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The Impacts of forest management practices on mercury contamination in small stream biota

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The Impacts of Forest Management Practices on Mercury Contamination in Small Stream Biota.

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Abstract

Mercury is a contaminant of global concern as it is present in all biota and ecosystems around the world. Small streams are influenced by the terrestrial systems that feed them. I examined the presence of mercury in small stream biota, the bioaccumulation of the mercury in higher trophic levels and the stream characteristics, including catchment disturbance that are associated with differences in mercury contamination among trophic levels. Sampling of periphyton, benthic invertebrates and fish occurred in 31 sites across 6 watersheds having different forest management histories. Mercury was present in all three biota types sampled with a wide range of mercury concentrations between and among sites and biota. Biota mercury concentrations were highest in the smaller size streams (small and medium) compared to the large streams with no differences between the different forest management histories. Biota mercury concentrations tended to have the highest association with local conditions including pH, conductivity, stream gradient and temperature. Brook trout [*Salvelinus fontinalis* (Mitchill)] had the lowest average concentrations of the two fish species collected with average mercury concentrations 50% less than dace species collected within the same stream. While biota mercury concentrations have been associated with disturbance in other studies, local stream conditions and stream size tended to have the highest association in my study.

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1.0 Introduction

Mercury is a toxin of global concern as it impacts all environments and life on earth. Atmospheric deposition of mercury is the primary source of mercury to terrestrial and aquatic systems with atmospheric mercury originating from natural and anthropogenic sources (Munthe *et al.* 1995, Pirrone *et al*. 2001). The distribution of mercury within an area can vary widely depending on disturbances to the environment, atmospheric conditions, or natural sources (Bacci 1989, Pirrone *et al*. 2001, Stein *et al.* 1996). Disturbances to the environment can include forest fires, forest management practices and factory emissions which can increase the mercury present in biota or influence the distribution of mercury (Garcia and Carignan 1999, 2005, Pirrone *et al*. 2001). Atmospheric mercury deposition can span the globe with inter- and intra-continental transportation possible based on winds, air-currents, temperature and topography (Shroeder and Munthe 1998). Mercury is naturally variable in the environment based on atmospheric deposition or terrestrial and aquatic sources which can all increase localized mercury concentrations (Shroeder and Munthe 1998, Ullrich *et al*. 2001).

Mercury present in the environment, as a result of natural and anthropogenic sources, may affect the biota. Mercury has been shown to have wide ranging effects on biota from reductions in populations or birth defects in amphibians to neurological disease and death in humans (Bank *et al*. 2006, McAlpine and Arake 1958). In Minimata Japan, a chemical company discharged methylmercury (MeHg) waste into the ocean resulting in the contamination of shellfish and fish. People consuming the shell fish and

fish suffered from neurological disease and death (McAlpine and Araki 1958). The World Health Organization (WHO) subsequently issued consumption guidelines for mercury contaminated fish and sea food because mercury contamination is not reduced by cooking (Mergler *et al*. 2007). In Ontario, the Ontario Ministry of Environment provides fish consumption guidelines for sport fish in many lakes and Health Canada restricts the commercial sale of fish with levels above 0.5ppm (OMOE 2009). The WHO has suggested that blood methylmercury levels of 200 µg/L or higher would cause neurological effects (WHO 2001). Kosatsky and Foran (1996) suggested that effects could occur at much lower blood concentrations. Research into mercury contamination is important due to the low concentrations of mercury necessary to cause birth defects or neurological damage.

Mercury in natural systems occurs as organic and inorganic mercury which may be present in various physical and chemical forms. (Ullrich *et al*. 2001). The vast majority is inorganic or elemental mercury and can constitute approximately 95% of atmospheric mercury (Lindqvist *et al*. 1991). While the majority of mercury is inorganic, methylmercury (MeHg) is the biologically available form and is passed between trophic levels because it binds in the adipose and muscle tissues of organisms (Laporte *et al.* 2002, Porvari 2003). Methylmercury is the most toxic form to biota (Lindqvist *et al*. 1991, Mergler *et al*. 2007, Sheuhammer *et al*. 2007). The sum of organic (MeHg) and inorganic mercury is expressed as total mercury (THg).

Atmospheric mercury can travel many thousands of kilometres before being deposited in areas that are not connected to the point sources (Morel *et al*. 1998). It is estimated that two thirds of all atmospheric mercury is from anthropogenic (industrial) sources (USEPA 2004) such as coal power generation, chlor-alkali plants, or mining and cement production. Coal generation has been estimated by the United Nations Environment Program (UNEP) to contribute 45 percent of all anthropogenic mercury (UNEP 2009). Up to two thirds of all anthropogenic mercury released in the year 2000 was from the combustion of fossil fuels (mainly coal; Pacyna *et al.* 2006). In 1995 an estimated 2427 tonnes of mercury was released into the atmosphere from atmospheric sources which was an increase over the 1990 levels (Pacyna *et al.* 2003).

Once mercury is transported to an area it is deposited to terrestrial environments through atmospheric deposition which is the primary source of mercury to terrestrial systems (Munthe *et al.* 1995). Most newly deposited atmospheric mercury is absorbed by soil and plant matter with little in runoff (Hintelmann *et al*. 2002). Mercury absorbed by plant matter has a high level of retention in the terrestrial environment without moving to the aquatic system (Boudou and Ribeyre 1997). St. Louis *et al*. (2001) found litterfall and throughfall had mercury concentrations 2 to 3 times that of wet deposition showing that the forest canopy increases the mercury flux to the terrestrial area. Litterfall is defined as the plant material dropped to the ground by terrestrial vegetation (leaves, twigs etc) while throughfall is the water that washes off the leaves. Mason *et al.* (2000) showed that litterfall had approximately 20 percent higher mercury concentrations than the wet

deposition to an area. While the mercury concentration relative to wet deposition can vary, it has been shown that litterfall has higher mercury level than wet deposition.

Terrestrial mercury that is not bound to the plant material is usually in the soil and humic layers of terrestrial systems (Lindqvist *et al*. 1991). Humic layers have high levels of mercury because litterfall and throughfall contribute to the humic layer by deposition of mercury bound to plant material (Lindqvist *et al*. 1991). Soils are the site of long-term mercury accumulation and can be a source or sink depending on the environment in the area (Harris *et al*. 2007). Mercury that does not become part of the mercury pool can be volatilized back into the environment (St. Louis *et al*. 2001) or transported to the aquatic environment (Allan *et al*. 2001). Soil mercury levels have been shown to directly influence the surface water mercury concentrations in nearby aquatic catchments (Åkerblom *et al*. 2008, Cooper and Gillespie 2001, Grigal 2002, Lindqvist *et al*. 1991). Cooper and Gillespie (2001) report soil mercury concentrations of 0.055 µg/g, which was over 3 times the level in lake sediments in the vicinity.

However, surface runoff from terrestrial sources is one of the biggest additions of mercury to aquatic systems (Allan *et al*. 2001, Bishop *et al*. 1995, Harris *et al*. 2007, Hintelmann *et al*. 2002). Bishop *et al*. (1995) showed that riparian zone soils and flora can increase the mercury concentrations of streams through litterfall. Sediments in aquatic systems are the major long term storage site of mercury (Harris *et al*. 2007) and, once mercury has been deposited, retention is high (Boudou and Ribeyre 1997, Mason *et al*. 2000).

Direct atmospheric deposition of mercury to aquatic systems occurs (Branfireun *et al*. 1996, 1998, Harris *et al*. 2007, Hintelmann *et al*. 2002, St. Louis *et al*. 1996), and can increase the mercury concentrations in the surface waters (Allan *et al*. 2001). Mercury deposited into aquatic and terrestrial systems can be redistributed to other areas of the ecosystem and re-volatilized into the environment. The USEPA (2004) estimated that one third of all mercury in the atmosphere once deposited is re-emitted from aquatic or terrestrial systems. Hintelmann *et al.* (2002) showed that fluxes of mercury from terrestrial systems occur from plants and soils. Mercury concentrations in disturbed areas can continue to be high even when anthropogenic sources have stopped adding new mercury to the area. Harris *et al*. (2007) showed that while newly deposited mercury was the most involved in the food web, old stored mercury can still enter into the food web. Reductions in mercury available to an area will quickly reduce the organismal mercury concentrations depending on the lifespan of the organism (large decreases within 5-10 years); however, it will take many years for overall mercury concentrations in an area to show a reduction due to generational turnover of species, flushing of sediments and releases from the sediment mercury bank (Harris *et al*. 2007, Francesconi *et al*. 1997).

Peatlands and wetlands can be sinks for total mercury and sources for methylmercury (St. Louis *et al*. 1996). Peatland mercury levels are influenced by the vegetation they contain. Liu *et al*. (2003) showed that mercury levels in wetland plant species were higher than that of the upland species. Mercury atmospherically deposited on the wetland and absorbed from the wetland soil was believed to be one potential reason why wetland plants had increased mercury concentrations over upland plants (Liu

et al. 2003). Wetlands differ in type, water column height and mercury concentrations. Wetlands can increase the mercury concentrations of fish downstream of their drainage (Branfireun *et al*. 1996, Castro *et al*. 2007, St. Louis *et al*. 1996). The concentration of mercury in water downstream of wetlands can be higher than expected background levels (Heyes *et al*. 2000). During times of high water levels (flooding of wetlands) there is evidence of much higher levels of methylmercury compared to lower water levels (Paterson *et al*. 1998, St. Louis *et al*. 1996, 2004).

Mercury methylation is the transformation of inorganic mercury to organic mercury (Morel *et al*. 1998). Methylation of inorganic mercury requires the transferring of a methyl group to the metal ion, with the assistance of either a photochemical or microbial process (Morel *et al*. 1998). Gilmour *et al*. (1992) showed that sulphate-reducing bacteria (SRB) are one potential agent for mercury methylation in aquatic systems. A decrease in sulphate-reducing bacteria can decrease the methylation activity even with an abundance of inorganic mercury (Gilmour *et al*. 1992). While SRBs have been shown to methylate mercury, it is believed other microbes and organisms can also methylate inorganic mercury.

Methylation rates in aquatic systems are related to several factors, including water temperature, pH, sediments and the level of dissolved oxygen. An increase in water temperature with a decrease in dissolved oxygen levels of a stream can cause increased methylation (Ullrich *et al*. 2001). Increases in levels of fine sediments can create anoxic zones that have increased methylation rates compared to those of oxygenated areas

(Francesconi *et al*. 1997). The pH of the water influences the microbial processes surrounding methylation rates (Kelly *et al*. 2003) with more acidic waters having increased methylation rates (Watras *et al*. 1995, Westcott and Kalff 1996).

Disturbance of forested catchments, either through fire or harvesting, may influence the factors associated with methylation rates. Impacts to the aquatic environment as a result of catchment disturbance have included higher sediment loads, lower dissolved oxygen (DO), higher water temperatures and increased dissolved organic carbon (DOC) (Davies *et al*. 2005, Francesconi *et al*. 1997, Garcia and Carignan 1999, Harriman *et al*. 2003, Hartman *et al*. 1996, MacDonald *et al*. 2003). Increased levels of dissolved organic carbon in runoff may increase the amount of mercury available to be methylated since dissolved organic carbon is known to bind and transport mercury (Kelly *et al*. 2003). Disturbance in the catchment increases the stream water temperature which can be a key factor in net mercury methylation rates in aquatic environments (MacDonald *et al*. 2003, Ullrich *et al*. 2001). Increased sediment levels as a result of catchment disturbance can lead to lower dissolved oxygen levels in streams which may result in higher mercury methylation rates in the anoxic zones (Hartman *et al*. 1996, Ullrich *et al.* 2001). Disturbances in the catchment can impact several factors that are associated with mercury methylation rates and potentially increase the amount of MeHg present in the area.

Catchment disturbance may result in an increase in the mercury supply to aquatic systems through surface runoff and increased methylation rates. Post-harvest, the amount

of water in terrestrial environments can increase because of a decrease in evapotranspiration leading to greater infiltration and surface runoff (Bosch and Hewlett 1982). Increases in deep soil water storage can persist for decades until such time as evapotranspiration rates have recovered (Perry 1998). Increased wet soil areas can create anoxic conditions with sulphate reducing bacteria (SRB) for methylation of inorganic mercury and can be considered a source of methylmercury to the aquatic system via runoff (Porvari 2003, Ullrich *et al*. 2001). Porvari (2003) found that post-harvest silvicultural treatment on an upland catchment increased the THg and MeHg flux to a lake by an order of magnitude compared to the reference site. Surface runoff from the catchment as a result of disturbance may increase available mercury for accumulation by periphyton and other biota (Branfireun *et al*. 1998, Desrosiers *et al*. 2006a).

Several studies provide support for the hypothesis that catchment disturbances increase mercury in aquatic systems and increase bioaccumulation in biota. Lakes with fire disturbed uplands have been shown to have increased nutrients and MeHg concentrations in biota (macroinvertebrates and fish) similar to those of harvested lakes after 2 years post disturbance (Allen *et al*. 2005). In studies conducted by Garcia and Carignan (1999, 2000, 2005) levels of mercury in zooplankton and fish were higher in harvested lakes than in reference or fire impacted lakes. Average levels of mercury in brook trout in the reference lakes were 0.53 µg/kg, 0.67 µg/kg in fire impacted lakes, and 1.35 µg/kg in logged lakes. On average logged lakes had more than twice the concentration found in fish in the reference or fire impacted lakes (Garcia and Carignan 2005).

Small streams may be more susceptible to disturbance and changes in mercury concentrations since they are so closely linked with their catchment. Small streams, especially headwater streams, are strongly influenced by direct lateral inputs from the terrestrial catchment since they receive little input from upstream communities (Montgomery 1999, Vannote *et al*. 1980). The close linkage between the aquatic and terrestrial environments that is present in small streams is important since disturbance anywhere in the catchment area of the stream will likely influence stream conditions and possibly biota mercury concentrations. Disturbance in a catchment increases both the surface runoff from the upland and the mercury concentration (MeHg and THg) within that runoff (Porvari *et al*. 2003). Since the flux of mercury to streams increases with disturbance in the catchment and small streams are so closely linked to their catchment, disturbance in the catchment of a stream has the potential to impact smaller streams more than larger aquatic systems.

Streams have a relatively simple food web structure which can bioaccumulate mercury and transfer mercury among trophic levels. The primary producer in streams is periphyton (algal complex with detritus and microbes) which is also largely responsible for the accumulation of mercury from the water into the aquatic food web (Cummins 1974, Boudou and Ribeyre 1997). Since diet is the primary mechanism of mercury bioaccumulation (uptake of mercury by biota) it is important to know what an organism eats (trophic level) to determine potential mercury contamination (Mason *et al*. 2000). Increases in contaminant concentrations at each trophic level by dietary uptake is known as biomagnification and can lead to potentially toxic concentrations in stream biota

(Mackay and Fraser 2000, Gobas *et al*. 1999, Sheuhamer *et al*. 2007). Since stream trophic levels are linked energetically, uptake of mercury in the primary producers may result in dangerous levels in any consumers (Trudel and Rasmussen 2006).

Periphyton and other primary producers are important to streams because they form the base of the food web (Cummins 1974). Periphyton is also the site of mercury uptake from the environment (water; Boudou and Ribeyre 1997), and a potential site for mercury methylation processes (Desrosiers *et al*. 2006a, b, Planas *et al*. 2000). Concentrations of mercury in primary producers (including periphyton) can be 100 to 10 000+ times that of the surrounding water column, and can be the single biggest input of mercury to higher trophic levels in aquatic sytems (Pickhardt *et al*. 2002, Bell and Scudder 2007). Since the primary method of mercury bioaccumulation is from the diet, mercury concentration in the periphyton of a stream is important to the trophic levels that consume it.

