) and child (n=10) samples were collected into serum tubes for trace metals, from which 0.5 mL of supernatant serum was analyzed for mercury content prior to being sonicated to a homogenous state and re-analyzed for mercury. Total mercury in these tubes was calculated via the addition of mercury from each portion of sample divided by the initial volume of total sample. All other blood samples were collected into trace metal tubes for whole blood analyzed directly after being vortexed. All samples were stored at -20°C in a locked freezer at the Aamjiwnaang First Nation Health Center before being relocated on ice to the University of Michigan.

3.2.3.3 Biological Sample Analysis

Biological samples were analyzed using the DMA-80. Accuracy (within 20% of expected values; mean recovery: 92.44% for urine, 95.07% for blood, 93.02% for hair) and precision (within 7% relative standard deviation; mean RSD was 5.56% for urine, 5.10% for blood, 8.74% for hair) were measured using standard reference materials including QMEQAS084-01(urine) and QMEQAS09B-02 (blood) from the National Public Health Institute of Quebec, CRM 13 (human hair) National Institute for

Environmental Studies, Japan, and DOLT-4(dogfish liver) National Research Council Canada. The theoretical method detection limit (TMDL; 3 times the standard deviation of the mean blank value) was 0.03 ng Hg for urine, 0.06 ng Hg for blood, and 0.04 ng Hg for hair. Samples for which concentrations were below limit of detection are noted in the results section with the measured value being retained.

3.2.4 Statistical Analysis

Biomarker concentrations were not normally distributed and transformations did not achieve normality. In order to retain maximum interpretability, biomarker data were analyzed and reported without transformations. Statistical analyses were performed in SPSS, using t-tests and Spearman correlations. Primary comparisons of interest were differences between mothers and children living on and off-Reserve. Comparisons of values on and surrounding the Aamjiwnaang First Nation are compared to benchmark values as seen throughout the text.

3.3 Results

3.3.1 Source Results

Overall releases of mercury from facilities within the "Chemical Valley" region have shown a general increase since the year 2000 (Figure 3.3; USEPA, 2012; Environment Canada, 2012a). Sources of mercury were located surrounding the Aamjiwnaang First Nation Reserve, in varying distances (Figure 3.3). In the most recent reporting year, 2010, nearly 94 thousand pounds of mercury were released or processed within the area. Of those releases, 700 pounds were emitted into the air, 25 pounds were discharged directly into water bodies, and upwards of 93 thousand pounds were disposed of on-site either via underground injections or into landfills. The primary sources

included waste water treatment plants, waste treatment and disposal facilities, and coal-fired power plants (Figure 3.3).

3.3.2 Ecological Results

Sediment samples were collected from each of the 24 stream sites during three seasons. The geometric means of all sediment concentrations at all sites across each collection timeframe ranged from 5.03 to 398.73 µg/kg d.w. (Figure 3.4). In general, mercury concentrations across communities were variable. Despite variability, there were significant differences in mercury sediment concentrations between communities ($p<0.001$), with the Reserve being significantly higher than the reference community ($p<0.001$) and eastern Sarnia ($p<0.001$). The seasonal collections were not significantly different from each other. Site 10 in Port Huron and site 2 on Aamjiwnaang First Nation Reserve had the highest concentrations of mercury in sediment (Table 3.1; Figure 3.4).

Soil samples were collected near streams from each of the 24 sites. Similar trends were seen in soil as were seen in sediment. The geometric means of all soil samples ranged from 1.24 to 696.20 µg/kg (Figure 3.5). When comparing soils from all communities using a Kruskal-Wallis test, significant differences were detected ($p=0.004$). The mean ranks of mercury soil concentrations was significantly higher on Reserve than the reference community ($p=0.041$) and eastern Sarnia ($p=0.003$). There were no significant seasonal differences ($p=0.690$). One particular site had higher concentrations of mercury in the soil and sediment than all the others (Site 2, Figure 3.4). The soil at this site exceeded the NOAA benchmark value for plant and invertebrate health (Buchman, 2008). There was a significant correlation between sediment and soil concentrations among all sites and seasons ($r_s=0.835$, $P<0.001$).

In general, there were no differences in water temperature, pH, or conductivity between communities. Soil mercury concentrations were not associated with water quality parameters. Among all sites and seasons, stream water temperature was positively correlated to sediment mercury concentrations (r_s=0.454, p=0.017). Among seasons, water temperature, pH and conductivity showed significant differences (p<0.001, p=0.001, p<0.001, respectively). As expected, water temperature and conductivity measures were highest in the summer (Table 3.2). Values of water pH were highest in spring.

3.3.3 Participant Demographics

In total, 43 mother-child pairs residing on the Aamjiwnaang First Nation Reserve and in the surrounding "Chemical Valley" area were recruited. Of these, three pairs were lost to follow-up (7.5%). 87% of mothers living on Reserve were of First Nations descent, while 23% and 77% of mothers living off the Reserve were First Nations and White, respectively (Table 3.3). There was not a significant difference in education between mothers living on and off Reserve. Mean ages of mothers living on and off Reserve were not significantly different.

Child participation was limited to those aged 4-14 years. On and off-Reserve child participants did not show any differences between age and gender (p=0.254; p=0.375; Table 3.4). Among on-Reserve children, 41% were male, while 46% of off-Reserve children were male. All on-Reserve children were of First Nation descent. Of the off-Reserve mother and child participants, 24% were First Nation, 70% were White, and 6% were Other.

3.3.4 Mercury Exposure Biomarkers

In hair, total mercury content was measured in each sample. Overall concentrations in children (126.7 ± 112.9 µg/g) were significantly lower than in mothers (242.1 ± 188.6 µg/g; $p<0.001$). Concentrations of hair mercury were similar for participants residing on and off-Reserve in both mothers and children. No associations among child age (Table 3.4) and hair mercury levels were observed. There were no observed differences in hair mercury between boys and girls. There were no observed effects of age or gender on hair mercury levels.

Concentrations of total mercury were measured in blood samples. Of the 43 mother-child pairs, we were unable to obtain blood from eight children (n=4 on and off-Reserve each) and six mothers (n=2 on-Reserve, n=4 off-Reserve). No single blood sample was below the level of detection. Blood mercury levels differed in children living on and off-Reserve ($p=0.008$) but not in mothers ($p=0.951$). Concentrations of blood in children were not correlated with blood levels in mothers ($r_s=.238$, $p=0.198$). There were no age-related effects observed for mothers or children. Across all children, blood mercury levels in girls (2.23 µg/L) was found to be higher ($p=0.034$) than in boys (0.73 µg/L). Blood and hair levels were correlated in mothers ($r_s=0.429$, $p=0.007$), but not in children ($r_s=0.145$, $p=0.401$).

Fish and seafood consumption is the main route of organic mercury exposure. Here, the mean consumption of fish was 0.96 servings per week (1.12) in mothers and 0.62 (1.01) in children, with off-Reserve children consuming significantly more fish servings per week than on-Reserve children ($p=0.037$). The top three consumed fish were tuna (canned and canned light), halibut, and shrimp. The main Great Lakes fish species consumed included walleye, perch, and pike. When the mercury content in each fish was

related to the survey information, the mean intake of mercury from fish was 0.03 ± 0.08 µg/kg bw/d in children and 0.05 ± 0.13 µg/kg bw/d in mothers. When the organic mercury biomarkers (hair, blood) were related to fish intake in both mothers and children, several interesting points were observed. Estimated mercury intake through fish consumption (µg/kg/bw/d) was correlated to hair mercury in children and in mothers (r_s=0.440, p=0.005; r_s=0.356, p=0.024 respectively). Children hair mercury differed significantly (p=0.019) when they were dichotomized into those consuming fish (mean= 343.40 µg/kg) or not (mean=107.98 µg/kg). However, no relationships were seen among blood mercury concentrations and fish consumption in mothers or children.

Concentrations of total mercury in urine were found to be higher in on-Reserve mothers and children compared to those off-Reserve (p=0.028; p=0.018; Figure 3.6). There were no significant gender or age-related differences in urinary mercury concentrations in either on or off-Reserve children. There was no correlation between urine mercury levels and number of dental amalgams, the main exposure route for elemental mercury.

3.4 Discussion

The primary aim of this study was to increase understanding of mercury exposures in the Aamjiwnaang First Nation Reserve. While the closure of the Dow Chemical chlor alkali plant in the 1970s marked the cease of the largest source of mercury discharge into water bodies, thorough analysis of the TRI and NPRI databases show that mercury is still being released in the region with values increasing over the past twelve years (Environment Canada, 2011; U.S. EPA, 2012).

Having documented that mercury is still being released in the region, the second aim of this study was to compare levels of mercury in sediment and soil in sites located on the

Reserve to sites in the surrounding "Chemical Valley" including a reference community. We found significantly higher levels of mercury in sediment and soil on-Reserve than in the reference site during three different seasons. In a Spanish petrochemical center, mercury concentrations in soil were elevated compared to reference sites, though not significantly (Nadal *et al.*, 2004). With the exception of the elevated on-Reserve site, the range of soil concentrations in "Chemical Valley" was similar to those found by Nadal *et al.* (2004). In the past, a mercury cell chlor-alkali plant was among the facilities located near the Aamjiwnaang First Nation Reserve. Elevated concentrations of mercury in soils and sediments located in close proximity to such plants have previously been observed to be upwards of 262 µg/kg directly near the source and 0.12 µg/kg spanning within 1km of the source (Gonzalez, 1991). One site (Site 2, 131 µg/kg) on Reserve was found to contain concentrations of mercury above benchmark levels in both stream sediment and nearby soil. While there was no significant difference, the seasonal collections at this site showed that concentrations decreased over time. Further monitoring should be performed at regular intervals along Talfourd Creek, which flows though the Reserve. One site in Port Huron, MI also contained high levels of mercury in sediment during each collection season. While all other sites in the study had sediment substrates comprised of clay and clay with rocks, this site had much more detritus within the clayey sediment. Mercury absorbed in allochthonous detritus is a likely explanation for the elevated mercury concentrations at this site (Herrick *et al.*, 1982), along with the increased atmospheric deposition from nearby industries.

Though it has been known for a long time that mercury is a pollutant of concern in the region, no biomarker study has been performed to gauge individual exposures. Here,

while all participants had detectable levels of mercury in their hair, blood, and urine, none of the levels were any different from the average U.S. or Canadian populations, and they did not exceed any health guideline values. Methylmercury exposures, as measured by total hair mercury concentration, among the Aamjiwnaang mothers (range: 8.62-876.93 µg/kg) were generally below those seen in other First Nations populations across Canada where a subsistence diet is consumed (range: 2200-27100 µg/kg Hg; Beuter and Edwards, 2004). Hair mercury levels in mothers and children living on and off-Reserve did not exceed average levels found in the U.S. (McDowell *et al*., 2004). Hair biomarker concentrations among Aamjiwnaang participants were also found to be lower than a Californian Native American Tribe located near a historic cinnabar mine site (range 0.03 – 1.80 µg/g; Harnly *et al.,* 1997). A small study performed in 2005 measuring blood mercury concentrations in three Aamjiwnaang members also showed low blood mercury concentrations, though in only three participants (Environment Defense, 2007).

Concentrations of total mercury in urine were higher among mothers and children residing on-Reserve than off-Reserve. A similar relationship was found among adults residing at varying distances from an active chlor-alkali plant in Poland (Jarosinska *et al*., 2006). Average concentrations found among and near Aamjiwnaang were above those seen in Poland for both the chlor-alkali and reference zones (mean chlor-alkali =0.40 µg/L, mean reference = 0.21 µg/L), though there is no currently active chlor-alkali plant within "Chemical Valley". In addition to the former chlor alkali plant located within "Chemical Valley" there are multiple active sources of mercury such as coal-fired power plants, carbon black production, and a hazardous waste facility (Figure 3.3). In

comparison to a Native American Tribe located in California near a cinnabar mine, the urinary mercury ranged much lower among the Aamjiwnaang (0.4 – 12.5 µg/L; Harnly *et al.*, 1997). Urine concentrations among on and off-Reserve children averaged below those seen across the US (mean=0.25 µg/L; CDC, 2009). On-Reserve mothers averaged concentrations above those seen in the US, though off-Reserve mothers did not (mean=0.46 µg/L).

The project showed that there were slight differences in biomarker concentrations between mothers or their children living on the Reserve in comparison to those living off the Reserve, but still near the industrial complex. Hair mercury concentrations were correlated to estimated mercury intake through fish consumption across all children, as expected since methylmercury exposure occurs mainly through ingestion of contaminated fish (Clarkson, 1993). Children living off-Reserve showed higher hair mercury concentrations that did on-Reserve children. This find was unexpected, as First Nations Peoples are suspected to be more highly exposed to methylmercury through eating fish than the general public (Harris and Harper, 1997). However, in the current study, we found that a significantly higher percentage of our children living off-Reserve reported eating fish than did children living on-Reserve.

Ojibwe people living a traditional lifestyle would be expected to consume local produce and game, fostering healthy diets and cultural connections. Such lifestyles would put Ojibwe populations at risk of being exposed to environmental pollutants such as mercury at disproportionately high rates in comparison to the general U.S. population (Harris and Harper, 1997). However, the current study suggests that members of the Aamjiwnaang First Nation are experiencing a dietary and cultural shift, seen in many

other Native and First Nations Peoples (Kuhnlein and Receveur, 1996). Aamjiwnaang members have reported eating less locally grown foods and fish in recent years. Within the participants on the Aamjiwnaang First Nation 88% of mothers and 64% of children reported anxiety and/or fear associated with contaminants released by surrounding facilities. Reports of anxiety among the Aamjiwnaang associated with living near the petrochemical center have been well documented (Luginaah *et al.*, 2010). A shift in diet, along with chemical, physiological, and emotional stressors could be of major health concern either individually or cumulatively among the Aamjiwnaang First Nation (Arquette *et al.*, 2002).

This study was performed as a community-based participatory research project in partnership with the Aamjiwnaang First Nation's Health and Environment Committee. Even with community collaboration, recruitment was limited making statistical samples size a major limitation for epidemiological studies. However, mercury was measured in a diverse range of sample media including human biomarkers of exposure which had not yet been well characterized in this population. Other limitations of the study were sampling bias, as participants were volunteers though we advertised the study in the broader Aamjiwnaang and Sarnia communities through a variety of methods, and recall bias as participants provided self-reported health and dietary information. This was a cross-sectional study and, as such, may not have captured exposures during certain windows of vulnerability (e.g. pre-natal exposures). Regardless of these limitations, we used diverse and robust field and laboratory methods in order to address the aims of the study. The current study characterizes data and trends that allow for a foundation upon which to develop further investigation.

3.5 Conclusions

This study was performed in response to requests made by and in collaboration with the Aamjiwnaang First Nation's Health and Environment Committee. Using multiple environmental and biological media, evidence of mercury contamination was found at specific sites within the "Chemical Valley" region, though evidence of elevated human (including children) exposures was not seen. Further investigation of environmental contamination and human exposures to multiple other contaminants and stressors is called for. Long-term spatial and temporal scales of exposures and health outcomes should be addressed. Further, lower dietary intakes of fish among Aamjiwnaang members may reflect movement away from culturally meaningful and healthful dietary practices, which in turn may have additional health implications. Projects should be performed such that specialists across multiple fields for transparent and inclusive methodologies to promote participation and education among all stakeholders.

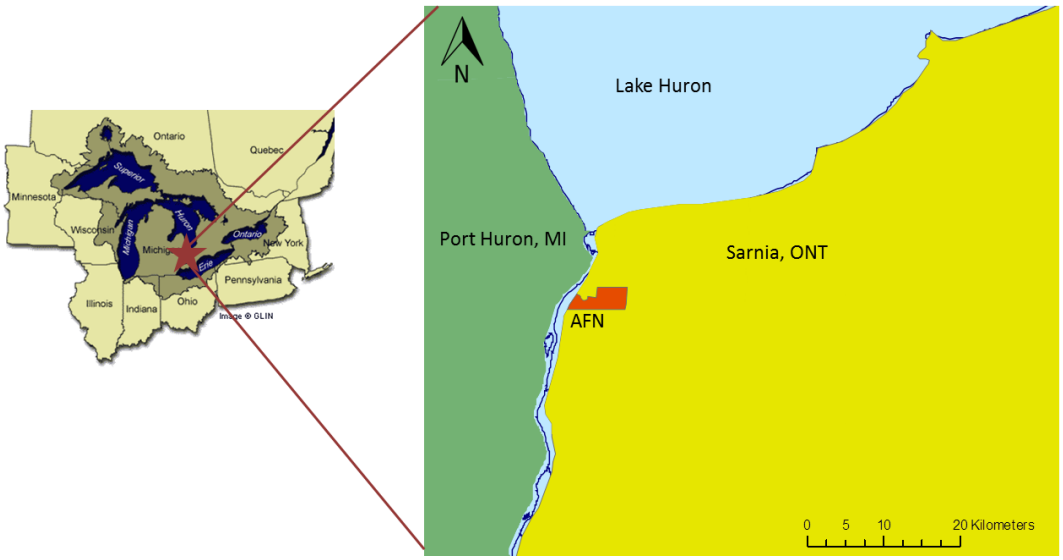

Figure 3.1 Map of the Aamjiwnaang First Nation and surrounding area. The Aamjiwnaang First Nation Reserve is highlighted in red on the map to the right. Maps and layer data provided by Geography Network Canada, Michigan Center for Geographic Information, and Great Lakes Information Network.

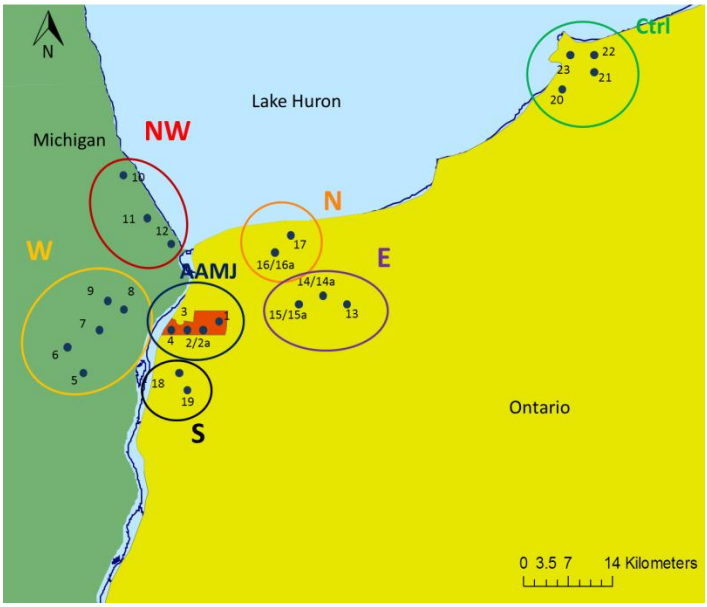

Figure 3.2 Communities from which soil and sediment samples were collected. The Aamjiwnaang First Nation (AAMJ) is indicated in red, and sampled communities are located in each direction from the Reserve: Port Huron, MI the north west (NW), Marysville, MI from the west (W), Corunna, ON to the south (S), northern Sarnia, ON to the north (N), eastern Sarnia, ON to the east (E), and Kettle Point , ON the control community (Ctrl). Maps and layer data provided by Geography Network Canada, Michigan Center for Geographic Information, and Great Lakes Information Network.

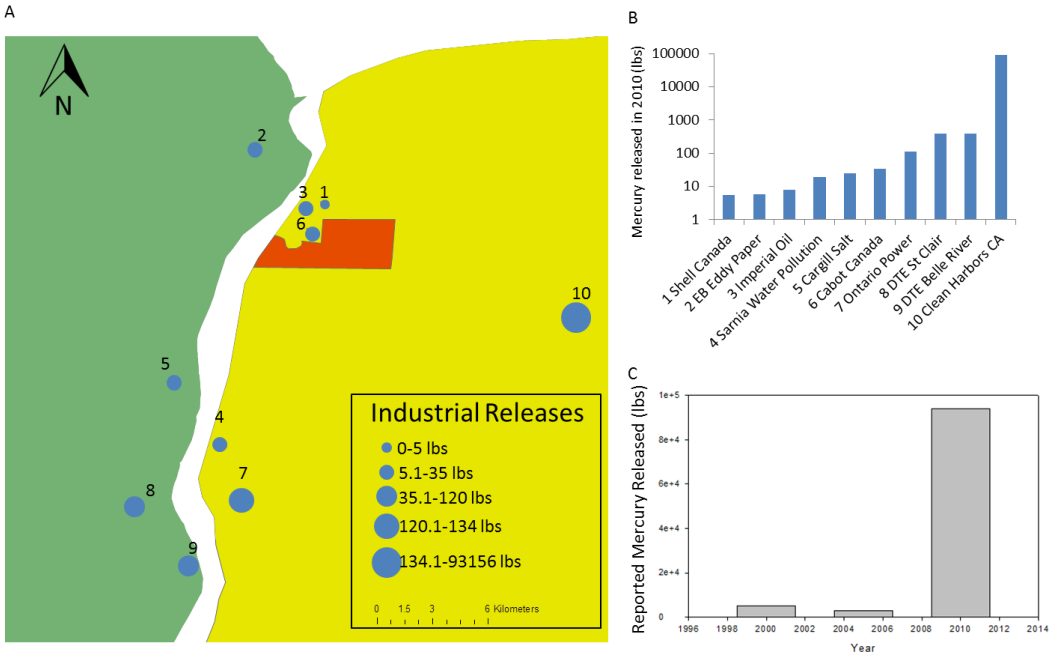

Figure 3.3 Mercury releases with "Chemical Valley" during 2010. A) Map of facilities that release mercury within the "Chemical Valley" region in the 2010 reporting year. Mercury releasing facilities are represented on the map by dots, with large dots representing a facility which releases more mercury. B) Bar graph of mercury released (lbs) by each facility. C) Cumulative mercury releases within "Chemical Valley" during 2000, 2005, and 2010 as based on a review of NPRI and TRI data.

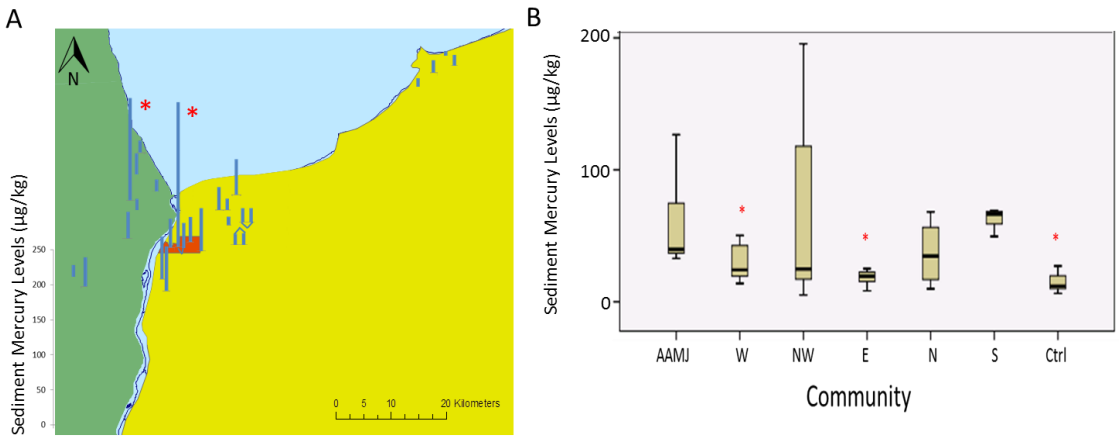

Figure 3.4 Sediment mercury concentrations. A) Map of sediment mercury concentrations (µg/kg). Each site is represented by its average mercury concentration during all three sampling sessions. Asterisks denote a site at which mercury levels were above the US EPA lowest effect level for freshwater invertebrates. B) Box and whisker plot of sediment mercury concentrations (µg/kg) from the 7 study communities. The horizontal line represents the median, the bar represents first through third quartiles, and the whiskers/error bars represent the minimum and maximum values within 1.5 times the length of the first to third quartiles.

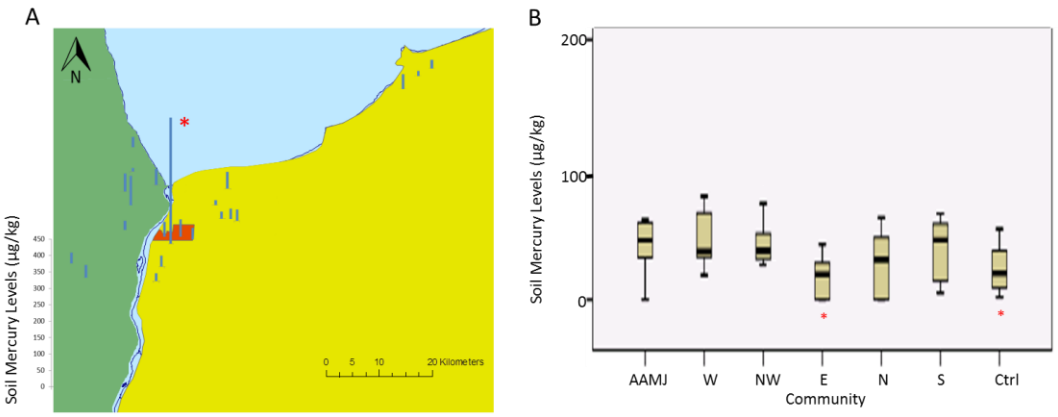

Figure 3.5 Soil mercury concentration. A) Map of soil mercury concentrations. Each site is represented by its average mercury concentration (ppb). Asterisks denote a site at which mercury levels were above the US EPA ecological soil screening levels for plant health. B) Box and whisker plot of sediment mercury concentrations (µg/kg) from the 7 study communities. The horizontal line represents the median, the bar represents first through third quartiles, and the whiskers/error bars represent the minimum and maximum values within 1.5 times the length of the first to third quartiles.

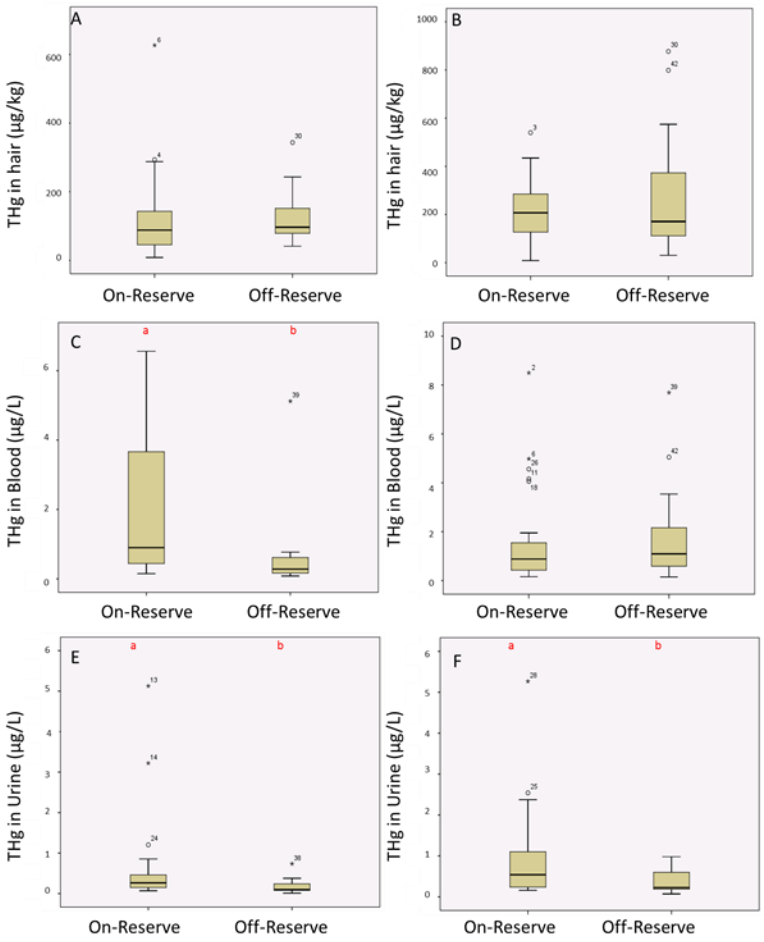

Figure 3.6 Biomarker concentrations of mercury in on and off-Reserve mothers and children. Concentrations (µg/kg) of hair mercury in children (A) and mothers (B). Blood concentrations (µg/L) of mercury in children (C) and mothers (D). Urine concentrations (µg/L) of mercury in children (E) and mothers (F). Levels of blood mercury in children, and urine mercury in mothers and children were significantly higher in those living on-Reserve than off-Reserve. Box and whisker plot of sediment mercury concentrations (µg/kg) from the 7 study communities. The horizontal line represents the median, the bar represents first through third quartiles, and the whiskers/error bars represent the minimum and maximum values within 1.5 times the length of the first to third quartiles.

Table 3.1 Stream site locations. Sites in which point sources were present (2, 14, 15, and 16) are represented by the site number as well "a" to denote that sediment samples were collected downstream of the point source. For each site, GPS coordinates and elevation were recorded using a Garmin Oregon 450.

Community	Site #	Steam Name	Nearest Intersection	lat	long	ele
Aamjiwnaang, Ont	1	Talfourd Creek	Scott Road	42.91467	-82.3967	176.6824
Aamjiwnaang, Ont	2/2a	Talfourd Creek	LaSalle Road	42.91231	-82.4228	176.3155
Aamjiwnaang, Ont	3	Talfourd Creek	MacGregor Road	42.91558	-82.3668	188.8931
Aamjiwnaang, Ont	4	Talfourd Creek	Pow Wow Grounds	42.91504	-82.4521	150.4393
Marysville, MI	5	Rattle Run Creek	Wadhams Road	42.87107	-82.5582	144.7957
Marysville, MI	6	Smiths Creek	Frith St	42.88853	-82.5778	131.4021
N Port Huron, MI	7	Huffman Stream	Minnesota Road	42.94371	-82.491	153.4232
N Port Huron, MI	8	Sanborn Creek	Sanborn Park	42.98066	-82.481	180.3463
N Port Huron, MI	9	Doe Creek	Brace Road	43.01213	-82.4418	175.9094
Port Huron, MI	10	Stocks Creek	Lapeer Road	43.06812	-82.4745	156.9773
Port Huron, MI	11	Stream #1	Parker Road	43.0372	-82.4765	126.9292
Port Huron, MI	12	Beach Creek	Beach Road	43.0019	-82.4884	166.5656
E Sarnia, Ont	13	Waddell Creek	Confederation Road	42.95896	-82.3031	188.7786
E Sarnia, Ont	14/14a	Perch Creek	Confederation Road	42.95926	-82.3105	190.1584
E Sarnia, Ont	15/15a	Stream #2	Confederation Road	42.95949	-82.326	191.6391
N Sarnia, Ont	16/16a	Wawanosh Creek	London Line	42.98374	-82.3397	213.946
N Sarnia, Ont	17	Wawanosh Creek	Michigan Line	43.00795	-82.3168	216.5777
Corunna, Ont	18	Marsh Creek	Hill Street	42.88802	-82.4284	172.2528
Corunna, Ont	19	Baby Creek	Rockeby Line	42.86382	-82.4355	182.7682
Ketle Point, Ont	20	Shashwanda Creek	Lakeshore Road	42.87759	-82.446	149.8063
Ketle Point, Ont	21	Ipperwash Creek	Ipperwash Road	43.19306	-81.9684	163.8
Ketle Point, Ont	22	Stream #3	Ipperwash Road	43.20496	-81.9739	174.8344
Ketle Point, Ont	23	Stream #4	Lakeshore Road	43.16201	-82.0182	205.9523

Table 3.2 Average water quality parameters for all sites during fall 2010, Spring 2011, and Summer 2011 sampling sessions.

	Average		
	Fall	Spring	Summer
Temperature (˚C)	6.09	10.57	20.78
pH	8.34	9.41	9.68
Conductivity (S)	0.38	0.54	1.58

Table 3.3 Demographics of mothers (n=43)

Demographic		On-Reserve (%)	Off-Reserve (%)
Race	First Nation	78.3	23.5
	Native Mix	8.7	0
	White	8.7	76.5
	Other	4.4	0
Education	Less Than High School	13	5.9
	High School/GED	26.1	5.9
	Some College	52.2	32.3
	Associates	4.4	41.2
	Bachelor	0	11.8
	Post Graduate	4.4	0
Age	<30	21.7	40
	30-40	39.1	46.7
	41-50	24.8	13.3
	>50	4.4	0
Smoke	Yes	73.9	80
Number of Hg Amalgams	0	81.3	62.5
	1 - 5	12.5	37.5
	6 - 10	6.3	0
Daily Hg Intake through Fish Consumption (µg/kg/bw/d)	0	38.5	44.4
	0.01-0.05	38.5	53.9
	0.05-0.1	23.1	38.5
	>0.1	0	38.5
Number of Fish Servings per Week	0	32.1	7.7
	<0.5	17.9	7.7
	0.5 - <1	17.8	30.8
	1 - 2	14.3	38.5
	>2	14.4	15.4

Table 3.4 Demographics of children, limited in age to 4 – 14 years (n=43)

Demographic		On-Reserve (%)	Off-Reserve (%)
Sex	Male	41.7	46.7
	Female	58.3	53.3
Age	4 - 8	43.5	73.3
	9 - 14	56.5	26.7
Race	First Nation	82.6	23.5
	Native Mix	17.4	0
	White	0	70.6
	Other	0	5.9
Local Foods	Yes	31.6	70.7
Number of Hg Amalgams	0	81.2	88.2
	2	12.5	0
	3	0	5.9
	4	6.3	5.9
Daily Hg Intake through Fish Consumption (µg/kg/bw/d)	0	66.7	23.1
	0.01-0.05	38.5	46.2
	0.05-0.1	15.4	7.7
	>0.1	7.7	15.4
Number of Fish Servings per Week	0	57.1	13.3
	<0.5	10.8	26.7
	0.5 - <1	7.2	26.7
	1 - 2	7.2	15.4
	>2	10.8	7.7

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Chapter 4

Biomarkers of Chemical Exposure and Self-Reported Health at the Aamjiwnaang First Nation

4.1 Introduction

The Aamjiwnaang First Nation, a Chippewa Tribe, is located within the region known as Canada's "Chemical Valley." Within a 25km radius of the Aamjiwnaang Reserve exists 58 petrochemical, chemical, and other industrial facilities (U.S. EPA, 2011; Environment Canada, 2010). Industries within the Chemical Valley region are known to release multiple classes of chemicals into the environment at varying concentrations, as determined from an analysis of data from the U.S. Toxics Release Inventory (TRI) and Canada's National Pollutant Release Inventory (NPRI) (Macdonald and rang, 2005; Cryderman *et al.*, Chapter 3). In studies on other dense industrial regions, metals such as vanadium, arsenic, and chromium have been demonstrated to be released into the atmosphere from petrochemical refineries (Hope, 1997). In such industrial zones others have also reported the release of a variety of polychlorinated biphenyls (PCBs), persistent organic compounds (POPs), and polycyclic aromatic hydrocarbons (PAHs) (Tsai *et al.,* 1995; Cetin *et al.,* 2003; Lin *et al.,* 2001).

The Aamjiwnaang have been actively requesting research regarding chemical exposures and potential health outcomes to be performed on the Reserve since the

1970's. Despite the potential for high exposures, little biomarker work has been performed in the area. A recent study on mercury contamination in the region has documented generally low levels in humans, but that hotspots do exist on Reserve (Cryderman *et al.*, Chapter 3). Only one other exposure assessment study has been performed in the region even though potentially many more chemicals are released in the region, though this study included only three participants (Environmental Defense, 2007). The aims of the current study are 4-fold: 1) to assess the exposures of individuals living on-Reserve to multiple chemicals across a variety of classes; 2) to make a comparison of exposures on-Reserve to the general population; 3) to determine if exposure to metals in on-Reserve participants show different trends than in off-Reserve participants; and 4) to characterize self-reported health outcomes of individuals residing on and off-Reserve.

4.2 Methods

4.2.1 Human Subject Interactions and Sample Collection

Human subject approval was gained from the University of Michigan Institutional Review Board (IRB: HUM00029363). Mother-child (children ages 4-14 years) pairs were recruited from the Aamjiwnaang First Nation Reserve and surrounding areas (n=43). Recruitment was performed via multiple methods including word-of-mouth, flyers, mailings, and newspaper ads. The study used a participatory based research design with the Aamjiwnaang First Nation Health an Environment Committee, and the Lambton County Health Department provided consultation. Prior to participating, each mother provided consent for herself and her child, and children provided assent to participate.

From each mother and child biological samples were collected. A licensed phlebotomist collected blood via venipuncture into trace metal and serum collection tubes

(BD Vacutainer). Urine was collected into pre-rinsed plastic cups for metals analysis (BD Vacutainer). Samples were frozen at the Aamjiwnaang First Nation Health Center in a secured freezer until shipment to the University of Michigan

4.2.2 Laboratory Analyses-metals

Metals were detected using an Inductively Coupled Plasma-High Resolution Mass Spectrometer (ICP-HRMS; Element2, Thermo Scientific) following methods we have previously described with some modifications outlined below (Basu *et al.,* 2010; 2011). All glassware and plastic ware were acid-rinsed prior to use. Samples were prepared in a class 100 and 1000 clean room. Here, blood copper, lead and manganese concentration are characterized in participants from on-Reserve (n= 24 mothers, 18 children) and off-Reserve (n=15 mothers, 12 children). 500µL of blood sample was combined with 1 mL of concentrate nitric acid (Optima grade, Fisher Scientific) and allowed to digest overnight. To these digests, 500 µL super pure hydrogen peroxide (Suprapur grade, Sigma –Aldrich) was added. 1 mL of final digest was then diluted 4-fold with milli-Q water (>18 megohm/cm resistivity) prior to ICPMS analysis. For urine, 1mL of sample was added to 1 mL concentrate optima nitric acid for overnight digestion and diluted 10-fold to a final acid concentration of <5% prior to ICPMS analysis. Concentrations of antimony, arsenic, cadmium, molybdenum, uranium, and vanadium in urine are reported for participants from on-Reserve (n=26 mothers, 24 children) and off-Reserve (n=17 mothers, 17 children). Urine samples were analyzed for specific gravity content using a pocket refractometer (PAL-10S, ATAGO, Tokyo, Japan).

All samples were batch processed according to sample type at the University of Michigan's Earth and Environmental Sciences department. The ICP-HRMS was auto-

tuned to achieve optimal sensitivity (~1.2Mcps/ppb In) and resolution (>300, >4000, >8000). Sample uptake was via peristaltic pump at ~0.3mL/min. An internal standard (5ppb In) was added at 0.05 mL/min prior to entering the MicroMist nebulizer and Scott double-pass spray-chamber. ~1.2L/min sample gas Ar, 80mL/min P10 gas was added after the spray chamber. Carrier Ar was added at 1L/min and coolant Ar set at 16L/min.