Since invertebrates and fish acquire the majority of their mercury from food (Hall *et al*. 1997, Mason *et al*. 2000, Watras *et al*. 1995), small changes in mercury concentrations in the lowest trophic level biota (periphyton) can result in rapid increases of mercury concentrations in invertebrate and fish tissues (Hall *et al*. 1997, Harris *et al*. 2007). Invertebrates generally have mercury concentrations 3 to 10 times that of the plant material they consume (Mason *et al*. 2000). The trophic transfer of mercury is measured by the bioaccumulation factor (BAF) and is the difference in Hg concentrations between two trophic levels. Concentrations of mercury in fish have been reported in the

order of 10^4 to 10^7 times that of water mercury concentrations. Methylmercury bonds strongly to protein sulphhydryl groups resulting in a long half-life for elimination (around two years in fish; Porvari 2003). It is this long half-life which results in transfer of MeHg between trophic levels, with upper trophic levels having concentrations up to 10^8 times higher than background water levels (Porvari 2003). While periphyton accumulates mercury from its environment, nearly all mercury present in invertebrates and fish is from the diet.

How an invertebrate feeds has an impact on the mercury concentrations it will have. Scrapers are invertebrates that shear off food that adheres to surfaces especially periphyton while shredders are organisms consuming coarse particulate organic matter (CPOM) such as leaves or macrophytes (Cummins and Klug 1979). Scrapers generally have very high mercury concentrations (0.05-0.2 μg/g THg; Castro *et al*. 2007) which can bioaccumulate in fish through predation since diet is the primary method of mercury transfer to fish. The insect Orders Ephemeroptera, Plecoptera and Trichoptera are known as the EPT complex and are commonly used in benthic bio-assessments of water quality (Barbour *et al*. 1999). The majority of taxa in the EPT complex belong in the shredder and scraper feeding groups (Cummins and Klug 1979) and can be considered primary consumers (Garcia and Carignan 2005).

Fish species are especially vulnerable to the effects of mercury contamination since they generally occupy the highest trophic level in a stream and nearly all of the mercury in fish is MeHg accumulated from their diet (Hall *et al*. 1997, Watras *et al*.

1998, Mason *et al*. 2000, Stafford *et al*. 2004). Fish like pike which are piscivorous generally have higher mercury concentrations than lower trophic level species like perch (Garcia and Carignan 2005). Yellow perch in Wisconsin lakes have a BAF value of approximately 500 000 while northern pike in Sweden have a BAF in excess of 1 million (Boudou and Ribeyre 1997) over water mercury concentrations. Fish mercury concentrations have been studied in depth because of the utilization of fish as a common food item by humans; however, the pattern of biomagnification and the relationship between environmental disturbance and the mercury concentrations is still poorly understood in stream environments.

Mercury contamination may occur at all levels of biota in streams and this contamination has been associated with neurological disease, birth defects and population decreases in aquatic biota and terrestrial organisms that consume them (Bank *et al*. 2006, McAlpine and Araki 1958). It is important to understand the factors that are associated with mercury concentrations present in biota and if disturbance influences these factors (Branfireun *et al*. 1998, Porvari 2003). Small streams may be more susceptible to this disturbance due to their close association with the terrestrial catchment they drain and their number across the landscape. Therefore, I have the following objectives and hypotheses:

1) Characterize the mercury levels in small stream biota in my study area north of Thunder Bay, ON. I hypothesize that mercury will be present in all trophic levels of small stream biota and, if mercury contamination levels are influenced by a

number of factors in the stream and its catchment area I expect that the levels of mercury present will vary among trophic levels and study sites.

2) Examine the trophic level differences in mercury of the small stream biota of Northwestern Ontario. I hypothesize that organisms at higher trophic levels will have higher levels of mercury, especially methylmercury, than organisms at lower trophic levels. Because mercury is biomagnified and transferred to the higher level organisms via the food chain higher trophic level organisms I predict there will be significant increases in the mercury between the three trophic levels studied.

3) Identify which local and catchment variables are associated with the presence and concentration of mercury. I hypothesize that catchment disturbance from forest management practices, which influence hydrologic characteristics of the catchment as well as habitat characteristics (e.g. temperature and sediment accumulation) will be positively associated with mercury levels in stream biota, possibly due to increases to methylation processes and increased flux of inorganic mercury into the stream.

2.0 Methods

2.1 Study Area and Site Selection

The study area is located northeast of Thunder Bay, Ontario, Canada and consists of streams with catchment areas of between 1 and 50 km^2 with the larger catchments draining into Lake Superior (Figure 2.1). The sites are contained within the Thunder Bay Plains, and Nipigon Plains Ecoregions (Wickware and Rubec 1989). The Thunder Bay Plains contains primarily diabase, greywacke and shale bedrock formations and is located along the north shore of Lake Superior. The Nipigon Plains ecoregion is dominated by diabase bedrock (Wickware and Rubec 1989**).** The climate of Thunder Bay, ON and area range from daily average temperatures of 17.6 ºC in July to daily averages in January of -14.8 ºC, with an average annual precipitation of the area is 711.6 mm (Environment Canada 2010).

Thirty-two study reaches were sampled within 31 separate streams (Table 2.1) with varying amounts of harvesting disturbance present in the catchment area. Two study reaches were located on the same 10 km stream because of the locations of the other nested streams within the catchment.

The study area is dominated by northern Boreal forest species with forest management being the primary land use impact (Sims *et al*. 2007). Sites were selected so that a variety of disturbance histories and characteristics would be included in the study (Table 2.2). An attempt was made to minimize variation in local and catchment scale characteristics among sites. Sites required a free flowing unobstructed reach of at least

30 meters (up to a maximum of 50 meters). All sites were free of direct beaver and mining activity.

Study sites were located within 5 large (30-50 km^2) catchments with small (1-3 km^2) and medium (5-10 km^2) catchments nested within each of the large catchments (Figure 2.1). Catchments were delineated using the filled Ontario Provincial 20 meter resolution Digital Elevation Model (DEM). An enhanced flow direction grid was generated from the DEM and forced to coincide with mapped hydrographic layers using techniques described by Kenny and Matthews (2005). Environmetal Systems Research Institutes (ESRI) ARC GIS (version. 9.1) with Spatial Analyst was used to delineate contributing areas above each study reach. All characteristics of the study catchments were quantified using ARC GIS.

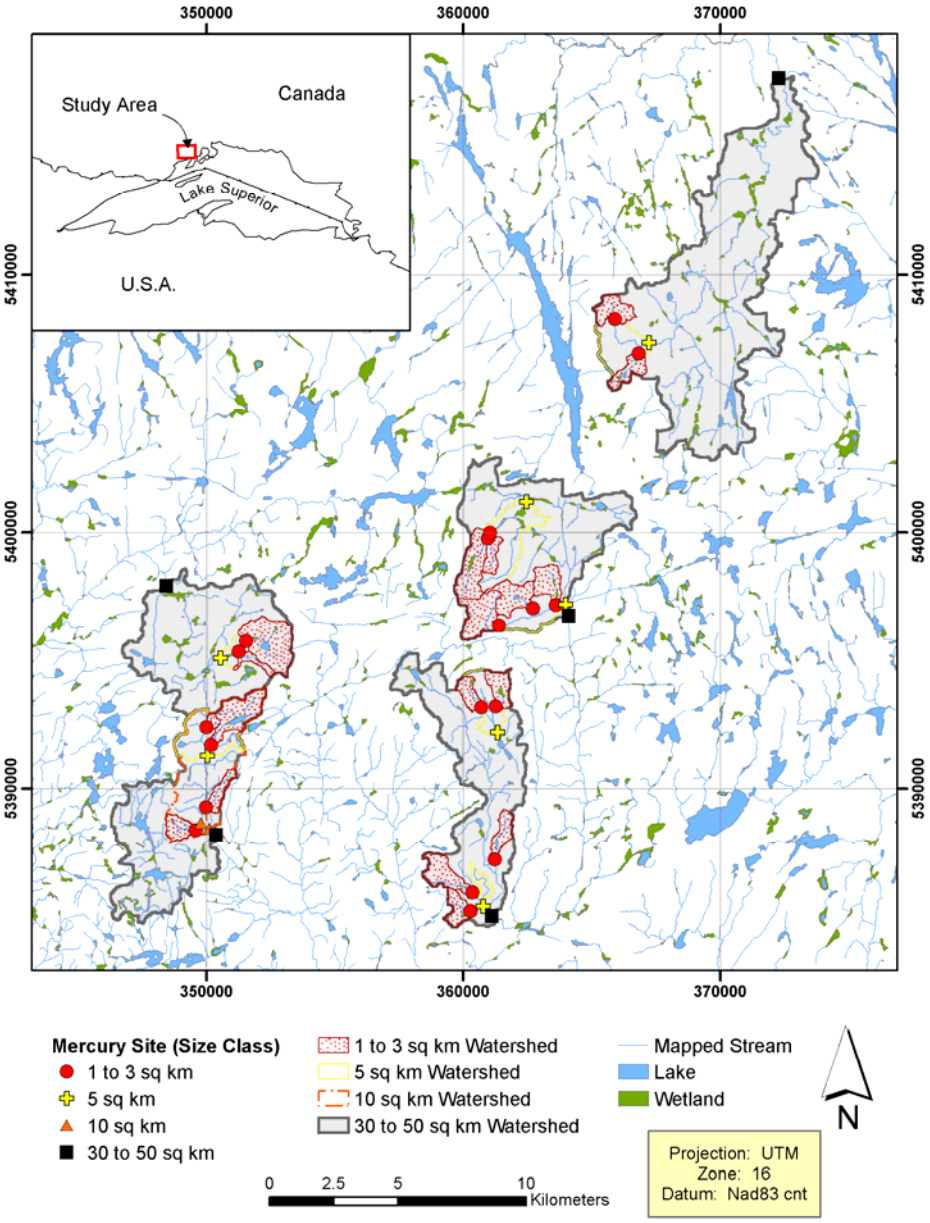

Figure 2.1 Study catchments delineated by stream size class catchment area.

Table 2.1 Catchment size and number of stream reaches of each sub-catchment stream size.

Catchment	Catchment Size (km^2)	Number of 1 km^2 stream catchments	Number of 3 km^2 stream catchments	Number of 5 km^2 stream catchments	Number of 10 km^2 stream catchments	Number of 30 km^2 stream catchments	Number of 50 km^2 stream catchments	Total Reaches Sampled
Beck	30	5	0	2	0	1	0	8
Walkinshaw	30	3	0	1	2	1	0	7
Northeast Current	30	1	1	1	1	1	0	5
Mackenzie West	30	5	0	2	0	1	0	8
Furcate	50	2	0	1	0	0	1	4

Table 2.2 Total number of streams of each size class broken down by the forest management history of the site (stream cut class).

Forest Management	Number of Streams	Stream Size Class (Catchment Size) Small 1 and 3 km^2	Medium 5 and 10 km^2	Large 30 and 50 km^2
No Cut	15	9	4	2
Low Cut (< 10% in last 10 years)	10	6	2	2
High Cut (>30% in last 10 years)	6	2	3	1
Total	31	17	9	5

2.2 Local Habitat Variables

Local habitat variables collected between June and July 2008 included canopy closure, riparian width, stream flow, woody debris counts, stream gradient, percent fine sediment, pH, conductivity and water temperature measurements (See Appendix 1 and 2 for a summary of local variables). Canopy closure was measured using a concave densiometer (%) mounted on a tripod. Densiometer readings were taken at the start, middle and end of each reach and were based on the average of readings taken while facing upstream, downstream, left and right. Riparian width was measured on both sides of the stream at the start, midpoint and end of the reach, using meter tapes (decimetre). The riparian widths were measured from the highwater mark to the distinct change in slope or a point of distinct change from riparian wetland vegetation to upland forest. Stream flow was measured at 3 positions per transect, with 5 transects within every stream study area. The measurements were taken at 25, 50 and 75 percent of the stream wetted width. The stream width was divided into 3 or 5 equally spaced points. Every flow reading was taken by a Marsh-McBirney Inc. flow meter (Flo-Mate Model 2000 Portable Flowmeter), according to manufacturers guidelines at the 60 percent depth mark in the stream (m^3/s). Large woody debris (greater than 5cm diameter) was counted within each 5 meter interval along the length of the stream reach. The sum of all 5 meter intervals provided the total woody debris count for a stream reach. Stream gradient was measured every 5 meters looking upstream using a clinometer (Suunto, PM5-360). The stream gradient was measured as the percent change from downstream looking upstream. Substrate classification was made by measuring 5 representative substrate samples equally spaced along transects that were established at every meter along the length of the

reach. Substrate classifications were based on Wentworth (1922). The pH (0.1), conductivity and the temperature (ºC) of the stream were collected using a YSI 650MDS multi-meter with a YSI 600QS multi-probe.

2.3 Catchment Scale Variables

Several catchment scale variables were measured using GIS including the percentage of lake, wetland, recent harvest, surface geology, and road density within the catchment (See Appendix 3 and 4 for a summary of catchment variables). The percent wetland and percent lake refer to the percentage of the catchment that is covered by lakes or wetlands. Recent harvest percent is the percentage of the catchment that has had forest harvesting within the last 10 years. The road density is the total of linear meters of road per square kilometre of catchment (m/km^2).

Levels of forest harvesting within each catchment were assessed using Ontario Forest Resource Information GIS data with updates from local forest companies. Surface water features, lakes, wetlands, roads, harvesting and mapped streams were assessed from Ontario's Natural Resources Values Information System (NRVIS) GIS database (OMNR 2005, 2009). Surficial geology was defined using digitized versions of Northwestern Ontario Engineering and Geology Terrain Study Maps (Mollard and Mollard 1981a, b).

All sites were classified according to their individual harvest histories (cut class), stream catchment size (stream size) and catchment (nests). There were three cut classes used: no cut, low cut and high cut. No cut includes all streams with less than 1% harvesting in the catchment basin in the last 10 years. Low cut streams had less than 10%

harvest in the last 10 years and high cut streams had more than 30% harvest in the catchment area of the stream within the past 10 years as of 2007.

2.4 Biota sample collection

2.4.1 Periphyton Collection

Three periphyton samples per site were collected using USEPA protocol for rapid stream assessment (Barbour *et al*. 1999). Rocks or substrate were scrubbed using plastic scrub brushes before the samples were placed in individual plastic sample jars for transport to the lab. Surface area scrubbed varied between samples but was measured by a 7.5 cm diameter section of plastic pipe to provide a rough estimate of area sampled. All samples were sorted for invertebrates or debris using a dissecting microscope before being filtered using Watman glass fiber filters (0.7 micron pore size). All samples were frozen (-20°C) in de-ionized water contained in single use glass sample containers with water prior to analysis for mercury.

2.4.2 Invertebrate Collection

Three invertebrate samples were collected per site using a modified Surber method consisting of a 500µm mesh D-frame dipnet, Teflon scrub brush and a 30 x 30 cm sampling square. The sampling square was placed immediately upstream of the D-net, which was placed in a position to collect all invertebrates and debris removed from the substrate upon sampling. All rocks and substrate within the sampling square were scrubbed to remove aquatic macroinvertebrates and debris for collection. Samples were placed in individual sample containers to be sorted in the lab under a dissecting microscope. All samples were sorted the day of collection to remove all Ephemeroptera,

Trichoptera and Plecoptera, which were placed in single use glass sample containers and frozen (-20°C) with water pending analysis for mercury.