Precision and accuracy were measured using certified reference materials that included U.S. National Institute of Standards and Technology (NIST) trace elements in water (1640a), the Institut national de santé publique du Québec (INSPQ) blood (QMEQAS09), and INSPQ urine (QMEQB2). For each metal, a detection limit was calculated as 3 times the standard deviations of the blank values added to blank averages (Table 4.1). Samples for which the concentration was below the detection limit were given a value of one-half the detection limit (U.S. EPA, 2000). Across all metals reported, average recovery rates (accuracy) ranged from 71.59-93.59% in blood and 82.66-111.43% in urine. Additionally, each batch contained procedural blanks and replicates. Average relative standard deviation (precision) ranged from 1.19-6.83% in blood metals and 1.19-4.11% in urinary metals.

4.2.3 Laboratory Analysis-perfluorinated compounds

Blood serum was collected from on-Reserve participants (n=12 mothers, 22 children) for analysis of 13 Perfluorinated compounds (Table 4.1). Blood was spun and serum decanted into amber glass vials. Samples were stored in a secured freezer on site until shipment to AXYS Analytical (Sydney, BC, Canada). Extraction and analysis methods have been described elsewhere (Frisbee *et al.,* 2009). In short, extraction was performed by adding 3mL formic acid to approximately 0.5mL blood serum followed by centrifugation. The supernatant was cleaned via solid phase extraction column

chromatography. The eluate was spiked and analyzed via high performance liquid chromatography mass spectrometry. Retention times ranged from 5-10 minutes. The congeners screened for are listed in Table 4.1.

Samples were batch analyzed. Systematic quality control protocols were followed during perfluorinated compound analysis such that analytical blanks, ^{13}C-labelled standards, and duplicates were analyzed at 5% frequency of samples. Detection limits for all compounds ranged from 0.5 – 1.0 ng/mL (Table 4.1). Samples for which concentrations were below detection limits are reported here as ½ the square-root of the detection limit. Average recovery rates for perfluorinated compounds ranged from 93.8-122%.

4.2.4 Laboratory Analysis-semi-volatile compounds and persistent organic pollutants

Semi-volatile organic compounds and persistent organic compounds (polycyclic aromatic hydrocarbons, organochlorine pesticides, and polychlorinated biphenyls, and polybrominated flame retardants) were analyzed in whole blood collected from on-Reserve participants (n=23 mothers, 19 children). Fifteen polycyclic aromatic hydrocarbons (PAHs) were analyzed, 21 organochlorine pesticides (OCPs), 81 polychlorinated biphenyls (PCBs) and 22 polybrominated diphenyl ethers (PBDEs) (Table 4.1).

Extraction and analysis of these chemicals has been previously outlined (Batterman *et al.*, 2007). In short, 1mL of whole blood was spiked with labeled standard. The solution was next extracted with 500 µL of a mixture of formic acid and acetone and 2mL of hexane-DCM prior to vortexing, sonication, and centrifugation. Organic layers were run through a Florisil column and analyzed on a gas chromatography-mass spectrometer (Agilent, Palo Alto, CA). Method detection limits were determined at 3

times the signal/noise ratio (Table 4.1). Average detection limits and relative precision for polycyclic aromatic hydrocarbons ranged from 0.005-0.087 µg/L and 6.3-56.2% respectively. Detection limits for organochlorine pesticides, polychlorinated biphenyls, and polybrominated biphenyl ethers ranged between 0.003-0.092 µg/L, 0.001-0.65 µg/L, and 0.005-0.068 µg/L, respectively. Precision ranged between 14.4-25.5% for organochlorine pesticides, 4.9-25.0% for PCBs, and 15.0-20.5% for PBDEs. Average participant lipid content was analyzed in order to adjust all SVOC and organic chemical concentrations. Lipid-adjusted whole blood values are reported and are compared to lipid adjusted serum concentrations from national surveys. Lipid-adjusted whole blood and serum concentrations of persistent organic chemicals have previously been shown to be comparable (Jotaki *et al.,* 2011; Schecter *et al.,* 2005).

4.2.5 Participant Survey

Written and oral surveys were conducted with mothers to increase understanding of possible determinants of exposure and self-reported health. Self-reported written surveys addressed diet, work history, tobacco and alcohol use, past and present maternal occupation, housing conditions, past and present known exposure history, as well as demographic information for each mother and child. In addition, oral interviews were conducted with each mother in order to gain data on number and outcome of mothers' pregnancies, complications during pregnancy and labor of participating child, mothers' and children's past and present medication use, and children's health history.

The survey was also used to understand exposure pathways. The leading source of lead exposure, particularly in North American children, is consumption of lead-based paint often found in older homes (ATSDR, 2007b). In order to address such lead exposures within study paint, age of the home and peeling paint present on participants'

properties were investigated. Mothers' smoking status was examined as a possible exposure sources for multiple metals such as arsenic and cadmium (Health Canada, 2010). A main exposure route of PFCs, PFCs, DDT, and PCBs is fish consumption, particularly in adults (Haug *et al.*, 2010; Health Canada, 2010; ATSDR, 2000). The presence of a wood stove or fireplace in the home, mothers' smoking status, and proximity to a major roadway were explored as exposure routes of PAHs (ATSDR, 1995).

Residential addresses were recorded and mapped on Google Earth (Version 5.1.3533.1731, Mountain View, CA) in order to identify on and off-Reserve participants (Figure 4.1). In order to investigate potential exposures through local releases, on-Reserve members were grouped into two clusters, east and west. Comparisons between biomarker levels for these two groups were made for both mothers and children.

4.2.5 Source Investigation

Local releases of multiple chemicals were investigated. Canada's National Pollutant Release Inventory (NPRI; Environment Canada 2011) and the U.S. Toxics Release Inventory (TRI; U.S. EPA, 2012) were quarried to identify current sources of metals and PAHs using a similar method to that previously described (Cryderman *et al.*, Chapter 3). PFCs, PCB, PBDE, and organochlorine pesticide releases were not investigated either because they are no longer used or produced in either country, or because their releases are not reported to the NPRI or TRI.

4.2.6 Statistical Analyses

Of primary interest, descriptive statistics are used to characterize chemical biomarkers in children and mothers living on-Reserve. Comparisons of metal biomarker concentrations between mothers and children living on and off Reserve are made using t-

tests. Biomarker values are also compared to reference populations as described in the paper. All statistics were performed using SPSS 20.0 software. Biomarker data were not normally distributed and transformations did not achieve normality. As such, all comparisons were made using non-parametric tests, such as Kruskal-Wallis, Mann Whitney, and Spearman on the untransformed data.

4.3 Results and Discussion

Although it is known that the "Chemical Valley" region is an area with several pollutant sources, there has not been an extensive biomarker study investigating human exposures to multiple contaminants. This study is the first in the region to characterize human exposures to metals, PFCs, PAHs, organochlorine pesticides, PCBs, and PBDEs. The study also aimed to identify key health outcomes of concern, as self-reported by participants.

4.3.1 Metals

Lead, manganese, and copper were detected in every participant's blood sample (Table 4.1). The mean levels and ranges of these three metals in children's blood were similar to values measured in children aged 6-11 from the Canadian Health Measures Survey (Table 4.2) (Health Canada, 2010). Likewise, levels of these metals in Aamjiwnaang mothers' blood samples were similar to women across Canada.

Urine samples were used to measure seven metals. In children, there were no samples below detection limits for arsenic, cadmium, and molybdenum. Antimony, cobalt, uranium, and vanadium levels were below detection limits in some samples (Table 4.1). In mothers, all samples were above detection limits for arsenic and molybdenum, with other metals having samples below detection.

Metal biomarkers of on-Reserve participants were compared by geographical cluster (i.e., participants residing on the east or west side of the Reserve; Figure 4.1) though no differences were found. Metal biomarkers were also compared between on and off-Reserve participants. In mothers, there were no observed difference in metal concentrations in blood and urine between on and off-Reserve participants. For children, besides urinary vanadium, no differences were found. For example, blood lead concentrations between on (9.39 ± 8.32 µg/L) and off-Reserve (9.84 ± 10.88 µg/L) children were similar (Figure 4.2). Urine vanadium concentrations among on-Reserve children (0.2 ± 0.19 µg/L) were 2-fold higher than those among off-Reserve children (0.11 ± 0.06 µg/L), a difference which remained significant even after adjustment for specific gravity (p=0.019). The children residing off-Reserve span a larger geographical area, and their homes are located further away from industry than on-Reserve children. Vanadium is used as a petrochemical cracking catalyst and is recycled from spent catalysts and residues in petrochemical productions (Moskalyk and Alfantazi, 2003). Little is known about human exposures to vanadium in relation to residing near petrochemical industries, though a study of soil and chard near such a site in Spain showed vanadium concentrations higher than control sites (Nadal *et al.,* 2004). Though, it should be noted that several vanadium measurements were below detection limits.

The distribution of urinary antimony among Aamjiwnaang children was significantly higher than the national average for children across Canada (p=0.002; Table 4.2). Aamjiwnaang mothers showed a general trend of elevation compared to the nation, though this was not statistically significant. For molybdenum, urinary concentrations in children were approximately 2-fold higher than those seen nationally, though

concentrations were within range; mother's concentrations were similar to national distributions. Antimony and molybdenum are both ubiquitous metals, with main exposure pathways being food and drinking water. It is feasible that elevated levels of these metals are present within "Chemical Valley", as they are both used in the petrochemical industry. Antimony is often used in the petrochemical industry, in the form of antimony trioxide, as a flame retardant for foam products (ATSDR, 1992; Dow Chemical Canada Inc., 2004). Molybdenum is used as a catalyst in many petrochemical processes, and it has also been associated with male reproductive adversities (Kar *et al.*, 2004; Meeker *et al.*, 2010).

Urinary cadmium concentrations in Aamjiwnaang children were approximately three-times greater those seen across Canada, while in Aamjiwnaang mothers they were about two-times that seen in Canadian women (Table 4.2). The leading exposure route of cadmium is through smoking and second-hand smoke (ATSDR, 2012), though in the current study there was no difference in mean cadmium levels between smoking and non-smoking families. However this may be linked to elevated cadmium levels in participants as a high percentage (approximately 75%) of mothers reported smoking, potentially masking effects of smoking in this study. Additionally, we did not attempt to estimate secondhand smoke exposures via other residents in the household. Though cadmium exposures among study participants are elevated compared to the national average ($p<0.001$ children, $p=0.003$ mothers;),urine concentrations are well below health benchmark levels set by the American Conference of Governmental Industrial Hygienists (5 µg/L; ATSDR, 2012).

Releases of lead, manganese, copper, arsenic, cadmium, and vanadium were all reported among the "Chemical Valley" area (Table 4.3). In addition, environmental media have previously been noted to concern elevated levels cadmium, chromium, lead, arsenic, and aluminum (Golder Associates Ltd, 2004; CWAIGG, 2005, Atkinson Davies, 2005). A previous study (n=3) demonstrated that exposures to metals do exist on Aamjiwnaang. Distributions of lead (5.4-6.9 µg/L) and manganese (6.5-16.48 µg/L) were similar in blood collected from these three participants to the current study (Environmental Defense, 2005). Presence of arsenic and cadmium in the blood of participants of the Environmental Defense study reinforces that metals exposures may be of concern.

In children's blood, none of the metal biomarkers correlated with each other (Table 4.4). In mothers, the only correlation of statistical significance was blood manganese with blood copper (r_s= 0.464, p=0.003). Within urine, there were a number of significant correlations in both children and mothers.

When comparing mean levels of metals in whole blood between mothers and children, no differences were observed. Differences were found in the urine. For example, urinary arsenic was two times larger in the children (15.94 ± 35.42 µg/L) versus mothers (6.06 ± 6.50 µg/L; p=0.027) (Table 4.2). Likewise, mothers and children showed differing concentrations of molybdenum (p=0.001), with values higher in children (117.29 ± 66.59 µg/L) than in mothers (61.82 ± 36.33). These differences remained significant after concentrations were adjusted for specific gravity.

Children's age was found to be negatively correlated with blood copper (r_s=-0.372, p=0.047). In mothers, urinary molybdenum concentrations were negatively

associated with age (r_s= -0.403, p=0.014). Age was not associated with any other metal biomarker in urine or blood among mothers or children. A significant difference was found between male and female children's concentrations of blood manganese (p=0.035). Differences between genders were not seen in any other metal biomarker in blood or urine.

4.3.2 Perfluorinated Compounds

PFCs are synthetic organic compounds used in a variety of industrial processes, and thus may be found in "Chemical Valley" (Kissa, 2001). PFCs, particularly PFOS and PFOA have been associated with carcinogenicity and adverse developmental outcomes in animal models (Trudel *et al.,* 2008).

In the current study, 13 PFCs were analyzed in serum. Nine of these PFCs were also measured in children (aged 12-19) and adult females across the U.S. (CDC, 2012) thus providing us with a basis for comparison. Among the Aamjiwnaang participants, concentrations of PFBS, PFDoA, and PFOSA were below detection for mothers and children (Table 4.1), as were those measured nationally across the U.S. PFUnA was measurable in Aamjiwnaang children (0.99 ± 0.17 ng/mL), but were below detection limits in all mothers (<0.5 ng/ml). In general, only PFDA in Aamjiwnaang mothers was above mean values seen in women across the nation (Table 4.3, Table 4.5; CDC, 2012). PFOA (3.19 ± 1.59 ng/mL) concentrations in children ranged slightly above those but within a similar range as those seen across the in the U.S. Children's serum concentrations of PFNA and PFDA were significantly higher than the national average (p<0.001, p<0.001 respectively). PFUnA values were above those seen in the U.S. in children by nearly 2-fold, though the national average was not reported due to the large

percent of samples below detection (CDC, 2012). . Our finding of elevated concentrations of PFCs among Aamjiwnaang members is consistent with a previous pilot study performed on one Aamjiwnaang family, in which total PFCs were found to be higher than other families in Ontario (23.49-86.93 μg/L serum; Environmental Defense, 2007).

In children, but not mothers, several of the PFCs were correlated (Table 4.6). When comparing values between mothers and children, there were no significant correlations. Though, PFNA in children's serum (3.48 ± 2.65 μg/L) was considerably higher than that in mothers' (1.05 ± 0.29 μg/L) ($p<0.001$). Differential exposures among children and adults have been suggested in the past, where children have shown higher biomarker levels of multiple PFCs (Calafat *et al.,* 2007; Kato *et al.,* 2009).

In children, no difference between boys and girls were seen for any PFC analyzed. However, the age of the child was found to be negatively correlated with PFOA (r_s=-0.505, p=0.016) and PFNA (r_s=-0.491, p=0.034). No other PFC compounds were found to be correlated with children's age. A positive relationship was seen between mothers' age and PFOS (r_s=0.589, p=0.034) and PFOA (r_s=-0.678, p=0.011). No other PFCs were found to be correlated with mothers' age. No relationships were found among reported weekly fish consumption and biomarker concentrations of any PFC in mothers or children. When grouped by geographical cluster, no differences were seen in PFC levels in mothers or children. PFCs are not reported to the Toxics Release Inventory or the National Pollutant Release Inventory, and thus local source information was not attained (Environment Canada, 2011; U.S. EPA, 2012).

4.3.3 Semi-Volatile Compounds and Persistent Organic Pollutants

Many studies measure persistent organic pollutants on a lipid-normalized basis in plasma or serum, rather than whole blood which was analyzed here. Nonetheless, lipid-adjusted whole blood and serum concentrations of persistent organics have previously been shown to be comparable (Jotaki *et al.*, 2011; Schecter *et al.*, 2005) and thus we report our data on a lipid and non-lipid adjusted basis. In Aamjiwnaang children, the average lipid content was measured to be 0.75% in whole blood, while in mothers it was 1.1%. Here we provide data on a non-lipid adjusted basis but provide lipid-adjusted PAHs and whole blood OCP, PCB, and PBDE distributions in (Table 4.15).

4.3.3.1 Polycyclic Aromatic Hydrocarbons

PAHs are released as by-products produced during the burning of biomass, coal, and oil, among others. These releases, along with emissions from smoking and barbecuing foods, serve as main exposure pathways for PAHs to enter the human body (CDC, 2009). Exposures to PAHs have been linked to effects of the immune system, and neurodevelopment, and are listed as possible carcinogens. Locally at Aamjiwnaang, PAH contamination of Talfourd Creek, a stream which runs through the Reserve, has been documented (CWAIGG, 2005). Total PAHs were measured in urine of Aamjiwnaang members (0.27-0.50 µg/L), though in only 3 individuals (Environmental Defense, 2005).

Few studies have measured levels of PAHs in whole blood, thus it was not possible to compare findings of Aamjiwnaang participants to national or provincial distributions. Among Aamjiwnaang children and mothers, no samples were above detection limits for indeno [1,2,3-c,d] pyrene, dibenzo [a,h] anthracene, or benzo [g,h,i] perylene (Table 4.1). All children's (90.81 ± 75.55 µg/g lipid) and mothers' (30.49 ±

39.14 µg/g lipid) samples were above detection for naphthalene (Table 4.15). Non-adjusted whole blood concentrations of PAHs in pregnant women living in an impoverished area on the U.S.-Mexican border were analyzed between 2005 and 2006 (Sexton *et al.*, 2011). Mothers residing on Aamjiwnaang showed slightly lower blood levels of naphthalene, phenanthrene, fluoranthene, and pyrene than mothers from this study in Texas (Table 4.7). Acenaphthalene and anthracene values averaged a little higher at Aamjiwnaang than in Texas.

There were multiple correlations among blood PAH levels in mothers and children (Table 4.8), though between mothers and children no correlations were found. When comparing concentrations of anthracene between mothers (0.04 ± 0.05 µg/L) children (0.07 ± 0.05 µg/L), a significant difference was found (p=0.010) but not for any other PAH. In children, there were no differences found between boys and girls for any PAH biomarker level. Association between age and PAH biomarkers were investigated for both children and mothers. In children, benzo[a]fluoranthrene was found to have a positive relationship (r_s=0.530, p=0.020). Age was not associated with any other PAH level.

Smoking and residential wood burning are known exposure routes of PAHs (ATSDR, 1995). Children whose mothers smoked were found to have higher concentrations of lipid-adjusted anthracene levels (10.94 ± 7.13 ng/g lipid) than children whose mothers did not smoke (3.40 ± 2.1 ng/g lipid; p=0.014). Smoking was not associated with any other PAH biomarker in mothers or children, though 75% of all mothers in the study reported smoking. There were no observed differences in blood PAH concentrations, among participants residing in homes reported to have a woodstove

or fireplace against those who did not report to have these items in the home, though only small percentage of participants lived in such a home (5%). Distance of the residence from a major roadway was not found to be associated with PAH biomarker levels. Disproportionate sample size may mask statistically significant differences between biomarker levels of participants reporting to smoke or reside in a residence that may cause increased PAH exposure and those participants whom did not report these exposure routes. However, it is likely that main exposure routes include ambient air contamination, such as traffic exhaust, and tobacco smoke (ATSDR, 2009). The major congeners present among Aamjiwnaang children and mothers have been reported to be released within "Chemical Valley" (Table 4.3). Interestingly, those PAH congeners that were reported to be released in higher amounts (e.g., acenaphthene, acenaphthylene, phenanthrene, and naphthalene) were also found to be present in higher concentrations in Aamjiwnaang participants. When grouped by residence location on-Reserve, no differences were seen in any PAH biomarker in mothers or children. With many exposure routes of PAHs, it's difficult to identify a single source of exposure.

4.3.3.2 Organochlorine pesticides

A variety (n=21) of OCPs was measured in Aamjiwnaang mothers and children. Of these, four were found at detectable levels in whole blood (ppDDT, ppDDE, HCH, and HCB). DDT and HCB are legacy pesticides and are no longer manufactured or in use in the U.S. or Canada, but remain in the environment and food sources, particularly fish, due to their persistence. The use of HCH has been restricted to the treatment of lice and scabies (Health Canada, 2010). Potential health effects of chronic low-dose exposures range from liver, kidney, and autoimmune disease, adverse neurobehavioral and

developmental outcomes, and cancers (ATSDR, 2002). Contamination of Aamjiwnaang and the surrounding area has been documented. Fish muscle sampled from the St. Clair River was found to have potentially hazardous concentrations of DDT and HCB (Gewurtz *et al.,* 2010). Within the Reserve, a local pond was found to have levels of DDT, DDE, and HCH harmful to human cell lines (CWAIGG, 2005).

Lipid-adjusted whole blood concentrations of ppDDT among Aamjiwnaang mothers (21.67 ± 18.46 ng/g lipid) were higher than lipid-adjusted levels in plasma of Canadian women, which were below the detection limit (0.05 ng/mL) (Table 4.9; Health Canada, 2010). ppDDT concentrations in Aamjiwnaang mothers were also above those seen in serum of U.S. women (50^{th} percentile: <LOD, 90^{th} percentile: 14.0 ng/g lipid; CDC, 2009). Total HCH (αβγ-HCH) was measured in Aamjiwnaang participants. When compared to national distributions of β-HCH, total HCH concentrations in Aamjiwnaang mothers' blood had a higher distribution (Health Canada, 2010). This trend, however, was not seen in comparing Aamjiwnaang mothers to the lipid-adjusted serum HCH of US women (CDC, 2009). Concentrations of HCB in Aamjiwnaang mothers were observed to be distributed at lower concentrations than women across Canada. In comparison to other First Nations women residing in Ontario concentrations of ppDDE and HCB among the Aamjiwnaang mothers were quite low. ppDDT concentrations among Aamjiwnaang women were slightly higher than those seen in other First Nations women (2.0 – 54.5 ng/g lipid; Tsuji *et al.,* 2006). In children, similar trends were seen in that Aamjiwnaang participants had higher distributions of ppDDT (29.40 ± 19.14 ng/g lipid) and HCH (8.91 ± 2.48 ng/g lipid) than seen across the US, but were comparable in concentrations of HCB and ppDDE (CDC, 2009). Organochlorine pesticides were not measured nationally

in Canadians less than 20 years of age, and thus a comparison could not be made. Organochlorine pesticides have previously been suggested to be higher in Aamjiwnaang members than other families across Ontario (0.15 – 1.91 total pesticide µg/L plasma), though the sample size of this study was quite low (n=3, Environmental Defense, 2005).

Associations between biomarker concentrations of OCPs within children and mothers were explored. In children, HCH and HCB were positively correlated (r_s=0.692, p=0.001; Table 4.10). The same relationship was also found among mothers (r_s=0.776, p<0.001). No other correlations were found among OCPs. When comparing concentrations of OCPs between mothers and children, HCH (p=0.017) was found to be different with values higher in children. No other differences between mothers and children were found to be significant. No correlations between concentrations of these chemicals in mothers and children were found. There were no differences found between boys and girls for any of the OCPs. In children, age was not correlated to concentrations of any of these chemicals in blood. Likewise, age was not correlated to concentrations of OCP biomarkers in mothers. Fish consumption, the main current exposure route, was not associated with levels of any OCP in mothers or children. No differences were seen between clusters of residency on Reserve. Since these chemicals are considered mostly legacy chemicals in the U.S. and Canada, releases within "Chemical Valley" were not investigated.

4.3.3.3 Polychlorinated Biphenyls

PCBs are synthetic organic compounds present in mixtures, and they are used for a variety of industrial purposes (ATSDR, 2000). They were manufactured in the U.S. prior to 1979 but have never been manufactured in Canada (CCME, 2001). Animal

studies have shown multiple systems effects when exposure to mixtures of PCBs, and the class of chemicals is monitored under Canada's Toxic Substance Management Policy (WHO, 2000; Environment Canada, 1997).

Of the 81 congeners of PCBs tested for, only 5 congeners (118, 126, 180, 138, and 153) were present in measurable concentrations among Aamjiwnaang mothers and children (Table 4.1). There is little data reported on the distributions of children's PCB concentrations across Canada. However, PCB congeners 180 (20.9 ± 8.0 ng/g lipid), 138 (14.1 ± 6.4 ng/g lipid), 118 (13.6 ± 7.6 ng/g lipid), and 135 (11.2 ± 5.8 ng/g lipid) all ranged 3 to 7-fold higher than those seen in children across the U.S. (Table 4.11; CDC, 2009) and were significantly higher than the national average (Table 4.3). In mothers, PCB 126, 180, 153, and 118 also ranged significantly higher than the average seen across Canadian women (Table 4.3, Table 4.11; Health Canada, 2011). Few studies have measured PCB exposures in First Nations populations. Biomarker concentrations in Aamjiwnaang women were lower than other adult First Nations women in polluted regions of northern Ontario for PCB 118 (1.7-194 ng/g lipid), PCB 138 (4.0-478.4 ng/g lipid), PCB 153 (5.7-909.0 ng/g lipid), and PCB 180 (2.2-857.9 ng/g lipid) (Tsuji *et al.*, 2006). Our findings of elevated PCB exposures among Aamjiwnaang residences is further strengthened by a previous study (n=3), which showed that PCB biomarker levers in one Aamjiwnaang family was higher than those found in other families across Ontario (Environmental Defense, 2007).

Relationships between concentrations of blood PCB levels were investigated. Many positive correlations were found among mothers and children (Table 4.12). However, no associations were found between mothers and children. In fact, when

comparing concentrations between mothers and children, significant differences were found in congeners 138 ($p<0.001$), 180 ($p<0.001$), 118 ($p=0.012$), and 153 ($p=0.008$), with values higher in children. This differentiation between mothers' and children's exposure is not surprising, as it has been established that children are often more susceptible to exposures to a variety of contaminants for multiple reasons (e.g. increased inhalation and food and water intake per pound, hand-to-mouth behaviors, and metabolic processes; Landrigan *et al*., 2004; Bearer, 1995). When comparing boys to girls, no differences were found of any PCB biomarker. Child's age was not associated with any PCB concentration. In mothers, however, age was associated with PCB 180 ($r_s=0.468$, $p=0.033$) and PCB 138 ($r_s=0.596$, $p=0.004$).

A primary exposure route of PCBs is through fish consumption. Here, there were no correlations found between number of fish portions per week and PCB biomarker concentration in mothers or children. The St. Clair River is known to contain contaminated fish stocks. Though fish muscle PCB concentrations have decreased in recent decades, such levels in larger predatory fish may still be of potential health concern for consumers (Gewurtz, *et al.,* 2010). Though fish is a source of nutrients such as polyunsaturated fatty acids and fishing is historically a cultural tradition among Ojibwe peoples, participants on the Aamjiwnaang Reserve reported to consume little to no fish (Mzaffarian *et al.,* 2006; Cryderman *et al.*, Chapter 3). Therefore, even though potential exposures through fish consumption exist, this is not likely the main source of exposures among Aamjiwnaang children. Additional exposure routes may include other contaminated food sources and inhalation of contaminated air, which often occurs through leakage of PCBs from outdated household appliances (ATSDR, 2000).

Additionally, though releases of PCBs among "Chemical Valley" is not documented, increased air concentrations of these chemicals have been found near petrochemical facilities in South Korea (Beak *et al.*, 2008). The recent data from fish samples (Gewurtz *et al.*, 2010), and documented evidence of PCB contamination along Talfourd Creek (Leadley and Haffner, 1996), which flows through the Reserve, can be combined with this initial assessment of human PCB exposure to conclude that these chemicals remain a concern in the region. We found that, in children, PCB 180 was different between residents of different on-Reserve clusters ($p=0.011$) with children living towards the west (25.34 ± 7.64 ng/g lipid) being higher than those on the east (17.33 ± 3.19 ng/g lipid). A difference was also found for PCB 118 in mothers ($p=0.046$), as west (9.55 ± 3.19 ng/g lipid) was higher than east (7.37 ± 1.90 ng/g lipid). These differences were not seen in other PCBs.

4.3.3.4 Polybrominated Biphenyl Ethers

PBDEs are used as flame retardants and are listed under the Canadian Environmental Protection act (Health Canada, 2010). The compounds have not been manufactured in Canada, but are imported for use as products or polymers for further processing. Congeners of PBDEs have been associated with health risks including neurobehavioral effects and possible carcinogenicity (Health Canada, 2006). Exposures to total PBDEs in three Aamjiwnaang members (0.12-0.94 µg/L) have been documented previously but were similar to those seen elsewhere in Ontario (Environmental Defense, 2005).

Of the 22 PBDEs tested for, congeners 47, 99, 100, 153, and 209 were measurable in Aamjiwnaang mothers and children. PBDE 47 in Aamjiwnaang women (0.9 ± 0.5 ng/g

lipid) ranged well below those seen across Canadian women (Table 4.3, Table 4.13; Health Canada, 2010). Similarly, there were no other PBDEs for which Aamjiwnaang women were more highly exposed than the general population. PBDE biomarkers suggest lower exposures among Aamjiwnaang woman than subsistence First Nations individuals residing across Canada (means for PBDE 100, 153, 47, and 99 were 2.7, 2.67, 15.00, and 2.03 ng/g lipid, respectively; Liberda, *et al.*,2011). Fewer data has been reported characterizing the distribution of PBDEs in children across Canada. However, the distribution of PBDEs among Aamjiwnaang children was observed to be much lower than 12-19 year old children in the general U.S. population (Table 13; CDC, 2009). For example, the average concentration of PBDE 153 among Aamjiwnaang children (2.9 ± 5.8 ng/g lipid) was nearly 10-fold lower than those seen in the U.S.

Relationships among concentrations of PBDE biomarkers were explored in both mothers and children. A variety of positive associations were found (Table 4.14). This is not surprising, as PBDEs are often present in the environment as mixtures, and concurrent exposures to individual congeners is likely (ATSDR, 2004). Associations between mothers and children were also found for PBDE 100 (r_s=0.545, p=0.029) and PBDE 153 (r_s=0.683, p=0.004). However, children were found to have higher concentrations of PBDE 99 (p<0.001), 100 (p<0.001), 153 (p<0.001) and PBDE 209 (p<0.001) than mothers, suggesting different exposure routes or metabolic processes. Age was not found to be a factor in biomarker concentrations of PBDEs in children, and was only associated with PBDE 47 (r_s=0.571, p=0.004) in mothers. Location of the home showed no differences among PBDE levels in mothers or children.

Fish consumption, along with contaminated house dusts, is known to be a major exposure route to PBDEs (Health Canada, 2002). No correlations between any measured PBDE biomarker concentration and number of fish serving per week were found in mothers or children. Although elevated air concentrations of PBDEs have been reported near petrochemical industry have been reported in South Korea (Beak, *et al.,* 2008), releases of this class of chemicals are not reported to government databases and were therefore not investigated in this study.

4.3.3.5 Survey and Questionnaire Data

The survey was intended to characterize the broad dietary and living habits of both on and off-Reserve participants. The questionnaire collected data on consumption of locally grown produce, wild game, and fish. The survey was designed to allow the participant to choose the portion size consumed per meal and list the number of times that portion size of multiple fish species were consumed within one month. Dietary results of this study are described elsewhere (Cryderman *et al.,* Chapter 3). Briefly, there were significantly more mothers living off-Reserve that reported consuming local produce and game, and off-Reserve children reported eating more fish meals in the past month than did on-Reserve children (Cryderman *et al.,* Chapter 3).

The written survey also addressed self-reported health information. The health portion of the survey was designed to capture self-reported assessments of general health. While it is limited in a number of ways, the data may help identify future areas of research and current health concerns. Mothers reported a binary "yes" or "no" response to each health outcome, for herself was well as for her child. When outcomes were compared between on and off-Reserve participants, in general no differences were found. Of the professed health outcomes, asthma and skin irritation among children were most

pronounced (Table 4.16). In general, children living on and off-Reserve were reported to have similar prevalence of asthma, which were approximately 2-fold higher than the Canadian national prevalence in children (13%; Garner and Kohen, 2008). While associations between health outcomes and exposures in this study were not seen, they have been found at increased rates in similar industrial petrochemical centers (Wichmann *et al.,* 2009; Yang *et al.,* 1998). Additionally, secondhand smoke within the household has been linked to childhood asthma prevalence (Vork *et al.,* 2007). It is emphasized here that general, self-reported health outcomes were not verified by clinical tests or physician-diagnosed assessments.

Mothers were asked to report on housing conditions and storage of chemicals and other agents, which can be an exposure route for many chemicals. Of all participants, 74% reported not having a garage, while 21% had a garage and 5% had a carport. A garage or shed was used as outdoor storage among 52% of participants, while 5% used an overhang, 30% reported to outdoor storage, and 11% reported using other types of outdoor storage spaces. Chemicals which were reported to be stored in outdoor spaces include gasoline, ammonia, pesticides, paint, woodworking supplies, and lawnmower supplies. Similar chemicals were reported to be stored in homes as in outdoors shed, with the most frequent being ammonia and paints. Ages of homes ranged between 11 and 122 years. Five percent of mothers in the study reported to have a woodstove or fireplace in the home. Mothers were asked to describe the distance of the home from a major roadway (paved road with considerable traffic), of which 2.5% reported living directly adjacent to such a roadway, 67.5% reported living one to four blocks away, and 22.5% reported living greater than four blocks from such a roadway. Among mothers, 50%

reported the presence of peeling paint on the property. Pesticide treatment was reported among 65.9% of mothers.

4.4 Conclusion

The study was designed in collaboration with the Aamjiwnaang First Nation's Health and Environment Committee to serve as a baseline investigation of chemical exposures and general health of Reserve members. Though multiple recruiting efforts were made, the small number of participating mother-child pairs may not be representative of Tribal members at large, especially adult men. This cross-sectional study captures only a snapshot of current exposures, possibly excluding windows of susceptibility and not addressing latency periods for any exposure-health outcome associations. We were also not able to compare each biomarker (e.g. PAHs) directly to reference populations, as these data are not largely present in the literature (Sexton *et al.,* 2011). Nonetheless, a wide array of biomarkers was collected to measure multiple chemicals, to more holistically assess chemical exposures in a highly industrialized area.

The study demonstrates that Aamjiwnaang members are exposed to a large number of chemicals. The findings suggest that cadmium, antimony, molybdenum, vanadium, PFCs, DDT, HCH, and PCBs are of elevated exposures among residents of Aamjiwnaang. Little is known about real-world exposure to multiple chemicals, especially in children (Carpenter *et al.,* 1998; Grandjean and Landrigan, 2006; Landrigan *et al.,* 2004). Further investigation into these chemicals should be performed, and should include those groups that were not recruited in this study but whom may be susceptible to exposure through cultural activities (Donatuto and Harper, 2008). Major releases of volatile organic compounds have been documented within this region (Miller *et al.,* 2009)

but were not investigated in this study. Exposures to these contaminants have been linked to childhood asthma in other petrochemical areas (Rumchev *et al.*, 2004) a reported health outcome of interest at Aamjiwnaang and similar industrial centers (Wichmann *et al.*, 2009). Addition of these chemicals into future biomarker studies would be of interest.

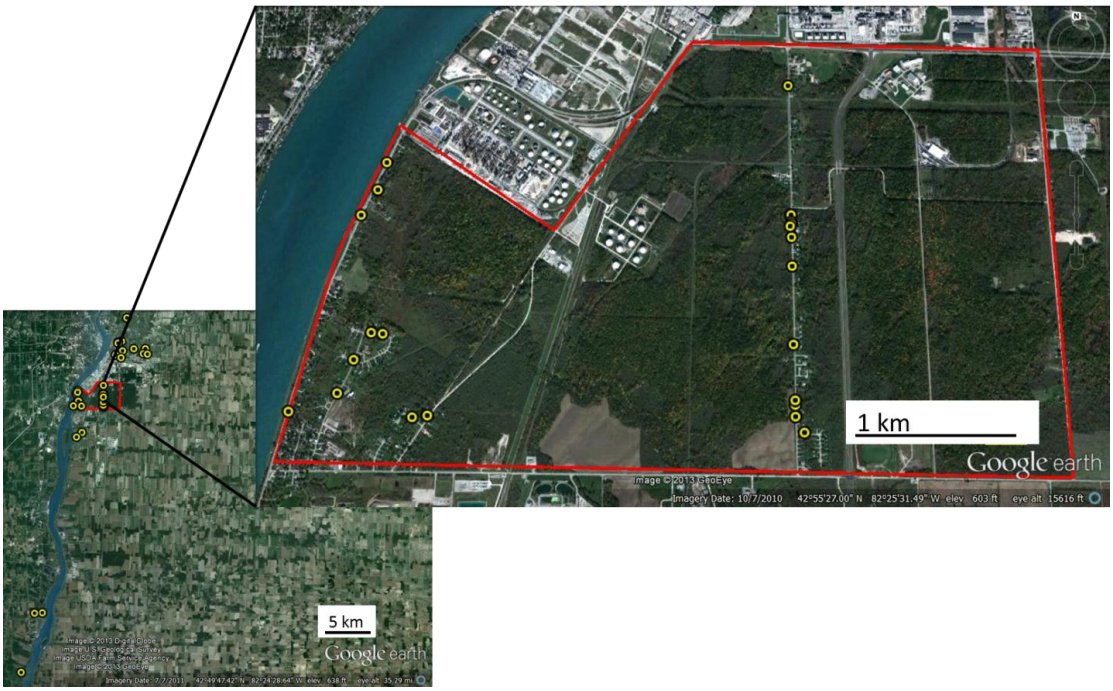

Figure 4.1 Map of participant location, represented by yellow dot. Aamjiwnaang First Nation is in excerpt highlighted in red.

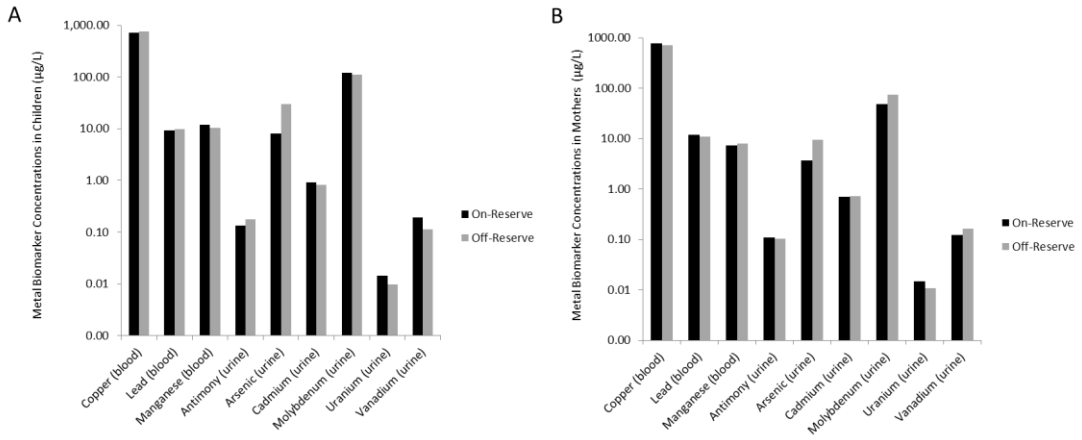

Figure 4.2 Comparison of on and off-Reserve metal biomarker concentrations. A) Mean concentrations (µg/L) of metals in blood and urine of on-Reserve (n=18 blood, 24 urine) and off-Reserve (n=12 blood, 17 urine) children. Levels of vanadium in on-Reserve children were significantly higher than off-Reserve children. B) Concentrations (µg/L) of metals in blood and urine of on-Reserve (n=24 blood, 26 urine) and off-Reserve (n=15 blood, 17 urine) mothers. No significant differences were found. Note for both Figures that the Y-axis is on a log-scale as concentrations of metals span several orders of magnitude.

Table 4.1 Detection limits and percent of samples below detection limits for all chemicals analyzed.