2.4.3 Fish Collection

All fish were collected by the Ontario Ministry of Natural Resources using a single pass upstream electrofishing protocol in July and August 2008. All streams had blocker nets at the top and bottom of the reach. A Smith–Root (model 15-B) generator powered backpack electrofisher was used for all fish sampling. The number of netters (1-4) varied depending on the size of the stream. All fish collected were identified stream-side, with all non-target fish weighed (grams) and measured (total length, mm) before being released back into the stream. All fish kept for tissue analysis were euthanized using an overdose of buffered MS-222 (tricaine methanesulfonate) mixed with stream water, before being put on ice for transfer to the lab. A maximum of 15 fish per site were collected consisting of 5 brook trout (*Salvalinus fontinalis*) and 10 *Phoxinus* dace [Finescale dace (*Phoxinus neogaeus*), Northern Redbelly dace (*Phoxinus eos*)]. If too few *Phoxinus* or no *Phoxinus* were present Black Nose Dace (*Rhynicthys atratulus*) were also collected.

Samples were weighed using a Sartorius scale (0.0001g) and total length (mm) and fork length (mm) measurements were taken. Tissue samples consisted of a dorsal skin-on fillet put into new individual Whirl-pak bags and frozen until analysis. See USEPA "Fish Sampling and Analysis Third Edition" for more details on dorsal sample collection (USEPA 2000).

2.5 Sample Analysis

All samples were processed by the Lakehead University Environmental Lab. A 0.2 - 1.5 g sample was digested with HNO_3/H_2SO_4 [7:3 ratio] in an I-CHEM 300 40ml vial, under reflux conditions at 100°C for 2 hours. The digestate was treated with 0.5ml of 0.2N BrCl solution to achieve a complete oxidation of the sample. The digestate was then diluted to 40 ml with double distilled water (ddw) and allowed to sit for at least 4 hours prior to analysis. The total mercury (THg) was measured using a Brooks-Rand Model III Cold Vapour Atomic Fluorescence Spectrophotometer. The procedures used are described in EPA Method 1631b "Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation" (USEPA, 2001).

2.6 Quality Assurance/Quality Control

The Lakehead University Environmental Laboratory demonstrates competency through participation in the National Water Research Institute [NWRI] proficiency testing programs for Mercury in water.

Protocols are followed to ensure the reliability of the results and consist of guidelines, procedures and practices developed and implemented to produce quality data. Blanks, certified standards and duplicates are used to verify the effectiveness of quality control procedures and to evaluate the quality of the data.

2.7 Analyses

Sites (n=31) were grouped within 3 categories: the size of the stream [small (n=17), medium (n=9) or large (n=5)], recent disturbance history [no (n=15), low (n=10), high (n=6)], and the 30 or 50km^2 catchment that they were in [nest (n=5)].

Mercury concentration in biota was analyzed using a full factorial ANOVA using SPSS 17.0.1 (SPSS Inc, Chicago, Illinois). The factorial ANOVA was run using the 3 categories (stream cut class, stream size class and nest) to evaluate the overall contribution of each category as well as interactions among categories, and variability in mercury concentration in the 3 biota type (periphyton, invertebrates and fish) mercury concentrations. Mercury concentrations (μg/g) were log transformed. A nested ANOVA was not used in this study as the unequal breakdown of the study sites into the different categories and some categories missing mercury concentrations would violate the assumptions of a nested ANOVA.

A paired t-test was performed using SPSS to determine if the differences in the fish mercury concentrations between brook trout and dace species within the 8 sites where both species were collected were significant.

A MANOVA was performed using SPSS to determine the influences of the different dependent variables on the among site groupings and to determine which variables were associated with the concentration of mercury. Variables that were contributing to the variability of the groupings were added to a discriminant function analysis (DFA).

A discriminant function analysis (DFA) was run using SPSS to determine if mercury concentrations could be classified according to the local and catchment variables. The variables run in the DFA were extracted using the MANOVA of variables in this study by site groupings. The DFA is the statistical opposite of the MANOVA.

Redundancy analysis (RDA) was performed to determine the relative association between the local and regional log transformed variables and the fish, invertebrate and periphyton mercury concentrations using Canoco 4.5 (Biometris, Wageningen, The Netherlands).

3.0 Results

At each of the 31 streams sampled 3 periphyton samples, 3 invertebrate and 15 fish samples (5 Brook Trout, 10 Dace) were collected if possible. A total of 92 periphyton samples was collected from the 31 sites sampled with only 2 samples from Beck1C. Aquatic invertebrate samples were taken from every site, however only 89 samples were collected in total with 3 sites (Walk 1D, Walk 10B, MW1A) unable to produce adequate invertebrates (enough mass for invertebrates of the PTE complex to be analyzed) for 3 samples per site to be analyzed. Fish samples were collected from 24 of the 31 sites with brook trout sampled from 10 sites. A total of 184 fish were collected 48 of which were brook trout (Table 3.0.1).

Table 3.0.1 Stream cut class, size class and the number of each type of biota mercury samples collected at each site with site code.

Site	Cut Class	Size Class	# of Periphyton Samples	# of Invertebrate Samples	# of Dace Samples	# of Brook Trout Samples
Beck 1A	1	1	3	3	0	0
Beck 1B	1	1	3	3	10	0
Beck 1C	1	1	2	3	0	0
Beck 1D	3	1	3	3	0	0
Beck 1E	2	1	3	3	5	0
Beck 5A	2	2	3	3	10	5
Beck 5B	3	2	3	3	10	0
Beck 30A	2	3	3	3	5	2
Walk 1A	1	1	3	3	0	5
Walk 1C	1	1	3	3	10	0
Walk 1D	1	1	3	1	3	3
Walk 5A	1	2	3	3	9	0
Walk 10A	1	2	3	3	2	5
Walk 10B	1	2	3	2	0	5
Walk 30A	1	3	3	3	5	5

Table 3.0.1 Continuation Stream cut class, size class and the number of each type of biota mercury samples collected at each site with site code.

Site	Cut Class	Size Class	# of Periphyton Samples	# of Invertebrate Samples	# of Dace Samples	# of Brook Trout Samples
NEC 1A	3	1	3	3	2	0
NEC 3A	3	1	3	3	10	0
NEC 5A	3	2	3	3	10	0
NEC 30A	3	3	3	3	10	0
MW1A	1	1	3	2	0	0
MW1B	1	1	3	3	0	0
MW1C	2	1	3	3	0	0
MW1D	2	1	3	3	9	0
MW1E	2	1	3	3	0	0
MW5A	1	2	3	3	5	0
MW5B	2	2	3	3	1	5
MW30A	1	3	3	3	5	5
Fur 1A	2	1	3	3	0	0
Fur 1B	1	1	3	3	10	0
Fur 5A	2	2	3	3	1	0
Fur 50A	2	3	3	3	4	8
Totals			92	89	136	48

3.1 Mercury Biota Concentrations

Mercury levels in periphyton were highly variable among the sites. There was a significant difference ($F_{(2,71)}$=7.115, p=0.002) in average periphyton mercury levels among the stream size classes with small streams (0.124 µg/g ± 0.232 SD) having lower periphyton mercury levels than medium (0.157 µg/g ± 0.318 SD) and higher than large streams (0.044 µg/g ± 0.077 SD; Figure 3.1.1). Periphyton mercury levels also differed significantly among the catchment nests ($F_{(4,71)}$=4.604, p=0.002) mainly due to high levels measured in the Furcate sites (0.219 µg/g ± 0.200 SD; Figure 3.1.2). There was no statistically significant difference in the periphyton mercury levels among the harvest treatments and no interaction effects among the factors (Table 3.1.1). Mean square values were used to interpret the relative contribution of each term to variance explained by the model.

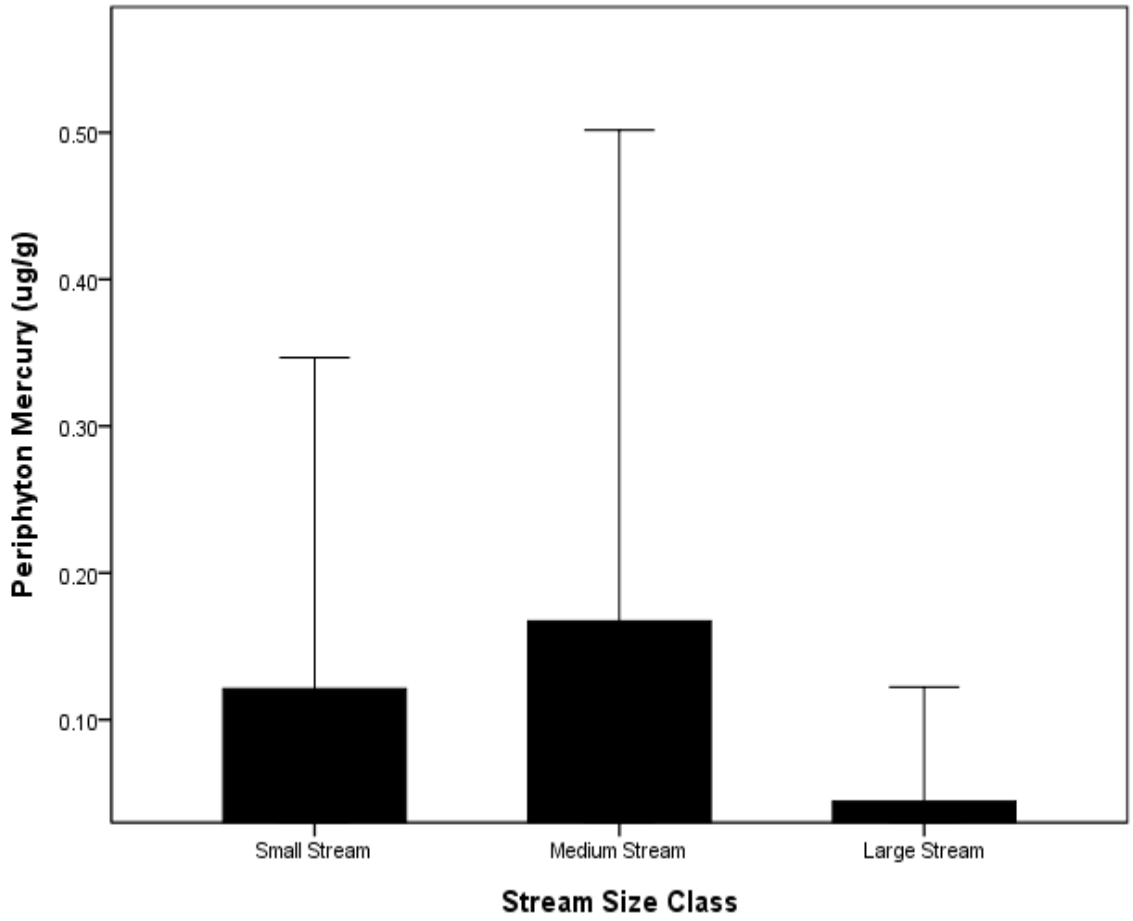

Figure 3.1.1 Mean (+ SD) periphyton mercury concentrations (µg/g wet mass) of streams by stream size class.

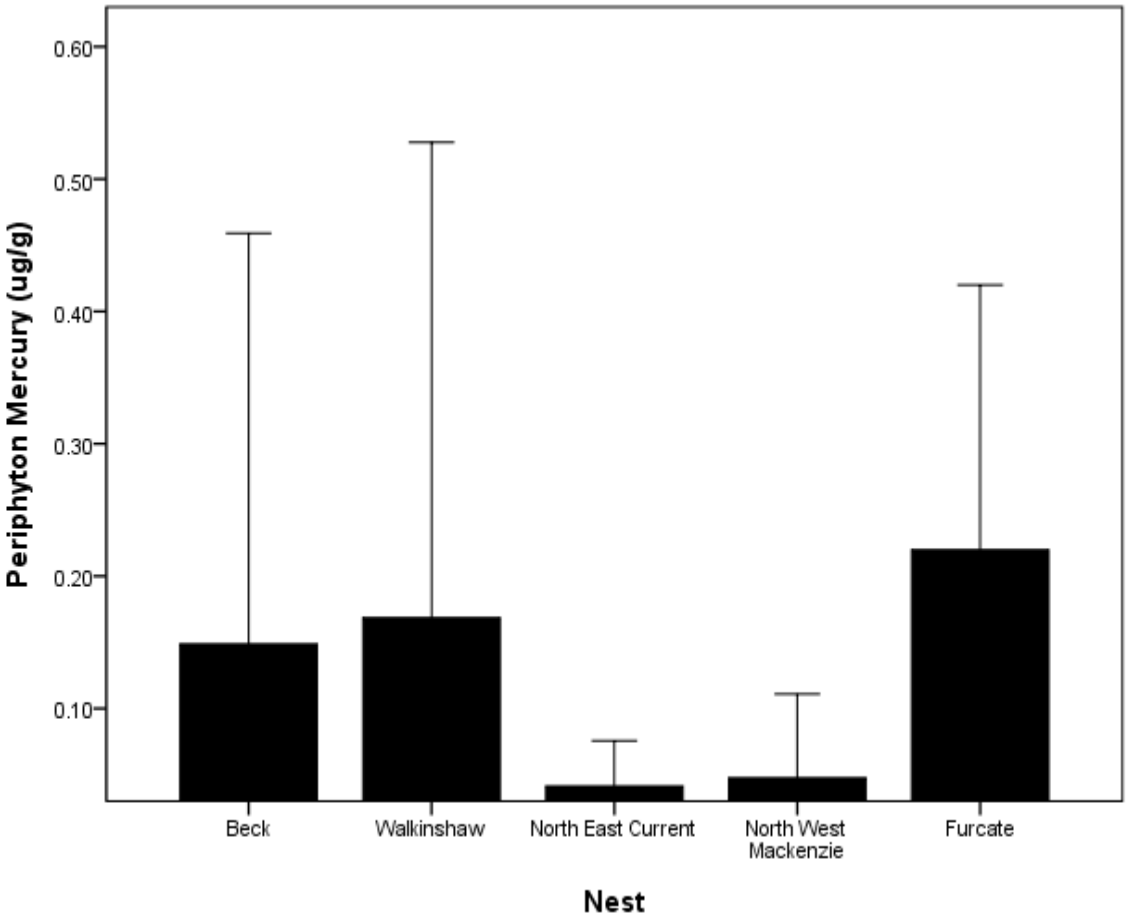

Figure 3.1.2 Mean (+ SD) periphyton mercury concentrations (µg/g wet mass) for each sample site nest.

Table 3.1.1 Summary of Factorial ANOVA showing sample significance values for the Periphyton Mercury Concentrations (log µg/g wet mass) of the three site classification groups. Interaction terms for the site classification groups are also included.