Chemical Class	Chemical Name	RSD (%)
	Mn	3.81
	Cu	4.49
	Pb	6.83
	V	1.99
	As	4.11
	Mo	2.96
	Cd	2.26
	Sb	1.96
Metals (µg/L)	U	1.19
	Naphthalene	16.60508
	Acenaphthylene	21.74011
	Acenaphthene	8.291199
	Phenanthrene	17.42005
	Anthracene	22.47322
	Fluoranthene	56.15998
	Pyrene	41.93651
	Benzo[a]anthracene	13.54007
	Chrysene	All <MDL
	Benzo[b]fluoranthrene	6.315013
	Benzo[k]fluoranthrene	14.23471
	Benzo[a]pyrene	10.82504
	Indeno[1,2,3-c,d]pyrene	All <MDL
	Dibenzo[a,h]anthracene	All <MDL
PAHs (µg/L)	Benzo[g,h,i]perylene	All <MDL
	HCB	22.27979
	Lindane	25.54455
	ppDDE	14.38815
	p,pDDD,o,pDDT	All <MDL
	ppDDT	16.65903
	Pentachlorobenzene	All <MDL
	α,β-HCH	All <MDL
	PCPM-ether	All <MDL
	Aldrin	All <MDL
	Dachtal	All <MDL
	Octachlorostyrene	All <MDL
	B-heptachloroepoxide	All <MDL
	Oxychlordane	All <MDL
	trans-y-chlordane	All <MDL
	cis-α-chlordane	All <MDL
	trans-y-nonachlor	All <MDL
	dieldrin	All <MDL
	Endrin	All <MDL
	cis-nonachlor	All <MDL
Organochlorine	Mirex	All <MDL
Pesticides(µg/L)	photo-Mirex	All <MDL
	BDE47	43.24
	BDE99	20.57466
	BDE100	14.98112
	BDE153	All <MDL
	BDE100	14.98112
	BDE209	All <MDL
	BDE4	All <MDL
	BDE17	All <MDL
	BDE28	All <MDL
	BDE75	All <MDL
	BDE49	All <MDL
	BDE71	All <MDL
	BDE66	All <MDL
	BDE85	All <MDL
	BDE166	All <MDL
	BDE138	All <MDL
	BDE183	All <MDL
	BDE190	All <MDL
	BDE203	All <MDL
	BDE208	All <MDL
	BDE207	All <MDL
PBDEs (µg/L)	BDE206	All <MDL

Chemical Class	Chemical Name	RSD (%)
	PCB126	24.95636
	PCB180	19.51589
	PCB138	20.28302
	PCB118	12.47562
	PCB153	4.933217
	PCB31+28	All <MDL
	PCB33	All <MDL
	PCB22	All <MDL
	PCB52	All <MDL
	PCB49	All <MDL
	PCB47+48	All <MDL
	PCB44	All <MDL
	PCB42	All <MDL
	PCB41+47	All <MDL
	PCB64	All <MDL
	PCB40	All <MDL
	PCB63	All <MDL
	PCB74	All <MDL
	PCB70+76	All <MDL
	PCB66	All <MDL
	PCB95	All <MDL
	PCB91	All <MDL
	PCB56+60	All <MDL
	PCB84+92+89	All <MDL
	PCB101	All <MDL
	PCB99	All <MDL
	PCB119	All <MDL
	PCB83	All <MDL
	PCB97	All <MDL
	PCB81+87	All <MDL
	PCB85	All <MDL
	PCB77	All <MDL
	PCB110	All <MDL
	PCB82	All <MDL
	PCB151	All <MDL
	PCB144+135	All <MDL
	PCB107	All <MDL
	PCB123	All <MDL
	PCB149	All <MDL
	PCB134	All <MDL
	PCB114	All <MDL
	PCB131	All <MDL
	PCB146	All <MDL
	PCB105	All <MDL
	PCB141	All <MDL
	PCB176+137	All <MDL
	PCB158	All <MDL
	PCB129	All <MDL
	PCB178	All <MDL
	PCB175	All <MDL
	PCB187+182	All <MDL
	PCB183	All <MDL
	PCB128	All <MDL
	PCB167	All <MDL
	PCB185	All <MDL
	PCB174	All <MDL
	PCB177	All <MDL
	PCB202	All <MDL
	PCB171	All <MDL
	PCB156	All <MDL
	PCB173	All <MDL
	PCB157	All <MDL
	PCB200	All <MDL
	PCB172	All <MDL
	PCB197	All <MDL
	PCB193	All <MDL
	PCB191	All <MDL
	PCB199	All <MDL
	PCB170+190	All <MDL
	PCB198	All <MDL
	PCB201	All <MDL
	PCB203+196	All <MDL
	PCB189	All <MDL
	PCB195	All <MDL
	PCB208	All <MDL
	PCB207	All <MDL
	PCB194	All <MDL
	PCB205	All <MDL
	PCB206	All <MDL
PCBs (µg/L)	PCB209	All <MDL

Table 4.2 Metal biomarker concentrations. Blood and urine metal levels measured in mothers (n= 39 blood, 43 urine) and children (n=30 blood, 41 urine) in comparison to values measured in Canadian women children aged 6-11 (Health Canada, 2010).

		Aamjiwnaang Participants (µg/L)					National Reference Range (µg/L)		
		Mean	Std. Dev	10th	50th	90th	10th	50th	90th
Children	Copper (blood)	730.71	109.19	597.20	741.54	847.15	824.63	971.55	1139.73
	Lead (blood)	9.56	9.16	4.23	6.60	21.25	5.30	8.70	16.10
	Manganese (blood)	11.41	3.47	7.69	10.34	16.60	6.94	9.74	14.14
	Antimony (urine)	0.15	0.16	0.05	0.14	0.20	<LOD	0.06	0.13
	Arsenic (urine)	15.91	35.42	2.88	5.08	29.68	2.46	9.63	35.42
	Cadmium (urine)	0.88	0.45	0.43	0.79	1.48	<LOD	0.25	0.59
	Molybdenum (urine)	117.29	66.59	50.16	108.11	179.64	19.42	60.31	146.49
	Uranium (urine)	0.01	0.01	0.00	0.01	0.02	<LOD	<LOD	0.01
	Vanadium (urine)	0.17	0.16	0.06	0.14	0.27	<LOD	<LOD	<LOD
Mothers	Copper (blood)	751.10	124.82	639.70	716.50	981.60	796.60	981.17	1419.10
	Lead (blood)	7.54	4.04	3.82	6.26	14.04	5.20	8.60	16.40
	Manganese (blood)	11.69	3.60	8.33	10.61	16.83	6.61	9.49	15.80
	Antimony (urine)	0.11	0.09	0.06	0.06	0.22	<LOD	0.04	0.11
	Arsenic (urine)	5.72	7.15	0.72	3.73	10.33	2.37	11.48	43.16
	Cadmium (urine)	0.71	0.56	0.15	0.58	1.57	<LOD	0.29	0.91
	Molybdenum (urine)	57.97	45.50	14.96	40.33	128.52	9.47	39.07	95.10
	Uranium (urine)	0.01	0.01	0.00	0.01	0.03	<LOD	<LOD	0.01
	Vanadium (urine)	0.14	0.12	0.06	0.06	0.33	<LOD	<LOD	<LOD

Table 4.3 Metal and PAH releases in “Chemical Valley” during 2011 as reported to NPRI and TRI databases (Environment Canada, 2012; U.S. EPA, 2012).

	Chemical	Total Released within Chemical Valley (kg)
Metals	Lead	9813.50
	Manganese	139710.95
	Copper	2.00
	Arsenic	194.00
	Cadmium	49.00
	Molybdenum	0.00
	Antimony	NR
	Cobalt	0.00
	Uranium	NR
	Vanadium	52522.85
PAHs	Acenaphthene	173.00
	Acenaphthylene	252.00
	Naphthalene	16.70
	Phenanthrene	144.00
	Anthracene	0.06
	Fluoranthene	5.90
	Pyrene	13.09
	Benzo[a]anthracene	1.10
	Chrysene	NR
	Benzo[b]fluoranthene	0.39
	Benzo[k]fluoranthene	0.06
	Benzo[a]pyrene	0.65
	Indeno[1,2,3-c,d]pyrene	0.24
	Dibenzo[a,h]anthracene	0.00
	Benzo[g,h,i]perylene	1.64

Table 4.4 Correlations between metal biomarkers in blood and urine for children and mothers.

			Copper (blood)	Manganese (blood)	Lead (blood)	Antimony (urine)	Arsenic (urine)	Cadmium (urine)	Molybdenum (urine)	Uranium (urine)	Vanadium (urine)
Children	Copper (blood)	p-value		0.977	0.713	0.159	0.638	0.653	0.597	(0.017	0.468
		(coefficient)		(0.006)	(-0.070)	(-0.268)	(0.091)	(0.087)	(0.102)	(-.441)*	(-0.140)
	Manganese (blood)	p-value	0.977		0.762	0.802	0.996	0.100	0.065	0.823	0.781
		(coefficient)	(0.006)		(0.058)	(-0.049)	(0.001)	(-0.312)	(-0.347)	(-0.043)	(0.054)
	Lead (blood)	p-value	0.713	0.762		0.079	0.070	0.092	0.811	0.238	0.140
		(coefficient)	(-0.070)	(0.058)		(0.332)	(0.341)	(0.092)	(0.046)	(0.226)	(0.281)
	Antimony (urine)	p-value	0.159	0.802	0.079		0.130	0.115	0.332	0.133	<0.001
		(coefficient)	(-0.268)	(-0.049)	(0.332)		(0.237)	(0.247)	(0.153)	(0.235)	(.550)*
	Arsenic (urine)	p-value	0.638	0.996	0.070	0.130		0.001	0.001	0.197	0.021
		(coefficient)	(0.091)	(0.001)	(0.341)	(0.237)		(.494)*	(.483)*	(0.203)	(.356)*
	Cadmium (urine)	p-value	0.653	0.100	0,636	0.115)	0.001		0.001	0.248	0.165
		(coefficient)	(0.087)	(-0.312)	(0.092)	(0.247	(.494)*		(.971)*	(0.182)`	(0.218)
	Molybdenum (urine)	p-value	0.597	0.065	0.811	0.332	0.001	<0.001		0.312	0.514
		(coefficient)	(0.102)	(-0.347)	(0.046)	(0.153)	(.483)*	(.971)*		(0.160)	(0.104)
	Uranium (urine)	p-value	0.017	0.823	0.238	0.133	0.197	0.248	0.312		0.014
		(coefficient)	(-.441)*	(-0.043)	(0.226)	(0.235)	(0.203)	(0.182)	(0.160)		(.378)*
	Vanadium (urine)	p-value	0.468	0.781	0.140	<0.001	0.021	0.165	0.514	0.014	
		(coefficient)	(-0.140)	(0.054)	(0.281)	(.550)*	(.356)*	(0.218)	(0.104)	(.378)*	
Mothers	Copper (blood)	p-value		0.003	0.734	0.469	0.433	0.173	0.231	0.951	0.425
		(coefficient)		(.464)*	(0.056)	(-0.123)	(-0.131)	(-0.226)	(-0.202)	(-0.010)	(-0.135)
	Manganese (blood)	p-value	0.003		0.779	0.198	0.245	0.248	0.089	0.841	0.419
		(coefficient)	(.464)*		(0.046)	(-0.217)	(-0.193)	(-0.192)	(-0.283)	(-0.034)	(-0.137)
	Lead (blooc)	p-value	0.734	0.779		<0.001	0.797	0.296	0.049	0.387	0.464
		(coefficient)	(0.056)	(0.046)		(-.545)**	(-0.043)	(-0.174)	(-.326)*	(-0.146)	(-0.124)
	Antimony (urine)	p-value	0.469	0.198	<0.001		0.021	0.002	0.001	0.078	<0.001
		(coefficient)	(-0.123)	(-0.217)	(-.545)*		(.360)*	(.462)*	(.505)*	(0.279)	(.530)*
	Arsenic (urine)	p-value	0.433	0.245	0.797	0.021		<0.001	<0.001	0.334	0.003
		(coefficient)	(-0.131)	(-0.193)	(-0.043)	(.360)*		(.618)*	(.731)*	(0.155)	(.450)*
	Cadmium (urine)	p-value	0.173	0.248	0.296	0.002	<0.001		<0.001	0.104	<0.001
		(coefficient)	(-0.226)	(-0.192)	(-0.174)	(.462)*	(.618*)		(.829)*	(0.257)	(.528)*
	Molybdenum (urine)	p-value	0.231	0.089	0.049	0.001	<0.001	<0.001		0.327	0.006
		(coefficient)	(-0.202)	(-0.283)	(-.326)*	(.505)*	(.731)*	(.829)*		(0.157)	(.423)*
	Uranium (urine)	p-value	0.951	0.841	0.387	0.078	0.334	0.104	0.327		0.015
		(coefficient)	(-0.010)	(-0.034)	(-0.146)	(0.279)	(0.155)	(0.257)	(0.157)		(.378)*
	Vanadium (urine)	p-value	0.426	0.419	0.464	<0.001	0.003	<0.001	0.006	0.015	
		(coefficient)	(-0.135)	(-0.137)	(-0.124)	(.530)*	(.450)*	(.528)*	(.423)*	(.378)*	

Table 4.5 PFC biomarker concentrations. PFC levels measured in mothers (n=12) and children (n=22) in comparison to values measured in Canadian women (Health Canada, 2011) and U.S. children ages 12-19 (CDC, 2012).

		Aamjiwnaang Participants (ng/mL)					National Reference Range (ng/mL)		
		Mean	Std Dev	10th	50th	90th	10th	50th	90th
Children	PFOA	3.19	1.59	1.53	2.79	6.20	ND	2.90	4.80
	PFNA	3.84	2.65	0.79	3.55	7.70	ND	1.30	2.70
	PFDA	0.90	0.23	0.52	1.00	1.00	ND	0.20	0.40
	PFUnA	0.99	0.16	0.74	1.00	1.00	ND	0.10	0.30
	PFHxS	5.30	10.31	1.16	2.36	9.82	ND	1.90	8.10
	PFOS	7.01	6.92	2.65	5.76	10.30	ND	6.90	14.40
Mothers	PFOA	2.42	1.41	0.87	1.70	4.69	0.95	2.10	3.76
	PFNA	1.05	0.29	0.67	1.00	1.49	ND	1.40	3.20
	PFDA	0.92	0.13	0.66	1.00	1.00	ND	0.30	0.70
	PFHxS	1.87	1.32	1.02	1.41	4.87	0.41	1.22	4.33
	PFOS	6.53	4.25	2.13	5.80	14.44	3.08	6.42	13.98

Table 4.6 Correlations between PFC biomarkers in serum for children and mothers. PFUnA was below detection limit for all mothers.

			PFOA	PFNA	PNDA	PFHxS	PFOS	PFUnA
Children	PFOA	p-value		0.046	0.001	0.185	0.003	0.242
		(coefficient)		(.430)*	(-.646)*	(0.294)	(.610)*	(-0.260)
	PFNA	p-value	0.046		0.181	0.472	0.805	0.257
		(coefficient)	(.430)*		(-0.296)	(-0.162)	(-0.056)	(-0.253)
	PFDA	p-value	0.001	0.181		0.716	0.087	0.336
		(coefficient)	(-.646)*	(-0.296)		(-0.082)	(-0.373)	(0.215)
	PFHxS	p-value	0.185	0.472	0.716		0.192	0.811
		(coefficient)	(0.294)	(-0.162)	(-0.082)		(0.289)	(-0.054)
Mothers	PFOA	p-value		0.037	0.317	0.282	0.001	
		(coefficient)		(.606)*	(-0.316)	(0.323)	(.824)*	
	PFNA	p-value	0.037		0.205	0.658	0.363	
		(coefficient)	(.606)*		(-0.394)	(0.143)	(0.289)	
	PFDA	p-value	0.317	0.205		0.710	0.426	
		(coefficient)	(-0.316)	(-0.394)		(-0.120)	(-0.254)	
	PFUnA	p-value	0.282	0.658	0.710		0.040	
		(coefficient)	(0.323)	(0.143)	(-0.120)		(.573)*	
	PFHxS	p-value	0.001	0.363	0.426	0.040		
		(coefficient)	(.824)*	(0.289)	(-0.254)	(.573)*		

Table 4.7 PAH levels measured in mothers (n=23) in comparison to values measured in women in Texas (Sexton *et al.,* 2001).

	Aamjiwnaang participants (µg/L whole blood)					Comparison Value (µg/L whole blood)
	Mean	Std. Deviation	10th Percentile	50th Percentile	90 Percentile	Mean (Std. Deviation)
Naphthalene	1.08	0.94	0.27	0.66	2.55	1.5 (1.3)
Acenaphthene	0.18	0.15	0.01	0.13	0.40	0.0 (3.5)
Phenanthrene	0.79	0.94	0.01	0.36	2.14	0.5 (2.4)
Anthracene	0.04	0.05	0.01	0.03	0.13	0.0 (3.1)
Fluoranthene	0.14	0.18	0.01	0.07	0.46	0.1 (3.3)
Pyrene	0.19	0.26	0.01	0.09	0.69	0.1 (3.3)

Table 4.8 Correlations between PAH biomarkers in blood for children and mothers.

			Naphthalene	Acenaphthylene	Acenaphthene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]anthracene	Chrysene
Children	Naphthalene	p-value		0.372	0.323	0.401	0.096	0.747	0.948	0.320	0.671
		(coefficient)		(-0.217)	(-0.239)	(-0.204)	(-0.393)	(-0.079)	(-0.016)	(0.241)	(0.104)
	Acenaphthylene	p-value	0.372		0.539	0.811	0.996	0.659	0.151	0.918	0.914
		(coefficient)	(-0.217)		(-0.150)	(0.059)	(0.001)	(-0.108)	(-0.343)	(-0.025)	(-0.027)
	Acenaphthene	p-value	0.323	0.539		0.643	0.989	0.231	0.939	0.877	0.024
		(coefficient)	(-0.239)	(-0.150)		(-0.114)	(-0.004)	(0.288)	(-0.019)	(-0.038)	(-.516)*
	Phenanthrene	p-value	0.401	0.811	0.643		0.614	0.185	0.117	0.222	0.160
		(coefficient)	(-0.204)	(0.059)	(-0.114)		(0.124)	(-0.318)	(-0.372)	(0.294)	(0.335)
	Anthracene	p-value	0.096	0.996	0.989	0.614		0.625	0.942	0.683	0.685
		(coefficient)	(-0.393)	(0.001)	(-0.004)	(0.124)		(-0.120)	(0.018)	(0.100)	(0.100)
	Fluoranthene	p-value	0.747	0.659	0.231	0.185	0.625		<0.001	0.262	0.504
		(coefficient)	(-0.079)	(-0.108)	(0.288)	(-0.318)	(-0.120)		(.844)*	(-0.271)	(-0.163)
	Pyrene	p-value	0.948	0.151	0.939	0.117	0.942	<0.001		0.652	0.776
		(coefficient)	(-0.016)	(-0.343)	(-0.019)	(-0.372)	(0.018)	(.844)*		(-0.111)	(0.070)
	Benzo[a]anthracene	p-value	0.320	0.918	0.877	0.222	0.683	0.262	0.652		0.057
		(coefficient)	(0.241)	(-0.025)	(-0.038)	(0.294)	(0.100)	(-0.271)	(-0.111)		(0.443)
	Chrysene	p-value	0.671	0.914	0.024	0.160	0.685	0.504	0.776	0.057	
		(coefficient)	(0.104)	(-0.027)	(-.516)*	(0.335)	(0.100)	(-0.163)	(0.070)	(0.443)	
Mothers	Naphthalene	p-value		0.980	0.937	0.821	0.261	0.516	0.631	0.029	0.262
		(coefficient)		(0.006)	(0.017)	(0.050)	(-0.244)	(-0.143)	(-0.106)	(.455)*	(-0.244)
		p-value		0.98	0.937	0.821	0.261	0.516	0.631	0.029	0.262
	Acenaphthylene	p-value	0.980		0.608	0.167	0.857	0.845	0.869	0.660	0.420
		(coefficient)	(0.006)		(0.113)	(-0.298)	(.-0.040)	(0.043)	(0.036)	(-0.097)	(-0.177)
	Acenaphthene	p-value	0.937	0.608		0.653	0.406	0.148	0.177	0.722	0.554
		(coefficient)	(0.017)	(0.113)		(-0.099)	(-0.182)	(0.312)	(0.292)	(-0.078)	(0.13)
	Phenanthrene	p-value	0.821	0.167	0.653		0.416	0.712	0.487	0.139	0.645
		(coefficient)	(0.050)	(-0.298)	(-0.099)		(0.178)	(0.081)	(0.152)	(0.318)	(0.101)
	Anthracene	p-value	0.261	0.857	0.406	0.416		0.810	0.607	0.965	0.037
		(coefficient)	(-0.244)	(-0.04)	(-0.182)	(0.178)		(0.053)	(0.113)	(-0.010)	(.437)*
	Fluoranthene	p-value	0.516	0.845	0.148	0.712	0.810		<0.001	0.265	0.620
		(coefficient)	(-0.143)	(0.043)	(0.312)	(0.081)	(0.053)		(.975)*	(-0.243)	(0.115)
	Pyrene	p-value	0.631	0.869	0.177	0.487	0.607	<0.001		0.604	0.403
		(coefficient)	(-0.106)	(0.036)	(0.292)	(0.152)	(0.113)	(.975)*		(-0.114)	(0.183)
	Benzo[a]anthracene	p-value	0.029	0.660	0.722	0.139	0.965	0.265	0.604		0.153
		(coefficient)	(.455)*	(-0.097)	(-0.078)	(0.318)	(-0.010)	(-0.243)	(-0.114)		(0.308)
	Chrysene	p-value	0.262	0.420	0.554	0.645	0.037	0.602	0.403	0.153	
		(coefficient)	(-0.244)	(-0.177)	(0.13)	(0.101)	(.437)*	(0.115)	(0.183)	(0.308)	

Table 4.9 OCP biomarker concentrations. OCP levels measured in mothers (n=23) and children (n=19) in comparison to values measured in Canadian women (Health Canada, 2011) and U.S. children ages 12-19 (CDC, 2012).

		Aamjiwnaang Participants (ng/g lipid)					National Reference Range (ng/g lipid)		
		Mean	Std. Deviation	10th	50th	90th	10th	50th	90th
Children	HCB	5.89	2.10	4.00	5.33	9.33	ND	13.40	20.70
	HCH	8.91	2.48	6.67	8.00	13.33	ND	<LOD	<LOD
	ppDDE	168.14	163.60	54.67	110.67	441.33	ND	93.60	341.00
	ppDDT	29.40	19.14	13.33	25.33	45.33	ND	<LOD	<LOD
Mothers	HCB	4.17	1.13	2.73	4.55	6.00	<LOD	6.48	15.34
	HCH	6.76	2.21	4.00	6.36	10.00	<LOD	3.01	55.97
	ppDDE	151.01	113.12	42.00	110.91	376.54	35.94	78.19	478.63
	ppDDT	21.67	18.46	4.50	17.27	57.82	<LOD	<LOD	<LOD

Table 4.10 Correlations between organochlorine pesticide biomarkers in blood for children and mothers.

			HCB	HCH	ppDDE	ppDDT
Children	HCB	p-value		0.001	0.446	0.002
		(coefficient)		(.692)*	(0.186)	(-.655)*
	HCH	p-value	0.001		0.981	0.008
		(coefficient)	(.692)*		(0.006)	(-.586)*
	ppDDE	p-value	0.446	0.981		0.580
		(coefficient)	(0.186)	(0.006)		(-0.136)
	ppDDT	p-value	0.002	0.008	0.580	
		(coefficient)	(-.655)*	(-.586)*	(-0.136)	
Mothers	HCB	p-value		<0.001	0.416	0.363
		(coefficient)		(.759)*	(0.178)	(-0.199)
	HCH	p-value	<0.001		0.260	0.522
		(coefficient)	(.759)*		(0.245)	(-0.141)
	ppDDE	p-value	0.416	0.260		0.353
		(coefficient)	(0.178)	(0.245)		(0.203)
	ppDDT	p-value	0.363	0.522	0.353	
		(coefficient)	(-0.199)	(-0.141)	(0.203)	

Table 4.11 PCB biomarker concentrations. PCB levels measured in mothers (n=23) and children (n=19) in comparison to values measured in Canadian women (Health Canada, 2011) and U.S. children ages 12-19 (CDC, 2012).

		Aamjiwnaang Participants (ng/g lipid)					National Reference Range (ng/g lipid)		
		Mean	Std Dev	10^{th}	50^{th}	90^{th}	10^{th}	50^{th}	90^{th}
Children	PCB 126	0.08	0.14	0.00	0.00	0.27	ND	<LOD	0.02
	PCB 180	20.87	8.01	11.07	21.33	30.67	ND	2.97	11.10
	PCB 138	14.07	6.38	8.00	12.67	22.54	ND	4.57	12.70
	PCB 118	13.60	7.58	4.71	14.00	23.73	ND	2.83	6.80
	PCB 153	11.19	5.78	3.93	10.67	18.67	ND	5.40	15.70
Mothers	PCB 126	0.16	0.17	0.06	0.06	0.51	ND	0.02	0.06
	PCB 180	13.28	3.59	8.18	12.73	18.36	2.02	5.94	13.16
	PCB 138	8.06	2.49	4.91	8.18	11.82	2.28	5.81	11.93
	PCB 118	8.04	2.85	4.91	7.27	12.91	<LOD	3.29	7.47
	PCB 153	6.97	3.46	3.64	6.36	12.91	<LOD	9.43	23.81

Table 4.12 Correlations between PCB biomarkers in blood for children and mothers.

			PCB 126	PCB 180	PCB 138	PCB 118	PCB 153
Children	PCB 126	p-value		0.395	0.984	0.887	0.563
		(coefficient)		(0.201)	(0.005)	(0.034)	(0.138)
	PCB 180	p-value	0.395		<0.001	<0.001	<0.001
		(coefficient)	(0.201)		(.848)*	(.871)*	(.807)*
	PCB 138	p-value	0.984	<0.001		<0.001	<0.001
		(coefficient)	(0.005)	(.848)*		(.846)*	(.720)*
	PCB 118	p-value	0.887	<0.001	<0.001		<0.001
		(coefficient)	(0.034)	(.871)*	(.846)*		(.940)*
	PCB 153	p-value	0.563	<0.001	<0.001	<0.001	
		(coefficient)	(0.138)	(.807)*	(.720)*	(.940)*	
Mothers	PCB 126	p-value		0.790	0.532)	0.859	0.625
		(coefficient)		(0.059)	(-0.137	(0.039)	(0.108)
	PCB 180	p-value	0.790		<0.001	0.001	0.039
		(coefficient)	(0.059)		(.845)*	(.626)*	(.432)*
	PCB 138	p-value	0.532	<0.001		0.001	0.006
		(coefficient)	(-0.137)	(.845)**		(.656)*	(.558)*
	PCB 118	p-value	0.859	0.001	0.001		<0.001
		(coefficient)	(0.039)	(.626)*	(.656)*		(.829)*
	PCB 153	p-value	0.625	0.039	0.006	<0.001	
		(coefficient)	(0.108)	(.432)*	(.558)*	(.829)*	

Table 4.13 PBDE biomarker concentrations. PBDE levels measured in mothers (n=23) and children (n=19) in comparison to values measured in Canadian women (Health Canada, 2011) and U.S. children ages 12-19 (CDC, 2012).

		Aamjiwnaang Participants (ng/g lipid)					National Reference Range (ng/g lipid)		
		Mean	Std Dev	10th	50th	90th	10th	50th	90th
Children	PBDE 153	1.5	0.9	0.9	0.9	2.7	ND	7.5	31.0
	PBDE 47	2.9	5.8	0.9	1.3	4.0	ND	27.2	104.0
	PBDE 99	1.4	0.7	0.9	0.9	2.7	ND	5.7	27.9
	PBDE 100	1.1	0.2	0.9	0.9	1.3	ND	4.9	19.3
	PBDE 209	0.7	0.2	0.7	0.7	1.2	ND	ND	ND
Mothers	PBDE 153	1.0	0.6	0.6	0.6	2.4	<LOD	<LOD	14.5
	PBDE 47	3.3	5.3	0.6	0.9	14.5	<LOD	11.0	50.6
	PBDE 99	0.9	0.5	0.6	0.6	1.5	<LOD	<LOD	7.5
	PBDE 100	0.7	0.1	0.6	0.6	0.9	<LOD	<LOD	9.1
	PBDE 209	0.5	0.2	0.5	0.5	0.5	ND	ND	ND

Table 4.14 Correlations between PBDE biomarkers in blood for children and mothers.

			PBDE 47	PBDE 99	PBDE 153
Children	PBDE 47	p-value		0.204	0.984
		(coefficient)		(-0.305)	(-0.005)
	PBDE 99	p-value	0.204		0.272
		(coefficient)	(-0.305)		(-0.265)
	PBDE 153	p-value	0.984	0.272	
		(coefficient)	(-0.005)	(-0.265)	
Mothers	PBDE 47	p-value		0.315	0.131
		(coefficient)		(-0.219)	(-0.325)
	PBDE 99	p-value	0.315		0.522
		(coefficient)	(-0.219)		(-0.141)
	PBDE 153	p-value	0.131	0.522	
		(coefficient)	(-0.325)	(-0.141)	

Table 4.15. Distributions of lipid-adjusted PAHs and whole blood OCPs, PCBs, and PBDEs in Aamjiwnaang mothers (n=23) and children (n=19).

		Mean	Std. Deviation	10th Percentile	50th Percentile	90th Percentile
Children (ng/g lipid)	Naphthalene	90.81	75.55	26.67	69.33	245.33
	Acenaphthylene	30.49	39.14	1.18	25.33	52.00
	Acenaphthene	19.41	19.84	1.18	10.67	52.00
	Phenanthrene	108.40	125.16	1.18	76.00	373.33
	Anthracene	8.96	7.02	1.18	6.67	20.00
	Fluoranthene	21.43	28.26	1.41	9.33	77.33
	Pyrene	24.06	22.30	0.85	21.33	60.00
	Benzo [a] anthracene	9.02	9.42	0.85	6.67	24.00
	Chyrsene	5.28	8.17	1.23	4.00	9.33
Mothers (ng/g lipid)	Naphthalene	102.17	84.80	25.72	76.37	238.82
	Acenaphthylene	14.47	12.84	0.80	13.64	28.91
	Acenaphthene	16.70	14.02	0.80	11.82	36.36
	Phenanthrene	72.16	85.12	0.80	32.73	194.18
	Anthracene	3.95	4.20	0.80	2.73	11.64
	Fluoranthene	12.70	16.58	0.96	6.36	42.18
	Pyrene	17.23	23.98	0.58	8.18	62.36
	Benzo [a] anthracene	9.94	12.37	0.58	4.55	30.55
	Chyrsene	3.01	3.90	0.84	1.82	7.63
Children (µg/L)	HCB	0.02	0.02	0.00	0.00	0.06
	HCH	0.07	0.02	0.05	0.06	0.10
	ppDDe	1.26	1.23	0.41	0.83	3.31
	ppDDT	0.22	0.14	0.10	0.19	0.34
Mothers (µg/L)	HCB	0.05	0.01	0.03	0.05	0.07
	HCH	0.07	0.02	0.04	0.07	0.11
	ppDDe	1.66	1.24	0.46	1.22	4.14
	ppDDT	0.24	0.20	0.05	0.19	0.64
Children (µg/L)	PCB 126	0.00	0.00	0.00	0.00	0.00
	PCB 180	0.16	0.05	0.11	0.16	0.23
	PCB 138	0.11	0.04	0.06	0.10	0.17
	PCB 118	0.11	0.05	0.04	0.12	0.18
	PCB 153	0.09	0.04	0.04	0.09	0.14
Mothers (µg/L)	PCB 126	0.00	0.00	0.00	0.00	0.01
	PCB 180	0.15	0.04	0.09	0.14	0.20
	PCB 138	0.09	0.03	0.05	0.09	0.13
	PCB 118	0.09	0.03	0.05	0.08	0.14
	PCB 153	0.08	0.04	0.04	0.07	0.14
Children (µg/L)	PBDE 47	0.01	0.03	0.00	0.00	0.02
	PBDE 99	0.01	0.00	0.01	0.01	0.02
	PBDE 100	0.01	0.00	0.01	0.01	0.01
	PBDE 153	0.01	0.01	0.01	0.01	0.02
	PBDE 209	0.01	0.00	0.01	0.01	0.01
Mothers (µg/L)	PBDE 47	0.04	0.06	0.01	0.01	0.16
	PBDE 99	0.01	0.00	0.01	0.01	0.02
	PBDE 100	0.01	0.00	0.01	0.01	0.01
	PBDE 153	0.01	0.01	0.01	0.01	0.03
	PBDE 209	0.01	0.00	0.01	0.01	0.01

Table 4.16. Self-reported health outcomes among participants (n=40).

	% Reported Yes			
	Mothers		Children	
Outcome	On-Reserve	Off-Reserve	On-Reserve	Off-Reserve
Asthma	21.4	13.3	28.6	15.4
Jiggling Vision	21.4	13.3	3.6	7.7
Itchy Eyes	35.7	20	10.7	7.7
Eyes Strain	32.1	13.3	21.4	15.4
Infection of Conjuctiva	3.6	13.3	0	0
Puffy Eyes	28.6	13.3	14.3	15.4
Teary Eyes	39.3	7.7	21.4	0
Eye Mucus	32.1	7.7	14.3	7.7
Poor Vision	14.3	13.3	10.7	7.7
Runny Nose	57.1	46.7	60.7	53.8
Itchy Nose	28.6	46.2	21.4	23.1
Dry Throat	21.4	23.1	17.9	15.4
Scratchy Throat	25	20	25	30.8
Sore Throat	25	38.5	32.1	33.3
Phlegm	35.7	38.5	28.6	20
Cough	42.9	53.8	46.4	33.3
Skin Swelling	14.3	13.3	7.1	0
Itchy Skin	42.9	40	25.9	30.8
Blisters	10.7	13.3	18.5	7.7
Flushed Face	17.9	13.3	10.7	7.7
Skin Irritation	25	26.7	22.2	30.8
Dizziness	39.3	23.1	10.7	0
Neausea	21.4	15.4	10.7	0
Headache	60.7	92.3	39.3	7.7
Palpatation	14.3	7.7	0	0
Loss of Appetite	17.9	30.8	7.1	0
Stomacheache	25	15.4	44.4	7.7
Obdominal Pain	32.1	23.1	14.3	0
Diarrhea	25	30.8	17.9	23.1
Constipation	21.4	23.1	7.1	23.1
Fatigue	39.3	53.8	10.7	15.4
Fever	21.4	7.7	17.9	23.1
Tingling Extremeties	39.3	23.1	17.9	0
Tremor of Extremities	14.3	0	10.7	0
Weak Extremeties	17.9	15.4	3.7	0
Insomnia	28.6	23.1	7.1	7.7
Loss of Concentration	35.7	15.4	25.9	23.1
Irritability	42.9	53.8	25	15.4
Lower Back Pain	53.6	38.5	21.4	7.7
Injury	10.7	13.3	14.3	0

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Chapter 5

Conclusion

5.1 Major Results and Discussion

For over thirty years it has been known that the lands of Aamjiwnaang are polluted, though little research has been conducted upon documenting the extent of this pollution. This dissertation is one of the first comprehensive characterizations of chemical contamination of the land and peoples at the Aamjiwnaang First Nation. Based on a exposure disease model of inquiry (sources-fate-exposure-outcome paradigm) and in close collaboration with community members, the dissertation characterized upwards of 200 distinct chemical pollutants of potential concern to the community in a number of samples, including water, sediment, soil, and human biomarkers (Figure 5.1).

5.1.1 Metals Contamination in Stream Systems

5.1.1.1 Multiple Metals in Stream Water

The first aim of the study was to address metals contamination in stream systems near and within the Aamjiwnaang First Nation Reserve. Stream sites were chosen on Reserve (n=4), in Marysville, MI (n=2), northern Port Huron, MI (n=3), Port Huron, MI (n=3), eastern Sarnia, ON (n=3), northern Sarnia, ON (n=2), Corunna, ON (n=2), and Kettle Point, ON (n=4). Kettle Point served as the reference community, as it is over 40 kilometers from the industrial center and upstream waters flow through a natural preserve. This is the first study in the area to address stream water concentrations of

seven metals at sites located on and off-Reserve, including locations in the U.S. and Canada. The current study is also the first in the area to analyze comparison samples from a reference community.

Screening for elevated levels of metals in stream waters showed many sites to have concentrations of particular metals above those estimated to be harmful to freshwater invertebrates (Buchman, 2008). Nearly all sites (88.5%) were above screening concentrations for aluminum (mean=358.7 µg/L compared to EPA LEL=87 µg/L; Table 5.1). Aluminum is widely used in the petrochemical industry during cracking and refining of crude oil (O'Neill *et al.,* 2001; ATSDR, 2001). It is therefore likely that the use and releases of aluminum in the region may be related to elevated concentrations in nearby stream waters. There were also multiple sites (17%) above benchmark concentrations of manganese (mean= 57.9 µg/L compared to EPA LEL=80 µg/L; Buchman, 2008). However, high variability between sites and sampling seasons suggest that further analysis should be performed in order to identify sites with continually high concentrations of manganese.

Steam water collected from the Aamjiwnaang First Nation Reserve was compared to those from surrounding communities. Concentrations of aluminum (mean=358.7 µg/L; p=0.001), cadmium (0.016 µg/L; p=0.002), cobalt (0.44 µg/L; p=0.031), and lead (0.65 µg/L ; p=0.032) were higher on Reserve than at the Kettle Point Reference community (Figure 2.4). Stream water concentrations of cobalt on Aamjiwnaang were also higher than those seen in Port Huron. Overall, metals concentrations in stream water were higher in communities within the "Chemical Valley" area than in the reference community. These findings, along with previous research, show that the area closest to the industrial

center in Sarnia, Ontario may be disproportionately exposed to contaminants (Atari and Luginaah, 2008, Miller and Luginaah, 2009).

5.1.1.2 Mercury Contamination in Stream Systems

It has been long established that the St. Clair River is a hot spot for mercury contamination (US EPA, 2009), however little is known about its concentrations in stream ecosystems in the region. This dissertation aimed to expand upon the knowledge that mercury contamination is occurring in the St. Clair River by addressing the issues in the surrounding tributaries. More specifically, it aimed to investigate the possibility that Talfourd Creek, which runs through the Aamjiwnaang First Nation Reserve, is overburdened with mercury contamination in comparison to streams in nearby communities. To account for seasonal variability, soils and sediment samples were collected during Fall 2010, Spring 2011, and Summer 2011.