Classification Term	Mean Square	F	df	Significance
Size Class	3.615	7.115	2,71	0.002
Cut Class	0.106	0.208	2,71	0.813
Nest	2.339	4.604	4,71	0.002
Size Class * Cut Class	0.493	0.971	2,71	0.384
Size Class * Nest	0.712	1.418	6,71	0.220
Cut Class * Nest	0.629	1.238	2,71	0.296

Invertebrate mercury concentrations (µg/g wet mass) were highly variable among the sites. Small (0.168 µg/g ± 0.243 SD) and medium (0.168 µg/g ± 0.141 SD) size streams had the highest invertebrate mercury concentrations compared to large streams (0.132 µg/g ± 0.043 SD; $F_{(2,68)}$=6.670, p=0.002; Figure 3.1.3). The stream size class and cut classes (cut class*size class) interaction was significant when comparing invertebrate mercury concentrations ($F_{(2,68)}$=4.787, p=0.011). In the small streams the high cut class had the lowest invertebrate mercury concentrations compared to the no and low cut classes. The no cut streams had the highest invertebrate mercury concentrations and were also highly variable (Figure 3.1.4). Medium size streams show large variation with the low cut streams having the lowest mercury but highest variation (Figure 3.1.5). The Northwest Mackenzie and the Beck catchments have the highest variability in the small and medium size streams for invertebrate mercury concentrations (Figure 3.1.6). The stream cut class and nest interaction explains the largest source of variability in invertebrate mercury concentrations ($F_{(2,68)}$=12.660, p<0.001; Table 3.1.2). The forest management history or the cut history of an area is reflected with different nests (catchments) having a different historical cut percentage (Figure 3.1.6).

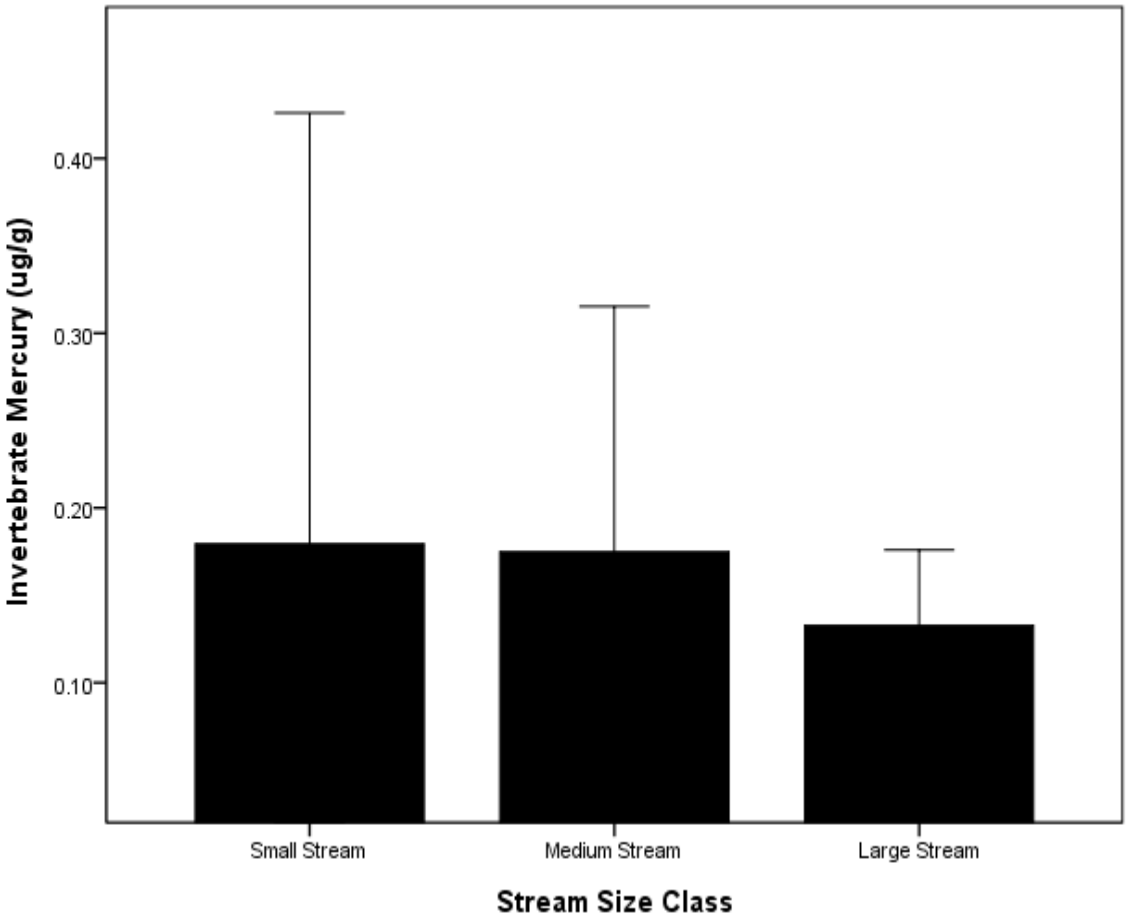

Figure 3.1.3 Mean (+ SD) invertebrate mercury concentrations (µg/g wet mass) for each stream size class.

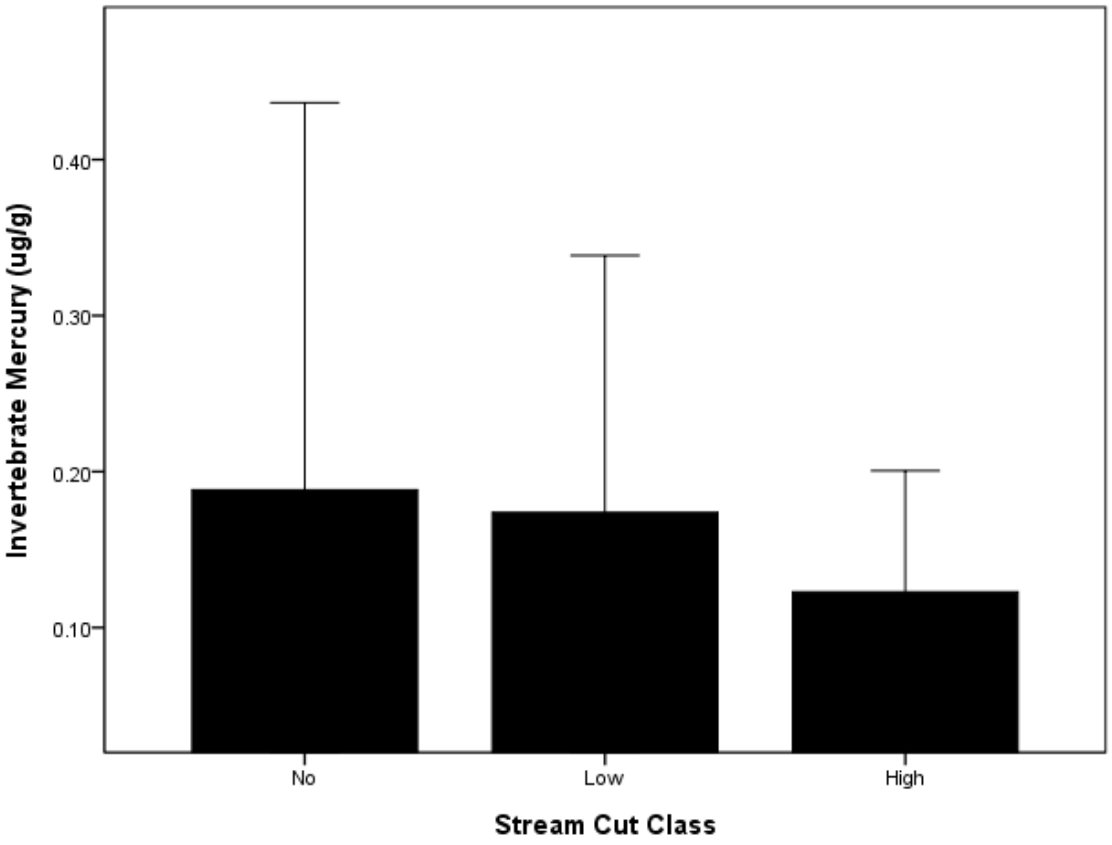

Figure 3.1.4 Mean (+ SD) invertebrate mercury concentrations (µg/g wet mass) for each stream cut class.

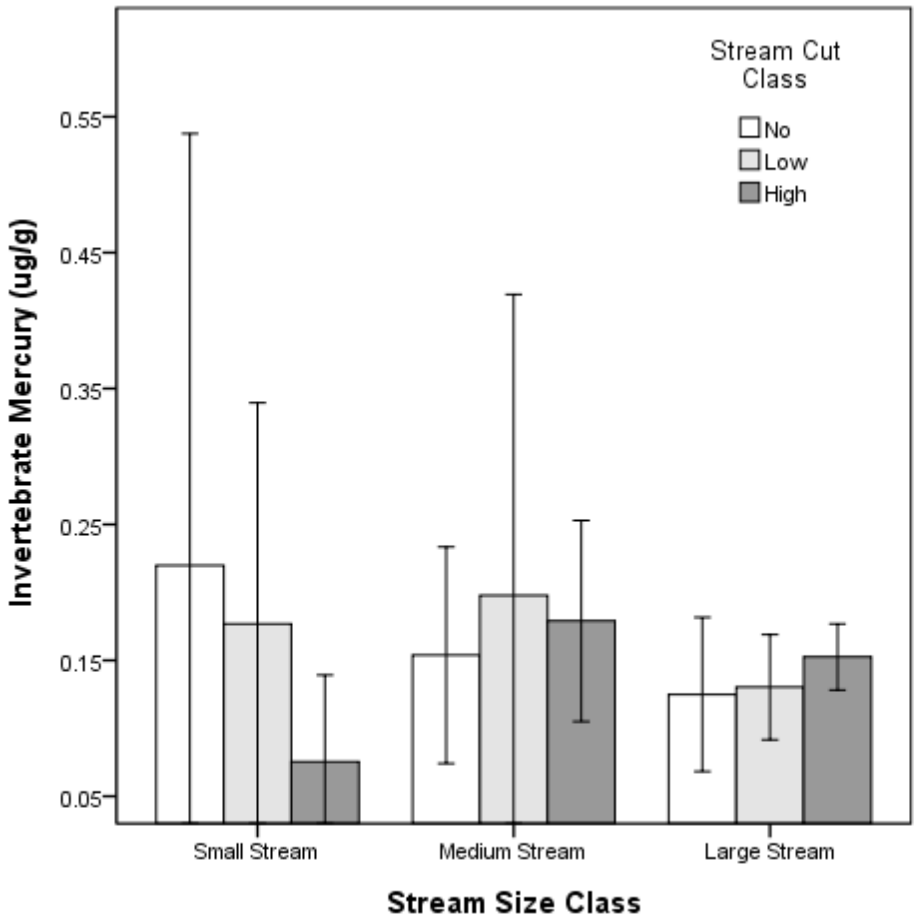

Figure 3.1.5 Mean (±SD) invertebrate mercury concentrations (µg/g wet mass) categorized by stream size and cut class.

Table 3.1.2 Factorial ANOVA table of the invertebrate mercury concentrations (log µg/kg) with the site classification terms and the interaction terms. All associated statistical values are reported for both classification terms and interaction terms.

Interaction Term	Mean Square	F	df	Significance
Size Class	3.890	6.670	2,68	0.002
Cut Class	0.541	0.927	2,68	0.401
Nest	1.215	2.083	4,68	0.093
Size Class * Cut Class	2.792	4.787	2,68	0.011
Size Class * Nest	1.657	1.657	6,68	0.016
Cut Class * Nest	7.383	12.662	2,68	0.0001

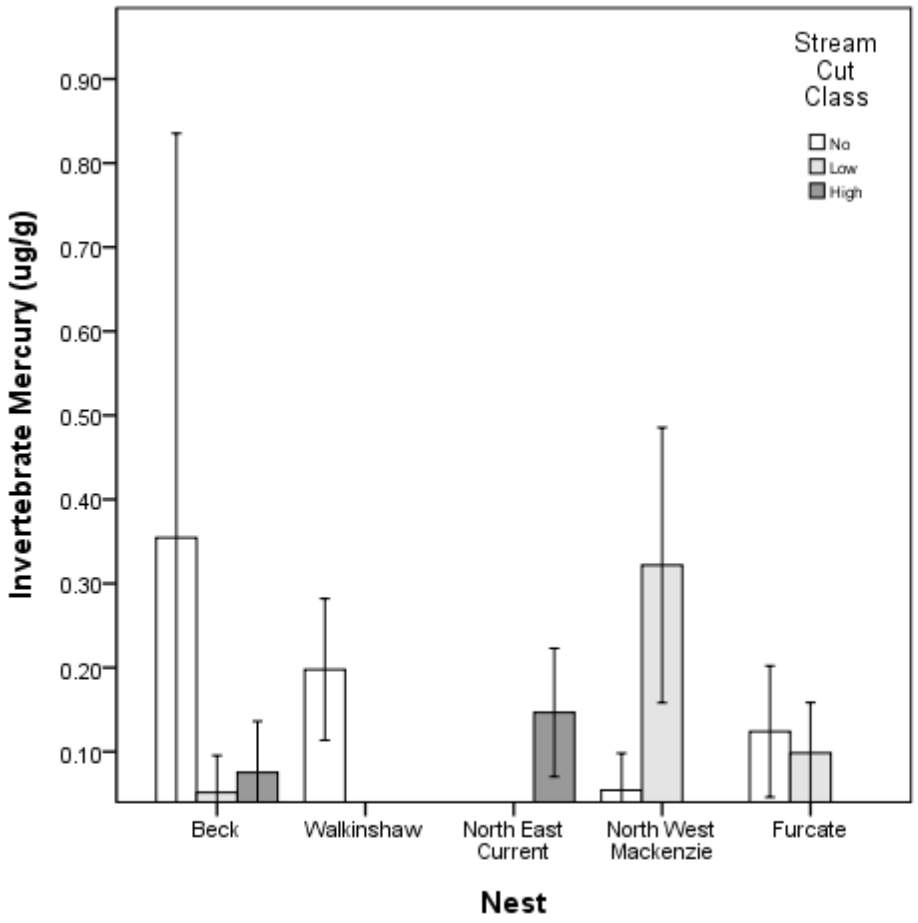

Figure 3.1.6 Mean (±SD) invertebrate mercury concentrations (µg/g wet mass) categorized by stream cut class and nest.

Fish were collected from 24 of the 31 study sites with 5 high cut class streams containing fish samples. Fish mercury concentrations were higher in small streams (0.176 µg/g ± 0.103 SD) compared to medium streams (0.142.74 µg/g ± 0.112 SD) and large streams (0.092 µg/g ± 0.049; $F_{(2,166)}$=6.491, p=0.002; Figure 3.1.7a). The no cut streams had the highest fish mercury concentration and variability (0.156 µg/g ± 0.132 SD) in comparison to the low cut class (0.113 µg/g ± 0.058 SD) and high cut class (0.141 µg/g ± 0.052 SD; $F_{(2,166)}$=7.025, p=0.001; Figure 3.1.7b). North East Current contained 4 of the 5 high cut class streams where fish were collected. More small size class sites were sampled than other size classes due to the number available in the catchments sampled and the nest grouping. Fish mercury concentrations were highest in the Beck catchment (0.172 µg/g ± 0.119 SD) with the Furcate catchment having the lowest fish mercury concentrations (0.109 µg/g ± 0.071µ SD; $F_{(4,166)}$=4.375, p=0.002; Figure 3.1.8). Interactions between stream size class and nest (size class * nest) were significant ($F_{(3,166)}$=5.779, p=0.001; Table 3.1.3) however, this does not explain as much variation in the fish mercury concentrations as stream cut class or stream size class alone.

Brook trout had lower average mercury concentrations (0.085 µg/g ± 0.043 SD) less than dace (0.128 ± 0.06 SD; Figure 3.1.9). Brook trout were found in 10 streams and may have contributed to the large variability of the fish mercury data. Brook trout were not found in any of the high cut streams. Eight study streams contained both brook trout (n=38) and dace (n=35) with a total of 73 fish collected from sites where both genus were present. Brook trout had mercury concentrations lower (0.079 µg/g ± 0.041) than the dace (0.128 µg/g ± 0.058; $t_{(1,72)}$=24.223, p<0.001) consistently over the sites where both were collected (Figure 3.1.10).

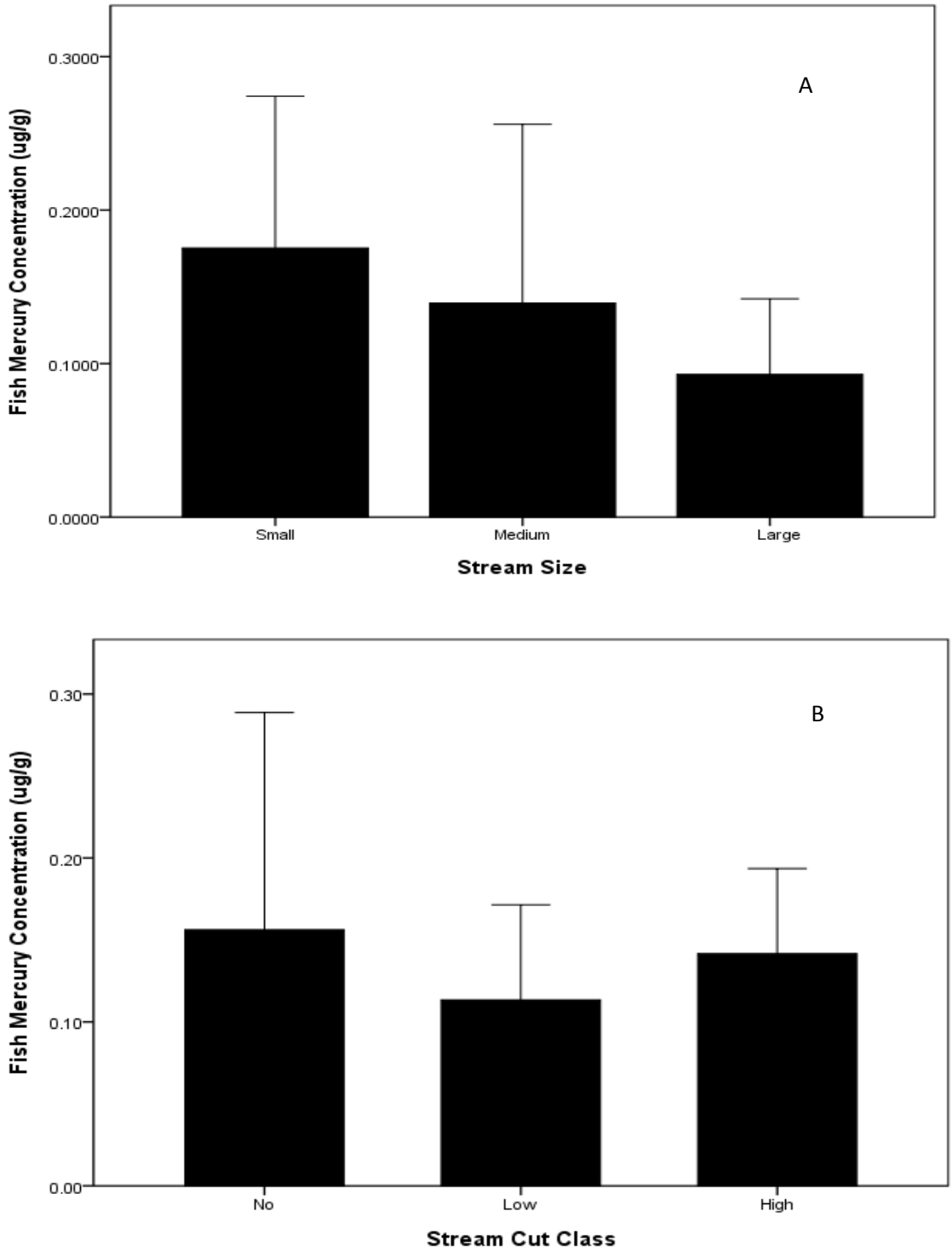

Figure 3.1.7 Mean (+ SD) fish mercury concentrations (µg/g wet mass) by A: stream size class and B: stream cut class.

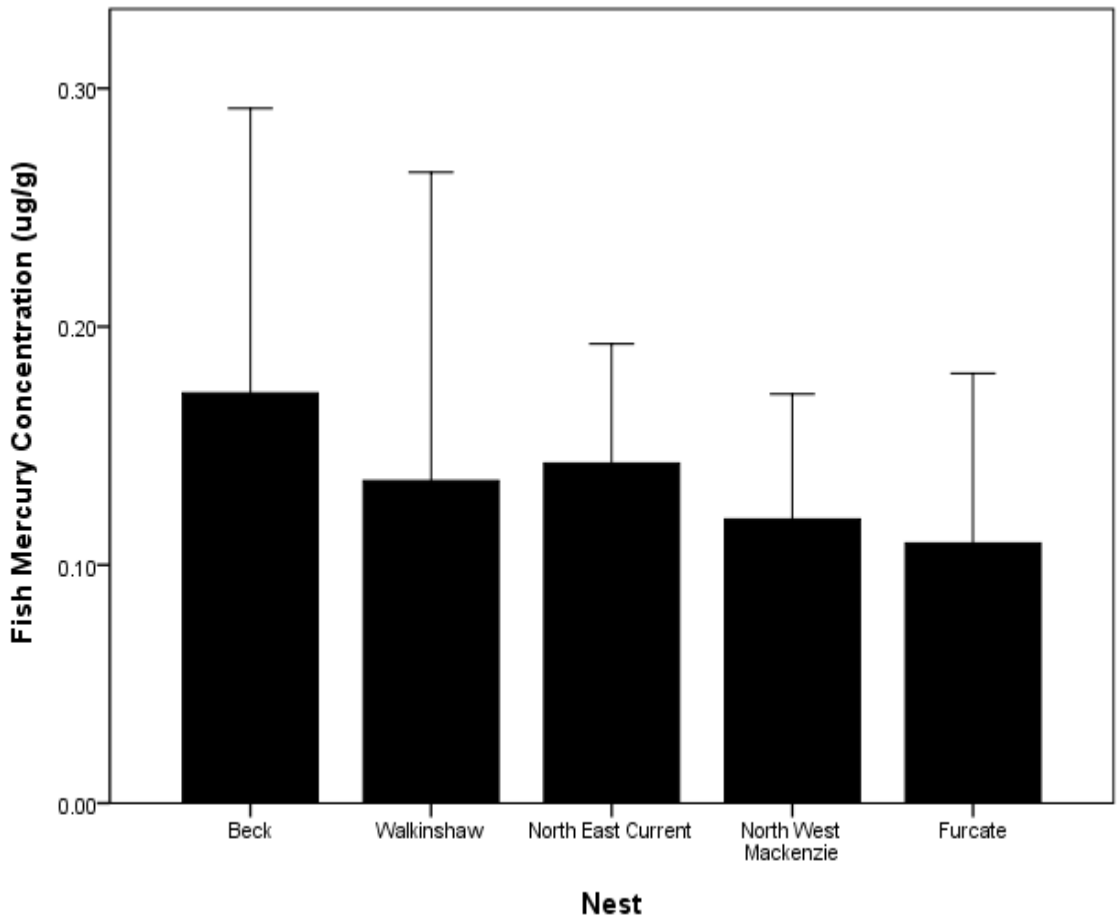

Figure 3.1.8 Mean (+SD) fish mercury concentrations (µg/g wet mass) for each nest.

Table 3.1.3 Factorial ANOVA table of the fish mercury concentration (log µg/g) with relevant statistics of the three site classification terms and the interaction terms.

Interaction Term	Mean Square	F	df	Significance
Size Class	0.232	6.491	2,166	0.002
Cut Class	0.251	7.025	2,166	0.001
Nest	0.156	4.375	4,166	0.002
Size Class * Nest	0.206	5.779	3,166	0.001

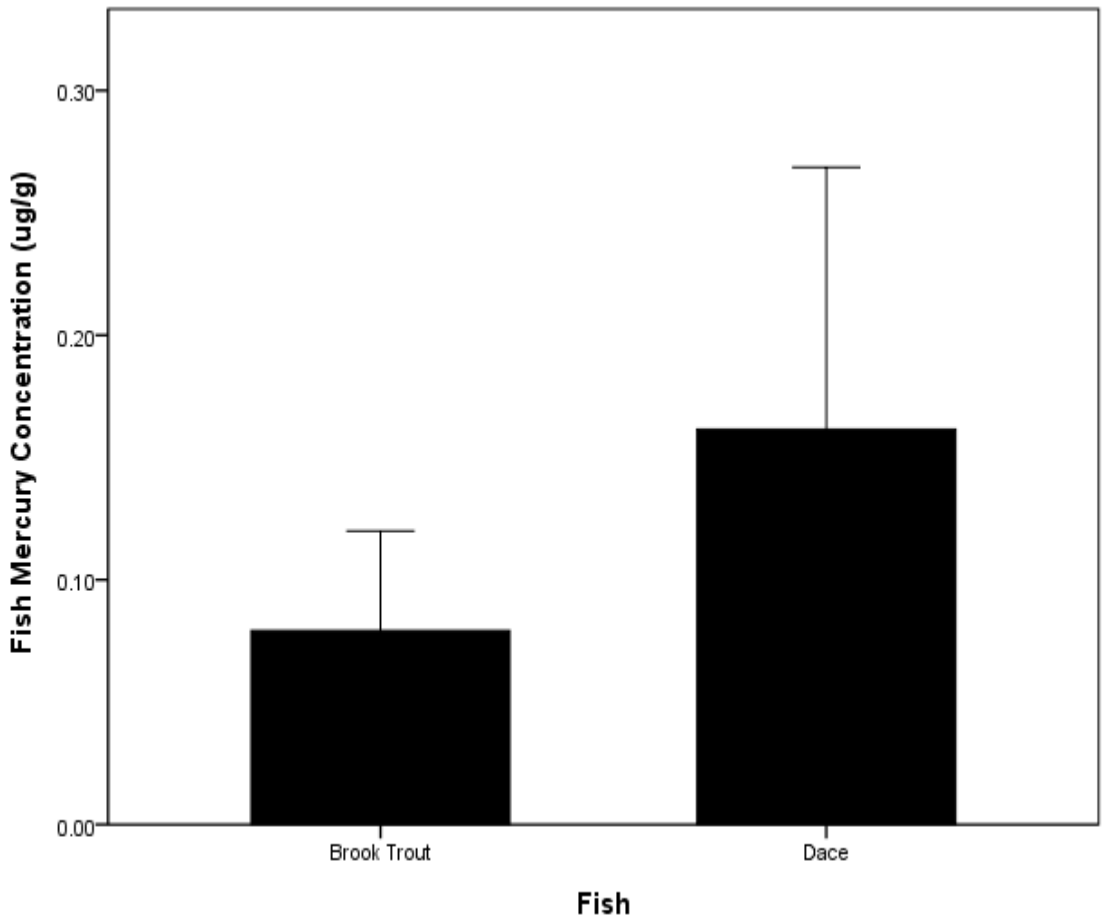

Figure 3.1.9 Mean (+SD) fish mercury concentrations (µg/g wet mass) by taxonomic group (brook trout and dace).

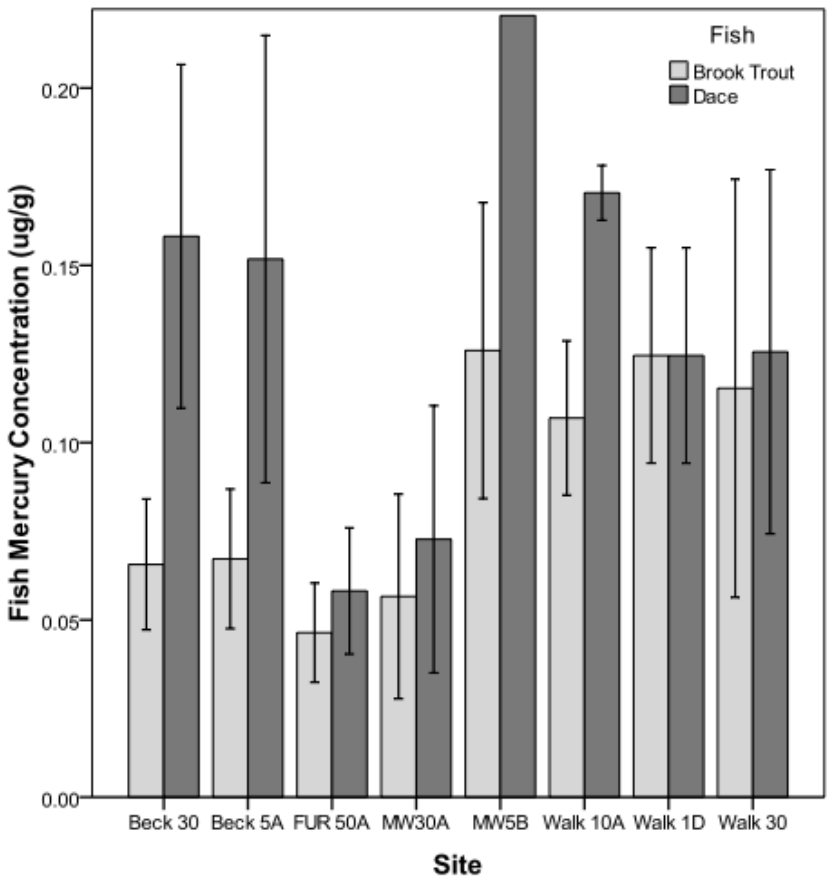

Figure 3.1.10 Mean (± SD) fish mercury concentrations (µg/g wet mass) of the 8 sites where both taxonomic groups were present. Light bars represent the brook trout and dark bars represent the dace mercury levels.

3.2 Trophic Level

Statistical analyses were not conducted to evaluate differences in mercury concentration in biota at different trophic levels due to large differences in the number of samples and samples not being collected for all categories. Rather than violating all assumptions under the ANOVA only mean comparisons were attempted in this section.

On average, invertebrate mercury concentrations (0.170 µg/g) were higher than the periphyton mercury concentrations (0.122 µg/g), but were also higher than fish mercury concentrations (0.140 µg/g; Figure 3.2.1). The small stream size class had similar invertebrate and fish mercury concentrations (0.179 µg/g and 0.176 µg/g) with similar sample sizes (n=48 and n=58).

The periphyton mercury concentrations, when compared among stream cut class, were consistently lower than the invertebrate and fish mercury concentrations (Figure 3.2.2). In the high cut streams there were higher mercury concentrations with the increase in biota trophic position from periphyton (0.044 µg/g; n=18 samples) to invertebrates (0.123 µg/g; n=18 samples) and fish (0.141 µg/g; n=42 samples).

The biota mercury concentrations did not follow the hypothesized trophic level increases from periphyton to invertebrates to fish in all of the nests (Figure 3.2.3), however biota mercury concentrations followed the predicted pattern in the Beck catchment with periphyton at 0.149 µg/g (n=23 samples), invertebrates at 0.171 µg/g (n=24 samples) and fish at 0.172 µg/g (n= 47). Other nests had similar invertebrate and fish mercury concentrations like the North East Current (0.147 µg/g and 0.142 µg/g) and the Furcate (0.105 µg/g and 0.109 µg/g) catchments respectfully. The Furcate nest was

especially unique since the periphyton mercury concentrations were higher than fish and invertebrate mercury concentrations combined.