Despite site and seasonal variability, concentrations in sediment and soil collected from on-Reserve were found to be significantly higher than those seen in the reference community (sediment $p<0.001$, soil $p=0.041$), as well as the eastern area of Sarnia (sediment $p<0.001$, soil $p=0.003$; Figure 3.4, Figure 3.5). In particular, a site along Talfourd Creek was found to contain sediment concentrations above the National Oceanic and Atmospheric Administration's lowest effect level set for freshwater invertebrate health (200 µg/kg d.w.; Figure 3.5). Similarly, soil collected near this site showed concentrations averaging above the ecological soils screening level for invertebrates and plants (100 µg/kg d.w, 300 µg/kg d.w., respectively; Figure 3.4). Mercury contamination near current petrochemical industrialization located in Spain has been documented (Nadal *et al.*, 2004). Similar to the case of "Chemical Valley," mercury concentrations near Spanish petrochemical facilities were found to be higher than those

at a reference site, though the finding was not significant. Concentrations of mercury in soils in "Chemical Valley," excluding the elevated on-Reserve site, were similar to those seen near the Spanish facilities.

Overall, mercury contamination in the region may still be of concern. Though the major historical source of mercury within "Chemical Valley" has been decommissioned for some decades, legacy hot spots of contamination still exist. The concentrations found at hot spots within Aamjiwnaang fall within those seen near chlor-alkali plants (Gonzalez, 1991). Moreover, the current releases and processing of mercury are possibly a cause for further contamination (i.e., emissions from coal-fired power plants, carbon black production, and waste facilities; Figure 3.3). Continued monitoring of the region is recommended.

5.1.2 Human Exposures to Multiple Chemicals

5.1.2.1 Mercury Exposures

Mercury exposures were estimated in mothers and children living on and surrounding the Aamjiwnaang First Nation Reserve. Hair, blood, and urine were collected from participants (n=43 mother-child pairs) and analyzed for mercury content. Exposures to methylmercury were estimated using total hair and blood concentrations. Participants on-Reserve (child mean=125.9 µg/kg, mother mean=220.8 µg/kg) were found to have similar concentrations to the general U.S. population, while off-Reserve participants (child mean=128.9 µg/kg, mother mean=281.8µg/kg) were found to have similar hair concentrations to the nation (Table 5.1, Table 5.2; McDowell *et al.*, 2004). Compared to subsistence Tribes across Canada, the Aamjiwnaang members showed slightly lower hair mercury concentrations (range: 2200-2710 µg/kg Hg; Beuter and Edwards, 2004). Concentrations among Aamjiwnaang mothers were also generally below

those seen in a Californian Native American Tribe residing near a cinnabar, elemental mercury, mining site (range: 0.03 – 1.80 µg/g; Harnley *et al.,* 1997).

Total mercury in urine is an estimate of exposure to inorganic forms of mercury. In both mothers and children, concentrations were higher in on-Reserve (child mean=0.61 µg/L, mother mean=0.95 µg/L) participants than off-Reserve (child mean=0.19 µg/L, mother mean=0.40 µg/L) and were significantly higher than the national mean (Table 5.2). Concentrations were similar to those seen near an active chlor alkali plant in Poland (near plant average = 0.40 µg/L; reference average = 0.21 µg/L; Jarosinska *et al.,* 2006). However, there is no epidemiological data referencing environmental exposures to inorganic mercury in residents residing near multiple other sources of mercury (i.e., coal-fired power plants) with which to compare Aamjiwnaang data. Concentrations among Aamjiwnaang and participants from the surrounding area were below those seen in the Californian Native American Tribe near a cinnabar mine (range = 0.40 – 12.5 µg/L) and on the lower range of those seen across the US for off-Reserve participants (Harnly *et al.,* 2006; CDC, 2012). However, on-Reserve mothers showed slightly higher urine mercury concentrations than the general U.S.

Methylmercury exposure occurs mainly through dietary fish consumption (ATSDR, 1999). Among Aamjiwnaang and surrounding areas, fish consumption patterns were examined through survey questionnaires. Estimated mercury intake through fish consumption was determined by multiplying the average amount of fish eaten per week by the estimated concentrations of mercury of each particular fish species consumed. Concentrations of hair mercury in mothers and children correlated to estimated mercury intake through fish consumption, as expected (Clarkson, 1993). Since fish consumption is

historically a large portion Ojibwe peoples' diets (Donatuto and Harper, 2008), it is expected that high mercury exposures would occur among the Aamjiwnaang. However, very low numbers of fish meals were seen among participants (57% of on-Reserve children and 32% of on-Reserve mothers reported eating zero servings of fish within the past 6 months; Table 3.3, Table 3.4), which was likely the reason for below average hair mercury levels. The potential implications of such a dietary change are addressed later in this chapter.

5.1.2.2 Multiple Metals Exposures

Multiple metals were measured in blood or urine collected from on and off-Reserve children and mothers (Table 5.1). Blood lead, manganese, and copper concentrations were fairly similar to Canadian national averages, though few children showed slightly elevated concentrations (Health Canada, 2010). Cadmium concentrations in children's urine (mean=0.88 µg/L; Table 5.2) were approximately 3-fold higher than those seen nation-wide and mothers' concentrations (mean=0.71 µg/L; Table 5.2) were nearly 2-fold higher. Elevated concentrations of antimony among Aamjiwnaang participants were noted, and were significantly higher in Aamjiwnaang children than the nation (p=0.002; Figure 5.2). Measurable concentrations of uranium (child mean=0.01µg/L, mother mean=0.01 µg/L) and vanadium (child mean=0.17 µg/L, mother mean=0.14 µg/L) were found among study participants, though these were below detection in national distributions.

5.1.2.3 Perfluorinated Compounds Exposures

Perfluorinated compounds (PFCs), a class of emerging chemicals, were analyzed in on-Reserve mothers and children. Thirteen compounds were measured in participants, of which six were measurable in Aamjiwnaang mothers and children (Table 4.1).

Distributions of PFNA (mean=3.48 ng/mL serum) and PFDA (mean=0.99 ng/mL serum) in Aamjiwnaang children varied above those seen in the US children ages 12-19 years (Table 5.2; CDC, 2012). Distributions of PFCs in mothers were similar to those seen across Canada and the U.S., with the exception of PFDA (Table 5.2; Health Canada, 2010; CDC, 2012). Mothers and children showed differing concentrations of many compounds, particularly PFNA and PFUnA. Children's PFNA was approximately 4-fold higher than mothers' (Table 4.5). There were no detectable levels of PFUnA in mothers, while there were in children. Such biomarker discrepancies suggest differences in exposures or metabolism and have been seen in the past (Calafat *et al.*, 2007; Kato *et al.*, 2009). In addition to reasons discussed previously (i.e., increased respiratory rates and increased ingestion rates per kilogram body weight), children may be exposed to PFCs at a higher rate than adults due to their increased contact with PFC-laden carpets and dusts (Trudel *et al.*, 2008).

5.1.2.4 Polycyclic Aromatic Hydrocarbons Exposures

Exposures to polycyclic aromatic hydrocarbons (PAHs) were estimated via concentrations in whole blood. Of the fifteen PAH congeners screened, twelve were found in measurable concentrations in Aamjiwnaang participants (Table 4.1; Table 4.7). Few studies have measured PAHs in whole blood (Sexton *et al.*, 2001). However, compared to an impoverished population near the Texas-Mexico border, concentrations among Aamjiwnaang mothers showed possible elevations of phenanthrene, acenaphthene, and anthracene. However, it is not well understood if these concentrations may be associated with health outcomes. Lipid-normalized anthracene was found to be higher among children whose mothers smoked than those whose mothers did not

(p=0.014). However, no other PAH biomarker in mothers or children was associated with smoking, wood burning, or distance to a major roadway.

5.1.2.5 Organochlorine Pesticides Exposures

A variety (21 congeners) of organochlorine pesticides (OCPs) was measured in on-Reserve mothers and children. Among them HCH, HCB, ppDDE, and ppDDT were found in measurable concentrations in both mothers and children. Compared to national distributions across the US and Canada, Aamjiwnaang children (mean=5.87 ng/g lipid) and mothers (mean=4.17 ng/g lipid) ranged fairly low in terms of HCB (Table 5.2; CDC, 2009; Health Canada, 2010). Concentrations of total HCH among Aamjiwnaang children (mean=5.89 ng/g lipid) were well above concentrations seen in the US (Table 5.2). This trend was also observed when comparing Aamjiwnaang mothers to women across Canada (mean=4.17 ng/g lipid; Health Canada, 2010). Likewise, ppDDE and HCB among Aamjiwnaang mothers were lower than levels seen in other First Nations women in Ontario, though ppDDT was slightly higher (Tsuji *et al.*, 2006). Further, DDT levels were much higher compared to background national populations for both mothers (mean=151.01 ng/g lipid) and children (mean=168.14 ng/g lipid; Table 5.2).

5.1.2.6 Polychlorinated Biphenyls Exposures

Polychlorinated biphenyls (PCBs) were measured in on-Reserve participants. In children, congeners 126 (mean=0.08 ng/g lipid), 180 (20.87 ng/g lipid), 118 (13.60 ng/g lipid), 138 (14.07 ng/g lipid), and 153 (11.19 ng/g lipid) were all found to be elevated compared to the general US population ages 12-19 years (Table 4.11, Table 5.2; CDC, 2009). Distributions of concentrations of PCB congeners 180 (13.28 ng/g lipid), 138 (8.06 ng/g lipid), and 118 (8.04 ng/g lipid) among Aamjiwnaang mothers were also above those seen in women across Canada (Table 4.11, Table 5.2; Health Canada, 2010),

though lower than those seen in First Nations women living in areas of Ontario known to be contaminated with PCBs (Health Canada, 2010; Tsuji *et al.*, 2006).

5.1.2.7 Polybrominated Diphenyl Ethers Exposures

Five of the twenty-two polybrominated diphenyl ethers (47, 99, 100, 153, and 209) were found in measurable concentrations in Aamjiwnaang mothers and children (Table 4.1). Concentrations of congener 153 in whole blood collected from mothers were found to be higher than the non-detectable levels of serum in Canadian women, but distributions among Aamjiwnaang spanned a similar range to those seen in plasma across women in the US (Health Canada, 2010; CDC, 2009). Congener 153 in Aamjiwnaang children's blood was lower than that seen in U.S. children (CDC, 2009). Distributions of other congeners among Aamjiwnaang mothers and children were below those seen nationally (Table 5.2).

5.2 Objective and Significance

5.2.1 Knowledge Gaps

The primary goal of my research was to conduct a broad screening of potential environmental contamination and human exposures among the Aamjiwnaang First Nation. Members of the Tribe reside amongst multiple industrial facilities, of varying proximities. Despite the numerous sources of chemical releases in the area, and attempts made by the Aamjiwnaang to initiate research, this is the first objective field study addressing contamination or exposures at Aamjiwnaang or the surrounding area. The project applied a holistic approach to understanding the many chemicals released, contamination of stream systems, human exposures, and human health in the area (Figure 5.1). We aimed at developing a basic understanding of the current conditions of contamination and exposures to multiple chemicals. Few studies of this kind have been

conducted investigating exposures to chemical cocktails at real-world concentrations, particularly in a heavily industrialized region such as Canada's "Chemical Valley," though such research has been called upon during the last decade (Sexton *et al.,* 2006). The U.S. National Research Council estimates that 41 million people live within a 4-mile radius of similar industrial pollution centers (Landrigan *et al.,* 1999), whom may be exposed to chemicals in a similar fashion to residents of the "Chemical Valley" area. In this study, we were able to characterize exposures in a First Nation Tribe comprised of 850 members. Measurable levels of metals (n=9), PFCs (n=6), PAHs (n=12), OCPs (n=4), PCBs (n=5), and PBDEs (n=5) were found in biomarkers collected from Aamjiwnaang participants. Moreover, many of these chemicals were elevated compared to national averages (Table 5.3). While no single chemical stood above established health benchmarks, the interactions among multiple chemicals, even at low levels, are not well understood in the environmental health sciences especially in susceptible sub-populations (Kortenkamp *et al.*,2007). Increased knowledge of mixture effects will help shape public health actions, as most guidelines are based off of information about exposure to a single toxic substance (ATSDR 1999; 2007).

Of particular note, this project addresses chemical exposures in adult females as well as children (ages 4-14). It was been well established that children may suffer higher risks and exposure rates than adults (Sexton and Adgate, 2001). Little is known about the potential health effects of complex mixtures in children (Carpenter *et al.,* 1998; Hu *et al.*, 2007). Furthermore, children's exposures are underrepresented in the literature. For example, the U.S. National Health and Nutrition Examination Survey (NHANES) did not measure PFCs, PBDEs, PCBs, or OCPs in children under the age of 12 years (CDC,

2009; CDC, 2011), and the Canadian Health Measures Survey measured these chemicals only in adults of 20 years of age and older (Health Canada, 2010).

Moreover, the project was aimed at measuring such chemicals in a high-risk group. First Nations, Native Americans, and Aboriginal groups of North America are under-represented in exposure research (Hightower *et al.*, 2006). It has been established that individuals practicing a subsistence lifestyle, such as traditionally seen among Ojibwe peoples, would be subject to exaggerated exposure rates in comparison to the general public (Harris and Harper, 2006).

For nearly half a century the Aamjiwnaang lands have been surrounded by the U.S. and Canadian multi-facility petrochemical industry. The Aamjiwnaang is accompanied by many other Tribes in the struggle of disproportionate environmental exposures (Nriagu *et al.*, 2012). Pollution effects more than health among Tribal members. Knowledge of a tainted environment has altered traditional practices and ceremonies such as hunting, fishing, and gathering that play a role not only in the diet and health of individuals, but also in economic, cultural, and spiritual aspects of Aamjiwnaang and other Native American communities (Smith, 2006). Specifically, among Aamjiwnaang participants in this study, little to no fish consumption was reported (Table 3.3, Table 3.4). This is a surprising finding given that the community has traditionally relied heavily upon local fish for sustenance. This shift away from a culturally and historically important diet has many potential health and lifestyle impacts, which will be discussed in depth (Section 5.2.3).

The project was designed in collaboration with the Aamjiwnaang First Nation Health and Environment Committee and commenced as a participatory-based project.

The Aamjiwnaang First Nation has been actively attempting to gain understanding of the chemical exposures, environmental contamination, and health concerns on-Reserve. All data and interpretations were reported to the Aamjiwnaang First Nation Health and Environment Committee and each participant received an individualized report about the levels of contaminants in their biomarkers. On-Reserve participants received a report describing the findings of the child's cognitive and behavioral assessment. Along with empowering Aamjiwnaang with personalized and overall results, the study also serves as a baseline understanding of the current state of environmental levels of multiple metals, human exposures to metals, PFCs, PBDEs, PCBs, and OCPs, and a variety self-reported health outcomes. This information will empower the Aamjiwnaang First Nation to play a role in developing regulatory laws aimed to reduce general amounts of chemicals released in the region.

5.2.2 Environmental Justice

Environmental Justice "embraces the principle that all people and communities are entitled to equal protection of environmental and public health laws and regulations" (Bullard, 1994). Equality reasons that no ethnic, racial, or socioeconomic population incur negative environmental consequences resulting from commercial, industrial, or municipal operations or of local, state, federal, and tribal policies at a rate disproportionate than any other population.

Environmental Justice incorporates cultural aspects of the population of interest as well as to promote communities in which individuals are afforded the confidence of a safe, productive, and nurturing environment (Bryant and Calleweart, 2008). Environmental Justice calls for the respect of both biological and cultural diversity. A wealth of literature has documented the unequal placement of coal-fired power plants,

chemical plants, refineries, incinerators, and hazardous waste landfills near economically afflicted communities (Bullard *et al.*2007; Mohai and Saha, 2007). Race of residents living in a neighborhood has been identified as the single most important predictor of position of hazardous waste facilities and penalties given to facilities for incurring pollution in white areas are reported to be higher than areas of other ethnicity (Bullard, *et al.* 2007).

As a tribe of the Chippewa band, the Aamjiwnaang Nation's land base was reduced from what was once greater than 2 million acres to 2850 acres now (Reynolds, 2002). Under land surrender with the Crown in 1827, the Chippewa Nations now live on four parcels one of which is the Aamjiwnaang Nation. These ancestral lands were settled prior to the region's post-war industrial boom. The disproportional placement of industry based on ethnic and economic factors, as occurred at Aamjiwnaang, is found in many regions of the U.S and exemplifies a common form of environmental injustice (Elliott *et al.*, 2004; Mohai and Saha, 2007, Oiamo *et al.*, 2011). The Aamjiwnaang community is surrounded by industry, may be underrepresented in decision-making committees, and is likely unable to gain availability of goods and services needed in order to respond to chemical spills (Schwartz, 1997). Historical pollution in the region is well documented (Ford, 2000). For example, mercury released into the St. Clair River between 1949 and 1969 by Dow Chemical's chlor-alkali facility resulted in the closure of the local commercial fishery in early-1970s (USEPA, 2009). This impacted 40 family businesses resulting in annual revenue losses of $2 million. Moreover, First Nation reserves are especially at risk for environmental inequality, as provincial jurisdiction may not apply on tribal lands (Schwartz, 1997). As of 2006, there were no regulations against moving

industrial wastes onto or storing it on tribal land and there was no bylaws in which to force the removal waste presently on Tribal lands (OECO, 2006). St Clair Chemical (more recently Welland Chemical), for example, was charged with using Aamjiwnaang lands as a waste disposal site in 1975 when an unknown amount of aluminum chloride was buried on the Reserve (Mallard, 1999). Within this project, 58 facilities within a 25 kilometer radius of the Reserve were reported to release multiple chemicals into the environment during 2010 (Figure 1.1). Furthermore, we found that residents of the Aamjiwnaang First Nation Reserve are subject to an over-burden of exposure to a variety of metals, PFCs, OCPs, and PCBs (Figure 5.1, Table 5.1, Table 5.2).

The Aamjiwnaang Nation is not alone; pollution of Tribal lands across the North America is well-documented (Schell *et al.*, 2003; Nriagu *et al.*, 2012). When considering the exposure of a particular community to contaminants of interest human health as well as environmental concerns should be reflected, especially in when pertaining to First Nations. It was noted through personal interactions that many participants and community members reported a general sense of fear in regards to pollution and exposures in the area. In fact, 95% of Aamjiwnaang mothers reported being worried or anxious about chemicals released within "Chemical Valley". Knowledge of pollution has limited activities, such as fishing, hunting and medicine gathering that play integral roles in the culture, spirituality, economy, and diet of Aamjiwnaang and other Native American communities (Smith, 2006). Tribal members often feel a sense of connectedness with wildlife and the environment (Donatuto and Harper, 2008). Many First Nations' belief is that the spirit, individual, family, community and environment are inter-related and belong equally to all generations (past, present, and future). The

presence of pollution not only affects human health, but also impacts the cultural traditions of the Aamjiwnaang people. In the words of an Aamjiwnaang member:

> "We are losing our people, losing our history. Our environment is affecting all life, not just humans" (CCI, 2010).

5.2.3 Dietary Changes

Fish consumption advisories and commercial fishing bans have been in place in the St. Clair River for the past four decades (US EPA, 2009). It is important to weigh the risks and benefits of fish consumption. Fish consumption is a major exposure pathway for a variety of toxic chemical including heavy metals, PBDEs, PCBs, and pesticides. Mercury, the chemical of particular concern, has been linked to adverse fetal brain development when exposed prenatally (ATSDR, 1999). For adult men and women not of child-bearing-age, negative health impacts remain unclear (Torpy *et al.*, 2006). Fish consumption has many benefits that potentially outweigh these risks (FAO/WHO, 2011; Torpy *et al.*, 2006). Fish and seafood are a known source of omega-3 fatty acids, which have been linked to a variety of positive health impacts including decreased blood pressure, decreased heart rate, and increased overall cardiovascular health. Docosahexanioc acid, one such fatty acid ingested through fish consumption, is linked to benefits during fetal brain development. Fish and seafood are also good sources of protein, energy, and other nutrients.