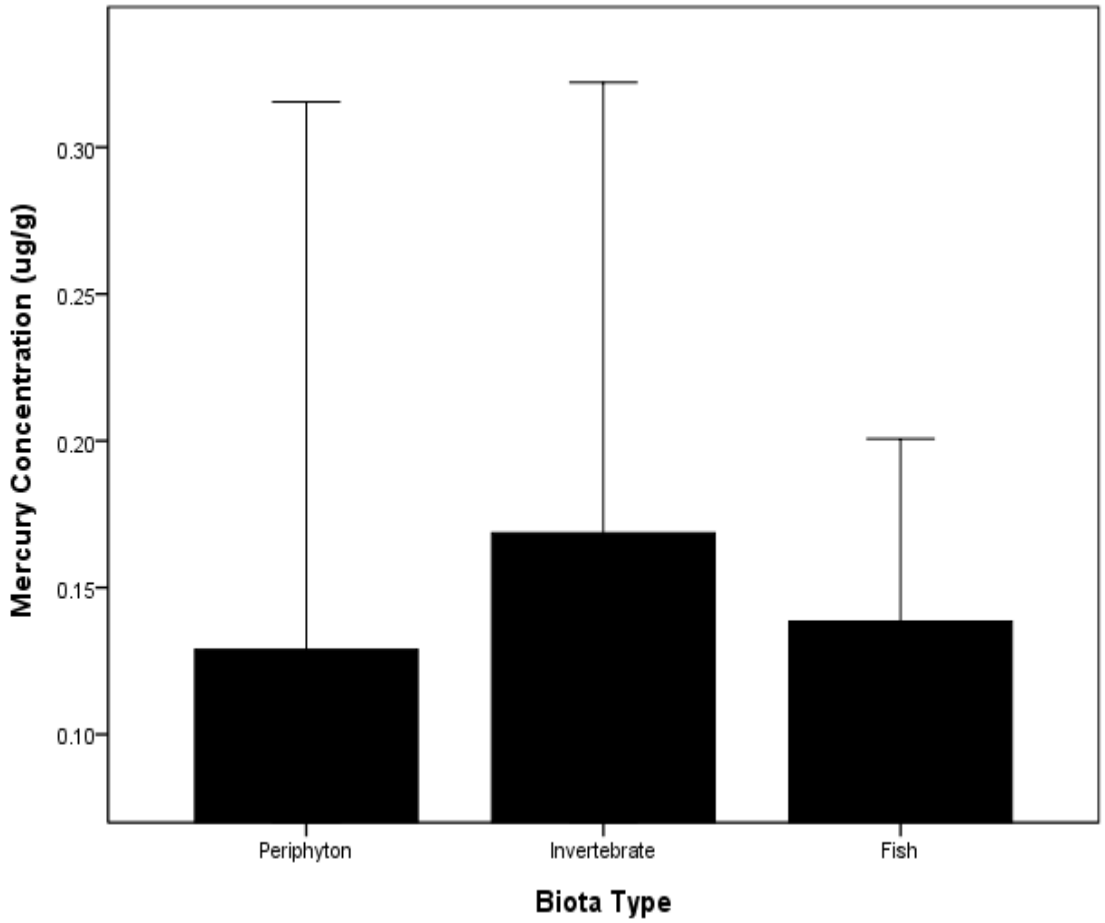

Figure 3.2.1 Mean (+ SD) biota mercury concentrations (µg/g wet mass) by biota type.

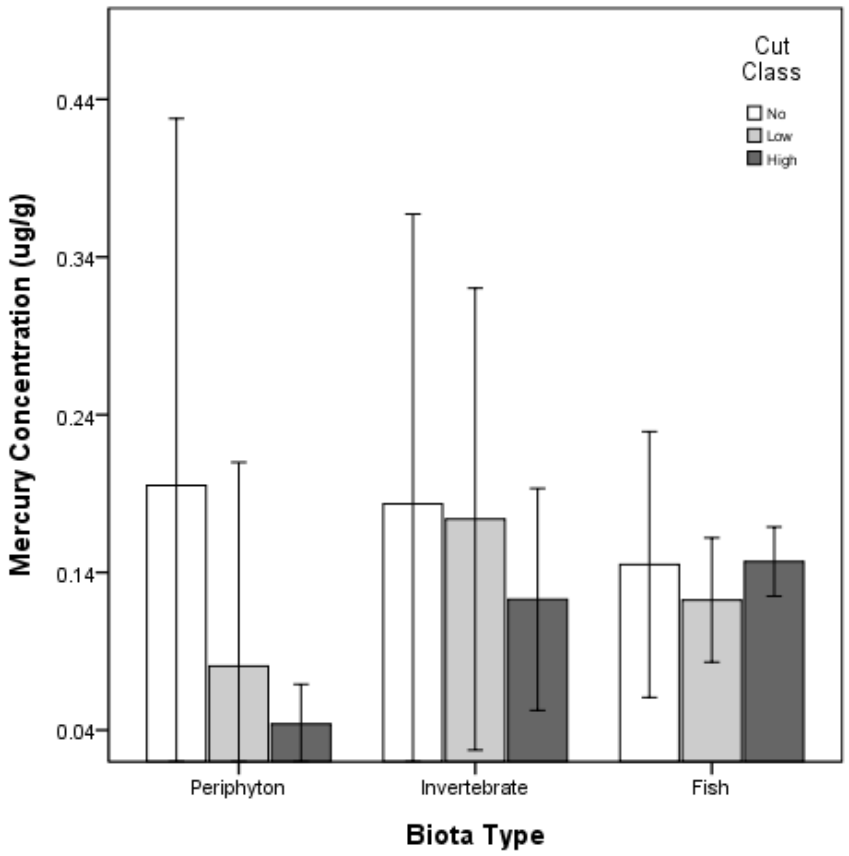

Figure 3.2.2 Mean (± SD) biota mercury concentrations (µg/g wet mass) for each cut class. No cut streams are shown with open bars, low cut with light grey and high cut with dark grey.

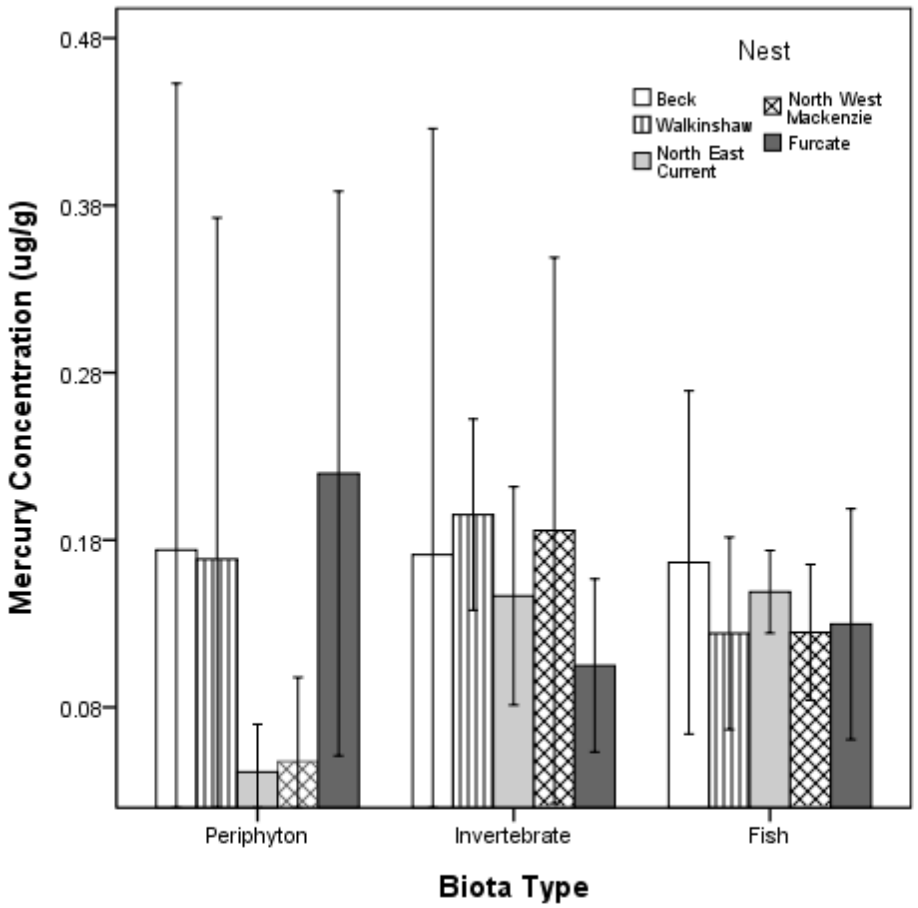

Figure 3.2.3 Mean (± SD) biota mercury concentrations (µg/g) for each nest. The Beck catchment is indicated by open bars, Walkinshaw by vertical lines, North East Current by a light grey, North West Mackenzie by a diamond pattern and Furcate by dark grey bars.

3.3 Stream Habitat

3.3.1 Local Variables

Local variables differed among streams in different size classes. Results of the MANOVA show that only stream size class results in separation of sites by local variables (MANOVA, $F=5.556$, $p < 0.001$; Table 3.3.1). Habitat characteristics did not differ among streams of different cut classes ($F=0.653$, $p=0.725$) or nests ($F=0.724$, $p=0.669$). No statistically significant difference was present in the pH of streams when grouped according to cut class (7.04-7.10).

Discriminate function analysis (DFA) showed that when sites were grouped by size class there was a significant separation of the groups (Wilks' Lambda $p=0.001$) in ordination space defined by functions 1 and 2 (Table 3.3.2; Figure 3.3.1). Size class explained 89.4% of the variance in discriminant function 1 scores and 10.6% of the variation in discriminate function 2 scores. The separation of the sites was dominated by differences in pH, temperature (ºC), conductivity (µS/cm) and average canopy density (%). Separation of the streams sizes was due to small streams having lower pH (mean 6.8 ± 0.3 SD), conductivity (mean 66.7 µS/cm ± 26.9 SD), lower temperature (14.3 ºC ± 1.7 SD) and a higher canopy density (75% ± 20 SD). The smaller streams (small and medium size classes) were further separated from the large streams by stream gradient (small 4.9% ± 1.9 SD, medium 4.1% ± 2.4 SD, large 3 ± 0.5 SD) and fine sediment % (small 24% ± 21 SD, medium 20% ± 24 SD, large 3 ± 6 SD). Small streams were classified correctly 88.2 % of the time while medium streams were classified correctly 77.8 % of the time by just the 6 local variables that were used in the classification in the

Redundancy analysis results indicated that local variables including pH, conductivity, canopy density and gradient had the strongest association with mercury concentrations ($F = 1.035$, $p = 0.293$; Figure 3.3.2; Table 3.3.3). Of the axes examined, a total of 42.2% of variation in mercury concentrations among sites was explained through axes 1 and 2. When all axes are considered 68.8% of mercury concentration variances are explained by the 5 local variables. Mercury concentrations had a greater association with stream specific variables (pH, conductivity and temperature) compared to the surrounding variables (gradient, canopy density). Periphyton and fish mercury concentrations were more closely associated with stream pH, conductivity and temperature, where cooler, more acidic (lower pH) and lower conductivity streams had higher fish and periphyton mercury. Invertebrate mercury was associated with the stream variables but seemed to be more closely related to stream gradient and canopy where steeper streams with higher canopy cover have higher mercury concentrations. The second axis shows a separation of streams with steep gradient, narrow riparian zone and lower fine sediment, which are at the positive end of the axis, from streams with low gradient, wider riparian zone and greater percent fine sediment which fall towards the negative end of the axis.

3.3.2 Catchment Variables

Redundancy analysis showed that catchment variables were separated on two gradients (F =1.310, p=0.252) with the first gradient showing that periphyton, invertebrate and fish mercury concentrations being positively associated with lake percent (Figure 3.3.3; Table 3.3.4). The second gradient separated streams with large percent wetlands, toward the positive end of the axis, from streams with large lake and recent cut percent at the negative end. Axes 1 and 2 explained a total of 34% of the variance in bioatic mercury with a total of 70.2% of variance in mercury being explained by all axes. Mercury was positively associated with the percent lake and temperature while it was negatively associated with the percent wetland and recent cut.

Table 3.3.1 MANOVA table of the 3 stream grouping variables and the contribution of each to explain the differences in local variables at each site.

	Nest (p=0.669)		Size Class (p=0.001)		Cut Class (p=0.725)	
Variable	F	p	F	p	F	p
pH	0.042	0.840	24.157	0.0001	0.040	0.842
Conductivity (uS/cm)	0.004	0.948	7.252	0.012	0.679	0.417
Gradient (%)	0.834	0.369	3.736	0.064	0.706	0.408
Woody Debris	3.263	0.082	1.792	0.192	4.232	0.049
Temperature (℃)	0.079	0.781	9.529	0.005	0.043	0.836
Riparian Width (m)	1.809	0.190	0.484	0.493	0.282	0.600
Canopy Density (%)	3.886	0.059	13.557	0.001	0.038	0.846
Fine Sediment (%)	0.835	0.369	3.486	0.073	1.120	0.299

Table 3.3.2 Standardized Canonical Discriminate Function Coefficients for the DFA of local variables.

Variable	Function 1	Function 2
pH	-0.661	0.264
Conductivity (uS/cm)	0.179	0.463
Stream Gradient (%)	0.288	-0.828
Temperature (C°)	-0.331	-0.386
Canopy Density (%)	0.571	1.007
Fine Sediment	0.595	-0.242

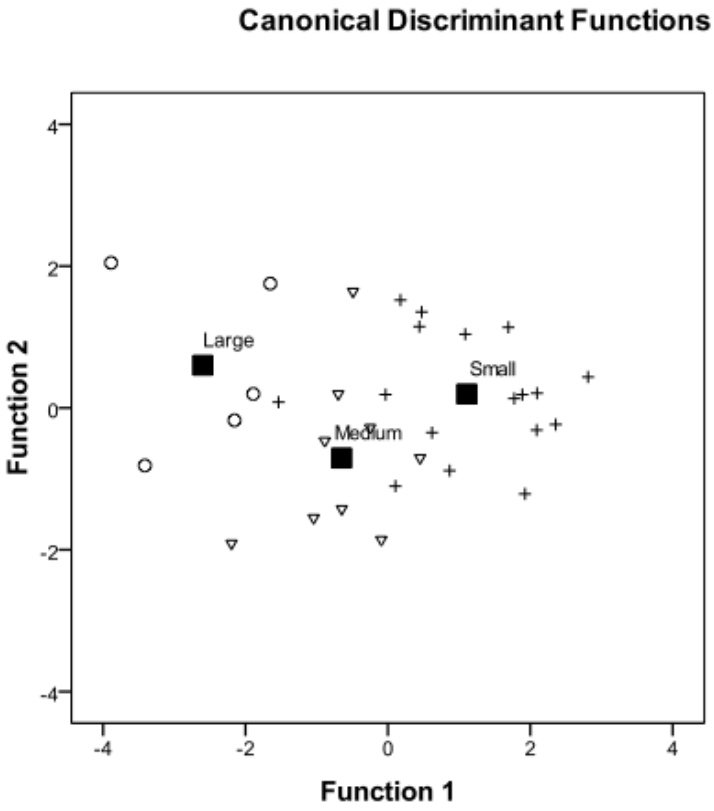

Figure 3.3.1 Discriminant Function Analysis (DFA) ordination plot illustrating the separation of the different stream size classes based on local scale habitat variables. The size class centroid is shown with a labeled black square. The small stream sites are shown as a plus sign, medium streams by a triangle and large streams by a circle

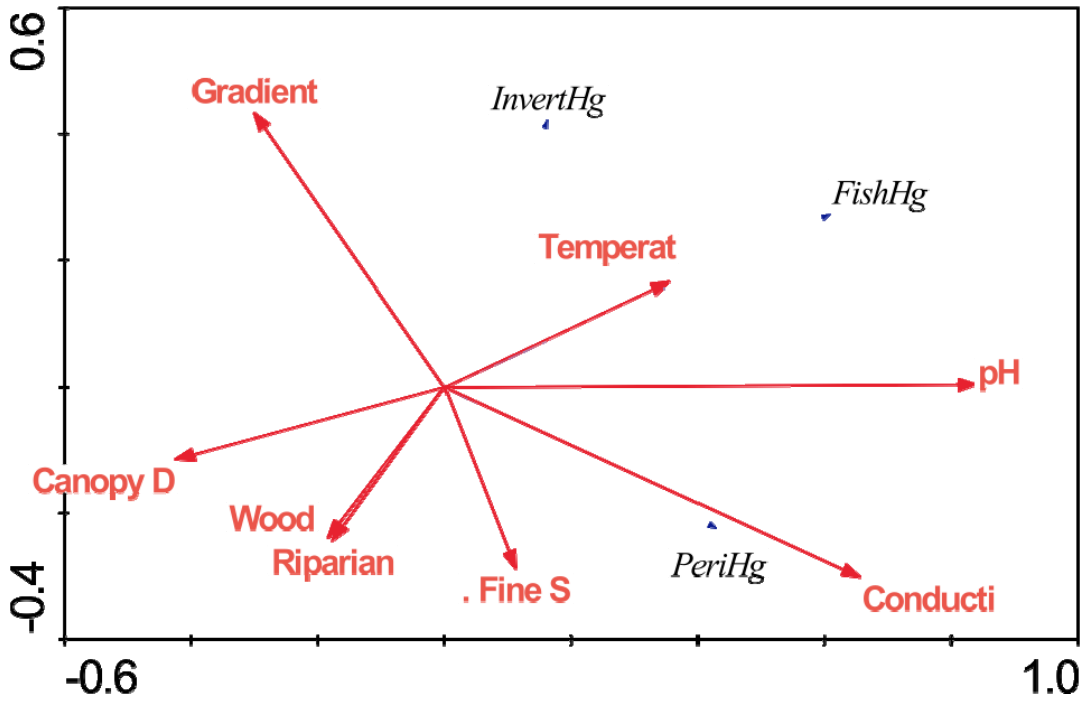

Figure 3.3.2 Redundancy analysis of local scale variables and biota mercury concentrations (F=1.035 p=0.293, all axis). The RDA found that 68 % of all variance in mercury concentrations were explained by differences in local scale habitat variables (See Table 3.3.3 for RDA statistics). The dark lines indicate the local variables with vector length indicating the strength of the relationship to the axis. The grey lines represent the biota mercury concentrations and the vectors indicate the strength and direction of the relationship to axes.

Table 3.3.3 Summary of the Redundancy analysis for local variables (Figure 3.3.2). The strongest correlations between the RDA axes and local habitat variables, as well as the variance in biota mercury explained by the analysis and it's significant, are presented.

Spatial scale	Variance Explained (%)		Strongest Variables	Axis Correlations		Significant Tests	
	All Axes	Axes 1&2		1	2	All Axes	First Axes
Figure 3.3.2	68.8%	42.2%	pH	0.5351	0.002	p=0.293, F=1.035	p=0.163, F=3.905
			Conductivity	0.4187	-0.1494		
			Gradient	-0.1921	0.2148		
			Temperature	0.2267	0.0823		
			Canopy Cover	-0.2703	-0.0567		

57

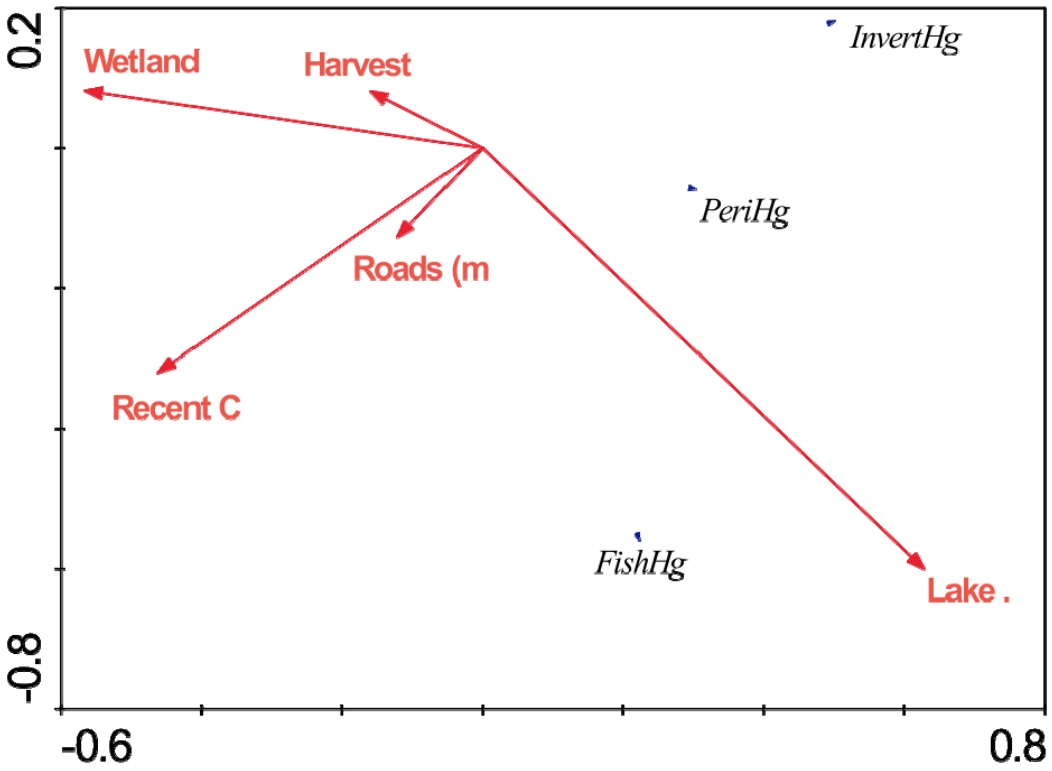

Figure 3.3.3 Redundancy analysis of catchment scale variables and biota mercury concentrations (F=1.31- p=0.252, all axis). The RDA found that 70.2 % of all variance in mercury concentrations were explained by differences in catchment scale habitat variables (See Table 3.3.5 for RDA statistics). The dark lines indicate the catchment variables with vector length and direction indicating the strength of the relationship to the axis. The grey lines represent the biota mercury concentrations and the vectors indicate the strength and direction of the relationship to axes.

Table 3.3.4 Summary of the Redundancy analysis for local variables (Figure 3.3.3). The strongest correlations between the RDA axes and catchment scale variables, as well as the variance in biota mercury explained by the analysis and it's significant, are presented.

Spatial scale	Variance Explained (%)		Strongest Variables	Axis Correlations		Significant Tests	
	All Axes	Axes 1&2		1	2	All Axes	First Axes
Figure 3.3.3	70.2	34	Lake %	0.3853	-0.3453	p=0.2520, F=1.310	p=0.3482, F=3.690
			Wetland	-0.3464	0.0471		
			Recent Cut	-0.2823	-0.1839		
			Roads	-0.0741	-0.0734		

4.0 Discussion

Mercury concentrations in biota and the factors that influence contamination are of global concern. Specific mercury concentrations in all three levels of biota (periphyton, invertebrates and fish) varied within and between sample sites with mercury concentrations in only 10 biota samples being below the detection limit (0.0004 μg/g). The highest biota mercury concentrations tended to be in the highest trophic level organisms but this pattern did not stand for all sites and samples with some periphyton samples having mercury levels higher than invertebrate and fish mercury concentrations. Several local and catchment variables were associated with the presence and concentrations of biota mercury concentrations including pH, water temperature (ºC), conductivity (μS/cm), percent lake and percent wetland. Forest management practices were not associated with differences in mercury concentrations and were also not associated with differences in local variables. The size of the stream seemed to have the greatest association between biota mercury concentrations and differences in local variable values.

4.1 Biota Mercury Concentrations

Mercury concentrations in biota varied between and among the sites and samples due to associations with different local and catchment scale variables. All samples were tested for total mercury (THg) with samples from only one site (MW1E) having concentrations below the detection limit (0.0004 μg/g). Periphyton mercury levels in my study varied as much as two orders of magnitude within and among sites. Periphyton mercury concentrations vary depending on the substrate they are found on, general stream conditions, location of the stream and species of periphyton collected (Bell and

Scudder 2007, Cleckner *et al*. 1998). There was a high level of variability in periphyton mercury concentrations with high levels at the Furcate sites (0.219 µg/g) compared to the North West Mackenzie which averaged below 0.05 µg/g. The Furcate sites had lower average conductivity, lower temperature and higher gradient than the North West Mackenzie sites. Variability of the periphyton mercury concentrations spanned orders of magnitude; it was higher in the smaller streams (small and medium) compared to the high streams and while not associated with different disturbance histories it was associated with the area of sampling (nest).

The variation in the invertebrate mercury concentrations may be due to the site specific methylation rates or differences in the size and/or species composition collected at different sites. Research by LeCraw (2009) showed different benthic invertebrates were present in different size streams when identified to the genus level. Different invertebrate species within the same location can accumulate mercury at different rates resulting in different mercury concentrations among species (Anderson and Depledge 1997, Hill *et al*. 1996). Since invertebrates were only identified to the order level of classification, invertebrate species composition differences associated with differences in stream size or substrate type may account for some of the variability between site and/or sample invertebrate mercury concentrations. While identification to species or even genus would be difficult without special knowledge and training during live picking of samples for mercury analysis, additional reference samples could be collected and preserved for identification later. Invertebrate mercury concentrations may also be lower due to enhanced periphyton growth dilution or invertebrate growth dilution (larger body size; Brinkman 2004, Mason *et al*. 2000). Invertebrate mercury concentrations varied by

orders of magnitude and this could be associated with the different growth conditions at sites (Fuller *et al*. 1986), different species present between sites (Anderson and Depledge 1997, Hill *et al*. 1996, Jackson 1988).

Dace species had average mercury concentrations approximately 50% greater than brook trout (0.128µg/g ± 0.006 SD, 0.085 µg/g ± 0.043 SD respectively). I assume that trout and dace are at the same trophic level as all fish used in my study were small, less than 100 mm in total length, which reduces the chances of piscivory by brook trout (Browne and Rasmussen 2009). Age of the fish can be a contributing factor in the mercury concentrations of fish with older fish tending to have higher mercury concentrations (Gorski *et al*. 1999, 2003, Harris and Bodaly 1998). I used backpack electrofishing to collect fish samples which tends to be biased towards capturing larger fish (Fièvet *et al*. 1999, Onorato *et al*. 1998). When fish were processed for samples in the lab, larger dace were chosen because of ease of processing. While fish were not aged in my study, sampling techniques may have favoured larger dace and younger brook trout. Dace in this study may have been as old as about 5 years old while brook trout were likely 1-2 years old based on the size at capture (Scott and Crossman 1973). Small brook trout were collected because they occur more commonly in all sizes of streams and their removal was less likely to impact the local populations than the removal of older, larger fish. Increased mercury uptake from food with slow mercury eliminations from the body (Porvari 2003) may be associated with why the potentially older dace had higher mercury concentrations than similar sized (but possibly younger) brook trout. Fish mercury was consistently lower in brook trout over dace with differences attributed to fish age.

Different size streams had different local variables and differed in biota mercury concentrations. The large streams in my study had catchments in all 3 cut classes and generally had lower mercury concentrations in all biota types. Biota sampled in small and medium streams had higher mercury concentrations than those from large streams. Large streams had less fine sediment which has been shown to be a potential mercury methylation environment (Francesconi *et al*. 1997) and can result in different invertebrate communities (Cummins and Klug 1979). Small and medium streams tended to have more woody debris, leaf matter and a higher canopy cover which may be associated with increased mercury available to the system due to litterfall increases (Munthe *et al*. 1995, St. Louis *et al*. 2001) or decreased dissolved oxygen due to sediments which increases methylation processes (Francesconi *et al*. 1997). Smaller streams in my study may have higher biota mercury concentrations due to many variables including the higher litterfall, fine sediment, woody debris, and leaf matter than larger streams. The biota mercury concentration differences may also be associated with differences among stream sizes in MeHg/THg ratios or different invertebrates composing the samples. Stream size is associated with differences in local variables and can be associated with large differences in mercury present in biota.

4.2 Mercury Bioaccumulation

Periphyton can be a potential site of mercury methylation (Desrosiers *et al*. 2006a, Mucci *et al*. 1995) and is an important component to the stream food web as the primary producer (Cleckner *et al*. 1998, Cummins 1974). While MeHg is the mercury that is bioaccumulated in higher trophic levels (Porvari 2003), the proportion of THg that is MeHg in periphyton varies with the sample, site and conditions with some samples

having as low as 2% MeHg (Bell and Scudder 2007, Hill *et al*. 1996). A number of aquatic macro-invertebrates feed on periphyton (Cummins and Klug 1979) including several species within the EPT complex analyzed in this study. Since food is the primary uptake route of mercury to invertebrates (Desrosiers *et al*. 2006b, Mason *et al*. 2000) herbivorous invertebrates should have MeHg mercury concentrations that are higher than periphyton.

Large variances in the biota mercury concentrations were observed when comparing samples from different size streams. The trophic level increases in mercury that were expected were not seen in the smaller streams in this study. The biota sampled in large streams showed had over a 3 fold difference in mercury concentrations between the two lowest trophic levels. The inconsistency in the pattern of differences between the base of the food chain (periphyton) and invertebrates among different stream sizes suggests that the pattern of mercury biomagnification may be influenced by a number of factors including the species present and the local and catchment scale characteristics of the sites. Periphyton is the base of the stream food web but the differences in stream size, local variables, variable ratios of MeHg to THg and the percent of the mercury passed to the higher trophic levels may be why the trophic level increases that were hypothesized were not observed.

Tsui *et al*. (2009) showed that MeHg/THg ratios increase with catchment size indicating that more MeHg is present as a percent of THg in larger streams. Porvari and Verta (2003) also report differences in MeHg and THg ratios in relation to catchments. Porvari and Verta (2003) attributed these differences to the type of catchment (mineral soil, mineral soil/peat, peat) but there were also differences in the sizes of the catchments

studied and so there may be an unreported influence of the catchment size in their MeHg/THg ratios as well. Differences in trophic level mercury concentrations in my study were variable between the smaller streams (small and medium) and the large streams with differences associated with the MeHg/THg ratios and local variables.

My study did not show the expected pattern of mercury biomagnification (fish Hg>invertebrate Hg>periphyton Hg). The lack of clear biomagnification pattern may be due to differences associated with the stream size classes having different biota mercury concentrations as a result of different mercury methylation rates. My study used THg testing of all samples which does not allow for the determination of the MeHg concentrations in biota with the lower trophic levels having different MeHg/THg ratios (% MeHg). Sites with different upland and upstream conditions may also have different MeHg/THg ratios present in biota.