Traditionally, fish consumption accounts for a large portion of foods eaten among Native American and First Nation peoples (Donatuto and Harper, 2008). However, very low numbers of fish meals consumed were seen among Aamjiwnaang participants; 57% of children and 32% of mothers reported eating zero servings of fish in the past six months (Table 3.3, Table 3.4). Off-Reserve children were shown to have significantly

more fish meals per week than on-Reserve children (p=0.007). Among Aamjiwnaang participants, only 27% reported fishing as a hobby. It should be noted, however, that many of these participants further explained that the fish caught were released, and not eaten.

Similarly, fewer on-Reserve participants reported consuming local produce or game than off-Reserve participants. Those Aamjiwnaang participants who ate local produce reported consuming garden tomato, cucumber, and peppers. These reports are in agreement with a prior community-led survey (Figure 1.5). Again, only 27% of Aamjiwnaang participants in the current study garden. The dietary shift away from country foods is not a phenomenon unique to Aamjiwnaang. Diet changes from local food consumption towards Westernized foods have been seen in Tribes across North America (Kuhnlein and Chan, 2000; Arquette *et al.*,2008). Such shifts have been observed in correlation with increased concern for contamination, decreased diversity and abundance of country foods, and decreased grounds and time for food collection (Kuhnlein and Recouveur, 1996). A variety of adverse health impacts have been associated with consumption of Westernized foods (including diabetes, alcoholism, heart disease, and cancers), while there are no known adverse health outcomes, but many nutritional benefits, of consuming uncontaminated country foods. Additionally, diet shifts are associated with a change in traditional lifestyles. Food insecurities among First Nations peoples are linked with decreases in time spent during cultural activities and a more sedentary lifestyle. Lifestyle changes may affect the economic, social, spiritual, educational, mental, and economic well-being of a Tribe (Donatuto and Harper, 2008; Kuhnlein and Chan, 2000).

The ability to carry out traditional dietary practices among First Nations peoples is recognized as an environmental health and justice concern. Such peoples are often under-represented but unequally exposed to contaminants (Hightower, *et al.,* 2006). Current regulatory trends call for the incorporation of Native activities and cumulative effects of exposures to low levels of chemical cocktails during law making (U.S. EPA, 2002). Governances of water bodies should be appropriate for all peoples using the water body and should incorporate all potential uses of that water body and the wildlife within it. Polluted waters once used for subsistence fishing should be cleaned in order to allow for such used, and future contamination of waters should be limited. Regulations following the described recommendations may protect the health and culture of First Nations and Native Americans.

5.3 Study Limitations

The first aim of the study measured metal contamination in stream waters on and off-Reserve. Chemicals in stream water represent a brief temporal window of contamination. In particular, seasonal concentrations of metals in stream waters may vary (Nimick *et al.,* 2005). To account for seasonal variability, samples were collected during fall, spring, and summer. To further account for variability within each stream site, an aggregate of three subsamples were collected at each location. Total concentrations of each metal were analyzed, which may be over representative of biologically available levels. Nonetheless, this is the first study to measure stream contaminations in "Chemical Valley" incorporating concurrent measures at a reference location.

Aims Two and Three of this dissertation incorporated a cross-sectional study of biomarker data in mothers and children living on and surrounding the Aamjiwnaang First Nation Reserve. The study captures only a view of current exposures, did not follow

participants over time, may not be representative of exposure events over a period of time, and may not have captured windows of vulnerability. As such, the timeframe of exposures captured rely heavily on the half-life of chemicals in the body. Whenever possible, biomarkers of chemical body burden were analyzed (e.g. the top 2cm of hair represents approximately 2-3 months of methylmercury exposures). However, exposures measured in the study would not represent those related to reported health outcomes, as latency periods suggest that concurrent exposures and adverse effects would not be associated. Biomarkers of exposure were collected from participants from January 2010 through April 2012. It is feasible that exposures to chemicals may vary seasonally, as individuals often spend more time outdoors during summer months and snow cover during winter months may limit children's access to soils (Metcalf *et al.,* 2004).

Biomonitoring is most informational when an adequate reference population or background range is available. Many chemicals have been measured nationally in Canada and the U.S., allowing for comparison of the Aamjiwnaang population to a larger body of data (Health Canada, 2010; CDC, 2012). However in the absence of such literature (e.g. polycyclic aromatic hydrocarbons in whole blood), it is difficult the put the Aamjiwnaang participants' exposures in perspective. Nonetheless, the study showed that Aamjiwnaang mothers and children are exposed to many classes of hazardous chemicals. The project also adds whole blood PAH biomonitoring data to the literature, a contribution that may be of use to future researchers (Sexton *et al.*, 2011).

Recruitment was performed using a variety of media and the project was performed with community collaboration. A sample size of 43 mother-child pairs was achieved, making statistical sample sizes a major limitation for epidemiological studies.

Comparisons of metal biomarkers between on and off-Reserve participants would likely be missed, as in many cases upwards of 300 participants in each group would be necessary to observe a statistically significant difference. It is possible that those who chose to participate were already conscientious of environmental health issues in the area and therefore may not be representative of the public at large. Despite these limitations, this was the first biomonitoring study in the area which captured exposures to upwards of 160 chemicals in Aamjiwnaang mothers and children.

5.4 Future Directions

Among the seven metals analyzed in stream water Nation Reserve, aluminum, cadmium, cobalt, lead, and manganese were higher on the Aamjiwnaang First Nation Reserve than the reference community (Kettle Point, ON). Concentrations of aluminum in the area were elevated at many sites and may be of concern. Additionally, mercury concentrations were elevated in stream sediments and soil at a Talfourd Creek site located on-Reserve. This dissertation measured total concentrations of each metal, which may only partially be reflective of the bioavailable metals present in the water (Li *et al.*, 2009). While this study serves as a screen for metals contamination, these are not the only chemicals of concern in the region and not all metals were analyzed. Vanadium has been shown to be elevated in such petrochemical super centers and may be of interest in this region (Nadal *et al.*, 2004). Additionally, atmospheric concentrations of volatile organics have been shown to be elevated near Aamjiwnaang (Miller and Luginaah, 2009). Future ecological monitoring should incorporate temporal trends of biologically available aluminum, cadmium, cobalt, lead, manganese, and mercury, and a baseline assessment of additional chemicals should be established.

As previously outlined, dietary shifts may play an important role in First Nations' community health. This dissertation suggests very little fish consumption on the Reserve. A previous study done on Reserve estimated approximately 30% of residents consume local game, and even less consume locally caught fish (CWAIGG, 2005). While there is potential for mercury exposure via consuming contaminated fish from the St. Clair River, the benefits of educated fish consumption may outweigh the risks (FAO/WHO, 2011). In recent years, fish muscle sampled from the St. Clair River has shown concentrations of mercury have declined, but still may be of potential health concern (Gewurtz, 2010). Although larger fish of top predatory species may exceed reference levels for children and women of child bearing age, smaller fish of lower trophic species can be consumed safely for most individuals (FAO/WHO, 2011). A more in-depth community dietary assessment, incorporating health and culture facets of traditional diets, would create a more holistic understanding of the impact that the contaminated environment has had on diets and lifestyles at Aamjiwnaang. Such a project should strive to include Tribal elders and those members who are most likely to rely upon a subsistence lifestyle, as these groups are the most at risk for chemical exposures through contaminated country foods (Donatuto and Harper, 2008). Community education on safe size and species of fish may help to continue minimal exposures via contaminated fishes while allowing for nutritional aspects related to fish consumption.

Biomonitoring of volatile organic compounds (e.g. benzene and styrene) was not attempted in this dissertation and has not yet been measured elsewhere. This class of chemicals may be of particular interest for future biomonitoring studies, as it has been suggested that Aamjiwnaang and neighborhoods in southern Sarnia, ON are

disproportionately exposed to concentrations of these chemicals in the air (Miller and Luginaah, 2009). Further investigation into human exposures to volatile organic compounds is needed in this region.

This dissertation measured biomarkers of upwards of 160 chemicals among members of the Aamjiwnaang First Nation. Among these chemicals, PFCs and PCBs in children, along with cadmium, and to some extent antimony, molybdenum, and vanadium among participants have been recognized as present in potentially high levels and exposures. Among children in the study, on-Reserve participants showed higher levels of urinary vanadium than off-Reserve children. While the small sample size of the study limits the significance of this finding, the literature suggests that environmental concentrations of vanadium is higher near petrochemical plants (Nadal *et al.*, 2004) . Molybdenum and antimony are also often used in petrochemical industry as catalysts, and flame retardants, respectively, suggesting that the presence of these metals may be elevated within "Chemical Valley" (ATSDR, 2004; Kar, 2004). Thusly, it is feasible to believe that exposures closer to such facilities may be higher than surrounding areas. However, as such exposures have not been studied elsewhere, further investigation is needed.

In general, the main exposure route for cadmium is through the use of tobacco products (ATSDR, 2012). In this dissertation, no differences in urinary cadmium concentrations were found among smokers and non-smokers, though within this sample a large percentage of mothers reported smoking (<75%), likely masking any statistically significant results. Since cadmium concentrations among Aamjiwnaang participants are similar to those seen in smokers in the US, this is likely the route for participants in the

study (McKelvey *et al.*,2007). Culturally appropriate tobacco cessation efforts have been effective in the past, and would likely aid to alleviate cadmium body burdens (Makoskey-Daley *et al.*, 2008; Gryczynski *et al.*, 2010).

PFCs are emerging chemicals used in industrial purposes as repellant coatings (ATSDR, 2009). Fish consumption, a major exposure route for PFCs and PCBs, was not associated with biomarker levels of either of these chemicals (ATSDER, 2000; 2009). Other exposure routes for PFCs include consumption of other contaminated foods, and potentially inhalation of contaminated air and drinking contaminated water (Fromme *et al.*, 2009). Lipid-adjusted PCB levels in children were higher than those seen in lipid-adjusted serum across the U.S. (CDC, 2009). A variety of health concerns have been linked to elevated PCB exposures, including reproductive effects which have been identified an issue at Aamjiwnaang (Mendes, 2002; Safe 2005; Mackenzie *et al.*, 2005). Further investigation of exposures of these chemicals, along with those not studied here, and is needed in order to fully understand the body burdens of Aamjiwnaang members. For simplistic comparisons to the literature, a more variety approach to biomarker media should be used. Such studies should be aimed at including members not represented in this study, but may be of particular exposure risks, as well as women and children (Donatuto and Harper, 2008). Identifying the main exposure route of these chemicals among the Aamjiwnaang First Nation will allow for the next steps in exposure reductions.

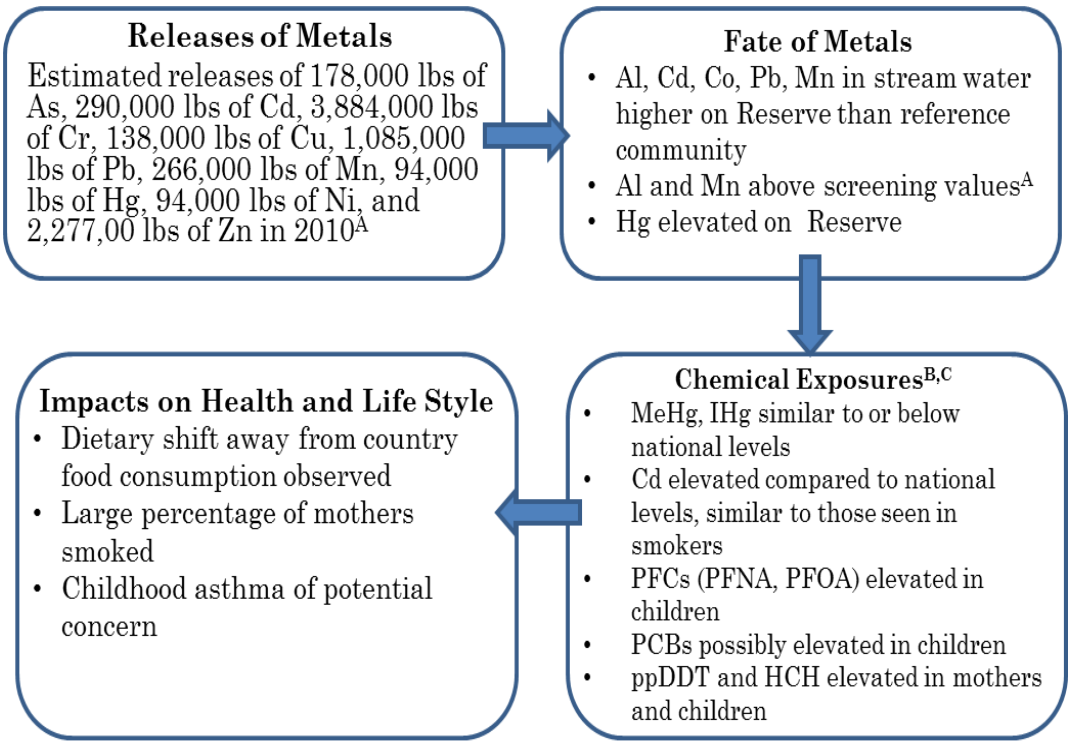

Figure 5.1 Major findings of sources and fate of metals, chemical exposures, and well-being issues.

A). Cryderman, D. Letourneau, L. Basu, N. Stream Metal Contamination in Canada's "Chemical Valley": Implications for the Aamjiwnaang First Nation, anticipated publication: Science of the Total Environment, fall 2013.

B). Cryderman, D. Letourneau, L. Johnston, S. Rogers, C. Basu, N., An epidemiological and environmental investigation of mercury contamination at the Aamjiwnaang First Nation, anticipated publication: Science of the Total Environment, summer 2013

C). Cryderman, D. Letourneau, L. Johnston, S. Rogers, C. Miller, F. Basu, N., Biomarkers of Chemical Exposure and Self-Reported Health at the Aamjiwnaang First Nation, anticipated publication: Environmental Health Perspectives, fall 2013

Table 5.1 Metal contamination in stream systems and exposures in humans at the Aamjiwnaang First Nation. Cited references are indicated in the table's footnote.

	Streams			Children			Mothers		
	Media	Locations above screening level [A]	Aamjiwnaang higher than reference	Biomarker	On-Reserve vs Off-Reserve	Above National Levels[B,C]	Biomarker	On-Reserve vs Off-Reserve	Above National Levels[B,C]
Aluminum	Water	Multiple, many on-Reserve	Yes	N/A	N/A	N/A	N/A	N/A	N/A
Antimony	N/A	N/A	N/A	Urine	No	Yes, but within range	Urine	No	No
Arsenic	Water	None	No	Urine	No	No	Urine	No	No
Cadmium	Water	None	Yes	Urine	No	Yes	Urine	No	Yes
Cobalt	Water	None	Yes	N/A	N/A	N/A	N/A	N/A	N/A
Copper	N/A	N/A	N/A	Blood	No	No	Blood	No	No
Lead	Water	None	No	Blood	No	No	Blood	No	No
Manganes	Water	One	No	Blood	No	No	Blood	No	No
Molybden	N/A	N/A	N/A	Urine	No	Yes, but within range	Urine	No	No
Zinc	Water	None	No	N/A	N/A	N/A	N/A	N/A	N/A
Mercury	Sedime	On-Reserve	Yes	Hair/Urine/Blood	No	No	Hair/Urine/Blood	No	No
Uranium	N/A	N/A	N/A	Urine	No	Yes	Urine	No	Yes
Vanadium	N/A	N/A	N/A	Urine	Yes	Yes	Urine	Yes	Yes

A) Buchman M. NOAA OR&R Report 08-1: NOAA Screening Quick Reference Tables. Seattle, WA. Office of Response and Restoration Division, National Oceanic and Atmospheric Administration 2008;34 pages.

B) Centers for Disease Control, Department of Health and Human Services. *Fourth National Report on Human Exposure to Environmental Chemicals, Updated Tables, September 2012* (2009) CDC, Atlanta, GA, pp 308. Available via http://www.cdc.gov/exposurereport/pdf/FourthReport.pdf Accessed 29 Oct 2012

C) Health Canada (2010) Environmental and Workplace Health Report on Human Biomonitoring of Environmental Chemicals in Canada. Results of the Canadian Health Measures Survey Cycle 1 (2007-2009). Ottawa, ONT. Health Canada; Available via http://hc-sc.gs.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/clms-ecms/report-rapport-eng.pdf. Accessed 29 Oct, 2012

Table 5.2 Comparison of Aamjiwnaang biomarker concentrations to national averages. Biomarker data for Aamjiwnaang mothers and children are compared to national mean when available. Chemicals for which there is no mean reported nationally are reported to have biomarker concentrations below detection for >40% of the national population (Health Canada, 2010; CDC, 2009).

	Children			Mothers		
	National Mean	Aamj Mean	p-value	National Mean	Aamj Mean	p-value
Sb (µg/L urine)	0.07	0.15	0.002	0.09	0.02	0.247
As (µg/L urine)	18.65	25.92	0.619	23.26	5.72	<0.001
Cd (µg/L urine)	0.31	0.88	<0.001	0.44	0.71	0.003
Cu (µg/L blood)	981.59	730.71	<0.001	1056.06	751.10	<0.001
Pb (µg/L blood)	10.20	9.56	0.703	10.20	7.54	<0.001
Mn (µg/L blood)	10.28	11.41	0.086	10.38	11.69	0.029
Hg (µg/L blood)	0.58	1.50	0.005	1.30	1.73	0.189
Hg (µg/kg hair)	220.00	126.00	<0.001	390.00	242.00	<0.001
Hg (µg/L urine)	0.30	0.46	0.255	0.43	0.76	0.027
Mo (µg/L urine)	75.52	117.29	<0.001	50.40	57.97	0.293
U (µg/L urine)	No national mean reported	0.01	N/A	No national mean reported	0.01	N/A
V (µg/L urine)	No national mean reported	0.17	N/A	No national mean reported	0.14	N/A
PFOA (ng/mL serum)	2.74	3.19	0.2	2.24	2.41	0.654
PFNA (ng/mL serum)	1.34	3.84	<0.001	1.43	1.04	0.001
PFDA (ng/mL serum)	0.22	0.90	<0.001	0.27	0.92	<0.001
PFUnA (ng/mL serum)	No national mean reported	0.99	N/A	No national mean reported	<LOD	N/A
PFHxS (ng/mL serum)	2.03	5.30	0.152	2.34	1.87	0.223
PFOS (ng/mL serum)	6.84	7.01	0.908	7.73	6.53	0.329
HCH (ng/g lipid)	No national mean reported	5.89	N/A	No national mean reported	4.17	N/A
HCB (ng/g lipid)	13.30	8.91	<0.001	15.80	6.76	<0.001
ppDDT (ng/g lipid)	No national mean reported	168.14	N/A	No national mean reported	151.01	N/A
ppDDE (ng/g lipid)	105.00	29.40	<0.001	241.00	21.67	<0.001
PCB 126 (ng/g lipid)	No national mean reported	0.08	N/A	17.80	0.16	<0.001
PCB 180 (ng/g lipid)	3.06	20.87	<0.001	9.31	13.28	<0.001
PCB 138 (ng/g lipid)	4.97	14.07	<0.001	6.98	8.06	0.049
PCB 118 (ng/g lipid)	3.06	13.60	<0.001	3.92	8.04	<0.001
PCB 153 (ng/g lipid)	5.86	11.19	0.001	12.28	6.97	<0.001
PBDE 153 (ng/g lipid)	8.05	1.50	<0.001	12.28	0.99	<0.001
PBDE 47 (ng/g lipid)	28.20	2.92	<0.001	22.08	3.28	<0.001
PBDE 99 (ng/g lipid)	6.88	1.39	<0.001	No national mean reported	0.89	N/A
PBDE 100 (ng/g lipid)	5.17	1.12	<0.001	No national mean reported	0.72	N/A
PBDE 209 (ng/g lipid)	No national mean reported	0.74	N/A	0.01	0.51	<0.001

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