4.3 Factors Associated with Mercury Concentrations

Several studies have shown that forestry management practices are associated with the overall biota mercury concentrations (Allen *et al*. 2005, Garcia and Carignan 1999, 2005) due to changes in variables that disturbance may cause. I originally hypothesized that forest management practices would have a large influence on biota mercury concentrations. The analyses indicated that other variables at the local and catchment scale explained more variation in overall biota mercury concentrations than forest harvest within the catchment. Changes to sediment load, pH, and stream temperature (Davies *et al.* 2005, Garcia and Carignan 1999, Harriman *et al*. 2003, Hartman *et al.* 1996) which may occur post harvest, because of changes in the hydrologic cycle and increased runoff (Bosch and Hewlett 1982), are commonly reported in the

literature. My study showed that there is an association between pH and mercury concentrations in biota with smaller streams having lower pH and higher biota mercury concentrations. However, there was not a significant difference in the mean pH among streams with different forest management histories. Biota mercury concentrations were higher in cooler streams, a result that differs from the previous observations of Bodaly *et al*. (1993) and Ramlal *et al*. (1993). Biota mercury concentrations were highest in streams with higher percent fine sediments, which is consistent with Ullrich *et al*. (2001). The higher percent fine sediments may result in higher mercury methylation rates or a greater release of mercury from sediments due to lower pH (Ullrich *et al.* 2001). Mercury concentrations in my study were closely associated to local stream variables which may vary based on the stream size or catchment disturbance.

Although few studies have focused on the mercury levels in periphyton following disturbance in streams, Hill *et al*. (1996) showed that post anthropogenic disturbance, mercury concentrations in periphyton and primary consumers were higher than in the undisturbed or slightly disturbed streams. I found biota mercury concentrations had a stronger association with the local variables than the catchment scale variables, including recent forest management. The low and no cut streams in my study had higher periphyton mercury concentrations with no and low cut streams present in several of the nests. High cut streams were present only in the Beck and North East Current nests while the highest periphyton mercury concentrations was observed in the Furcate nest. I found lower canopy cover at the disturbed sites which may result in increased light penetration and increased periphyton growth (DeNicola *et al*. 1992) as well as differences in invertebrate community structures (Fuller *et al*. 1986). Higher periphyton growth levels

may lower the overall level of total mercury present in sites with a catchment disturbance because of dispersion of the mercury across more periphyton (Brinkman 2004, Pickhardt *et al*. 2002). While disturbance may have an influence in other studies, my study showed that specific local variables were associated with biota mercury concentrations and that those variables were not impacted by disturbance.

Catchment disturbances were not strongly associated with local variables in my study but the disturbed sites did show different invertebrate mercury concentrations. There were significant differences in invertebrate mercury concentration among cut classes of streams; however, contrary to expectations disturbed sites had lower invertebrate mercury concentrations. Forest management practices have been associated with differences in the invertebrate community structure including in the abundance of the EPT complex (higher % in small cut streams) and in the families making up the Ephemeroptera and Trichoptera orders (some orders only found in cut streams; LeCraw 2009). All nests were associated with different catchments and as a result, small differences in catchment or local variables may influence mercury available to the local biota. Collective differences in local variables may influence mercury concentrations more than forest management practices alone.

More acidic waters can have higher mercury methylation rates and higher organic (MeHg) mercury levels (Mason *et al*. 2000, Watras *et al*. 1995; Westcott and Kalff 1996). The pH of study sites ranged from 6.23-8.26 and was associated with biota mercury concentrations more than any other local or catchment variable with the smaller (small and medium) streams having the lowest pH and highest biota mercury concentrations. Lower pH in the smaller streams may result in higher mercury methylation rates (Kelly *et*

al. 2003), increased release of mercury from sediments (Ullrich *et al*. 2001) and may partially explain why biota in the larger streams had lower mercury concentrations. Higher methylation rates at lower pH resulted in increased methylmercury uptake by higher trophic organisms (Kelly *et al*. 2003).

Higher biota mercury concentrations were also associated with lower conductivity. McMurtry *et al*. (1989) showed that smallmouth bass mercury concentration had a negative relationship with the conductivity of the water. Allard and Stokes (1989) showed that 54% of all mercury variability could be explained through a negative association between the mercury concentrations of crayfish tissue and conductivity alone. The streams with the highest mercury in my study were smaller streams that also had cooler water, lower pH, higher percent fine sediments and lower conductivity. Conductivity measurements are assumed to have a positive relationship with total dissolved solid (TDS) measurements (McManus *et al*. 1992). The total dissolved solids in streams may stabilize the mercury in solution by complexation or sorption with humic-hydrous oxide (Nevado *et al*. 2009). This stabilization of the mercury with humic-hydrous oxide may make the mercury less available to biota to uptake with lower conductivity streams having more mercury available to the biota. While conductivity did not vary between disturbance levels in my study it did vary with stream size.

Factors associated with biota mercury concentrations such as the percent fine sediment of a stream vary depending on local stream conditions including stream gradient, woody debris and catchment disturbance. Sediment in aquatic systems has been shown to be an important methylation environment releasing mercury from the sediment

mercury bank in lower pH environments or having a higher ratio of MeHg to THg (Francesconi *et al*. 1997; Ullrich *et al*. 2001). Small and medium size streams had higher percent fine sediments in my study which may be a primary driver for the higher mercury concentrations obsereved relative to large streams. In my study the amount of woody debris present was associated with stream cut classes with larger amounts of woody debris being present in the higher cut class streams. The higher percent fine substrate and woody debris volume may be due to input from the riparian zone. Higher levels of fine substrate and woody debris decrease the dissolved oxygen level of the stream and increase the methylation potential of the nitrogen reducing bacteria (responsible for mercury methylation; Ullrich *et al*. 2001).

Stream water temperatures have been shown to be influenced by disturbance in the catchment and to be associated with mercury methylation rates and biota mercury concentrations. I found there were no differences in water temperature between any of the cut classes, based on average stream temperatures, in part because there was only a 5% difference between the no and high cut stream classes. Bodaly *et al*. (1993) and Ramlal *et al*. (1993) showed that the mercury concentrations and methylation rates were positively associated with water temperature. Temperatures in streams have also been shown to be higher as a result of forest management practices (Curry *et al*. 2002, Harriman *et al*. 2003, Hartman *et al*. 1996). The lower temperature streams in my study had higher biota mercury concentrations which is contrary to expectations, but this pattern was only observed in the smaller size streams which is most likely because of other local variables impacting mercury uptake in biota. Streams with higher biota mercury (small and medium size classes) had lower pH, lower conductivity and higher

percent fine sediment which may indicate that the collective influence of these variables may be greater on biota mercury concentrations than just temperature.

Many studies have reported that wetlands influence the mercury flux in streams and are a potential site of methylation or source of mercury to aquatic biota. The runoff as a result of forest management has been shown to increase the flux of mercury to a system (Porvari *et al*. 2003, Porvari and Verta 2003), with runoffs from uplands into wetlands increasing the MeHg mercury flowing through the system (Heyes *et al*. 2000). The specific type of wetland was not determined although wetland type may influence site specific mercury concentrations in my study. Different types of wetlands have different MeHg/THg ratios and mercury fluxes to streams (Porvari and Verta 2003). I selected study areas that were similar and where it was possible to electrofish so the wetlands may have been outside the main sample collection areas further reducing positive association between wetlands and biota mercury concentrations. I calculated wetland percent at sites using data from the NRVIS database (OMNR 2005, 2009); while wetlands were observed at some sites during sample collection, the wetlands were not quantified on site. Wetlands showed an association with biota mercury concentrations but it may be the result of a few sites having a relatively high percentage of wetlands compared to the majority of sites. In my study only 10 sites that had more than 2% wetland in the catchment and only 1 site (Beck 1E) had more than 4% wetland in the catchment. While wetlands may have had an important influence on aquatic mercury levels, this study was not designed to evaluate or collect the appropriate data to properly evaluate this influence.

Catchment disturbance has been shown to influence biota mercury concentrations; in my study forest management practices were hypothesized to be positively associated with biota mercury concentrations. While some studies have shown biota mercury concentration increases as a result of forest management practices and disturbances in lakes (Bodaly *et al*. 1993, Garcia and Carignan 1999, 2000), my study examined forest management practice impacts on biota mercury concentrations in streams. No differences in biota mercury concentrations among sites with different forest management histories were detected in my study. In an addition/spike experiment, mercury additions in the upland resulted in very small increases in mercury downstream, or in traditional methylating environments (Harris *et al*. 2007). The lack of additional MeHg entering the system from upland disturbance may explain why I found no differences in the biota mercury concentrations among the catchments. This apparent lack of biota mercury response to forest management history may be a result of mercury not making it into the stream, or mercury being flushed through the system without bioaccumulating.

In addition to no differences in biota mercury concentrations as a result of forest disturbance, I found no differences in variables that normally result in increased methylation rates across the different cut classes. Local variables linked to forest disturbance and mercury methylation rates include higher sediment loads (% fine sediment), lower pH, and higher stream temperature (Davies *et al.* 2005, Garcia and Carignan 1999, Harriman *et al*. 2003, Hartman *et al.* 1996). Local variables are all linked to changes in the catchment and in the hydrologic cycle (Bosch and Hewlett 1982) with the impacts of disturbance decreasing with time. Studies on forest management practices and disturbances in streams typically take place close to the disturbance date and look

only at water mercury fluxes (Desrosiers *et al.* 2006a, Porvari *et al.* 2003, Garcia and Carignan 1999, 2000). While variables were not shown to have been impacted by the different cut classes of streams in my study, disturbance in the catchment may still have been present immediately after disturbance prior to sampling.

A study by Buttle and Metcalfe (2000) showed initial streamflow increases post harvest but limited streamflow changes were noticeable after more than 5 years post-disturbance. Stream temperatures in a study by Quinn and Wright-Stow (2008) on harvested streams show a return to reference conditions after less than 8 years post harvest. Furthermore, differences in stream temperature were noticeable only in highly disturbed catchments (48-100% harvest) after less than 3 years post disturbance (Quinn and Wright-Stow 2008). The forest management histories used in my study were based on the past 10 years as of 2007, with sampling occurring in 2008. The most recent disturbance used in my study was at least 2 years old and only 6 sites had more than 30% disturbance in their catchments. Enough time since disturbance may have passed that conditions had returned to pre-disturbance levels in my study. In addition, the percent of the catchment disturbed may not have been enough to result in stream level changes in local variables, methylation rates or biomagnification. Since small streams are so closely linked to their catchments, a fast response to disturbance may also result in a fast recovery from disturbance.

Future studies of the relationship between biota mercury concentrations and forest disturbance should identify invertebrates to the genus or family levels to better account for differences in invertebrate community structure among different size streams or in disturbed vs. undisturbed streams. Different species of invertebrates may have

different mercury concentrations or MeHg/THg ratios (% MeHg) with different size streams possibly having different invertebrate communities. Higher taxonomic resolution in the identification of invertebrates would allow for a direct comparison between the sites and invertebrates present especially given the species differences in mercury levels observed in fish sampled in this study. Lower trophic levels should also have MeHg testing done to more accurately measure how much mercury is available to the higher trophic levels since diet is the primary method of mercury biomagnification and the mercury present in invertebrates and fish is almost entirely from diet.

5.0 Conclusion

This study examined the patterns of mercury bioaccumulation by organisms in small stream environments and the factors that are associated with differences in biota mercury concentrations. Mercury was present in biota at all sites sampled although concentrations were variable within trophic levels and among sites. Periphyton mercury samples ranged from below detection levels to sites having periphyton average concentrations of 0.219 μg/g. Invertebrate mercury concentrations differed between sites with invertebrates in larger size streams having lower average mercury concentrations (0.043 μg/g) compared to those in small and medium streams (0.168 μg/g and 0.168 μg/g respectively). Fish mercury concentrations varied between the species sampled and among the different sites. Brook trout had approximately 50% lower mercury concentrations than dace, a difference that was consistent across all sites with both species present. No brook trout were found in any of the high cut class streams so although biota mercury levels and local variables did not differ between cut classes of streams, the fish communities did differ. Mercury biomagnification was difficult to

identify due to different biota mercury concentrations associated with stream size and similar mercury concentrations between fish and invertebrates. Forest management practices have been shown in previous studies to increase biota mercury concentrations and impact variables like temperature or fine sediment. The results of this study did not support the hypothesis that forestry management practices would impact biota mercury concentrations and local scale variables. Stream size had more influence on biota mercury concentrations than the cut class with smaller streams having higher biota mercury concentrations than the large streams. The differing stream conditions (variables like pH and percent fine sediment) had strong associations with biota mercury concentrations. Results suggest that local conditions, which may influence both mercury methylation potential and the growth rate and mercury uptake of organisms, may have a greater influence on mercury bioaccumulation than catchment disturbance.

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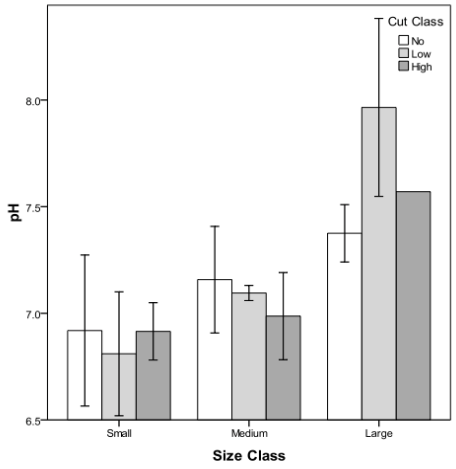
7.0 Appendix

a)



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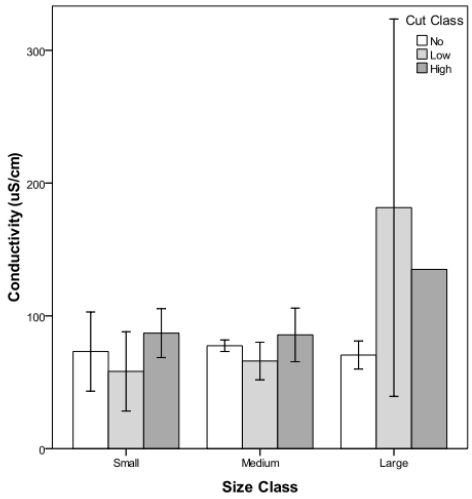

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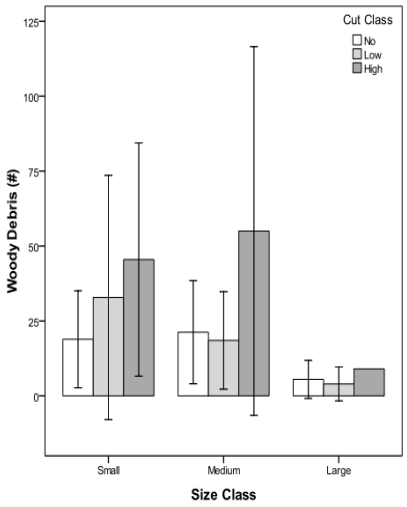

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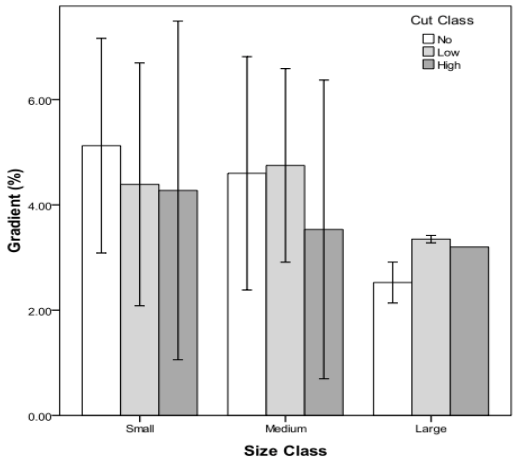
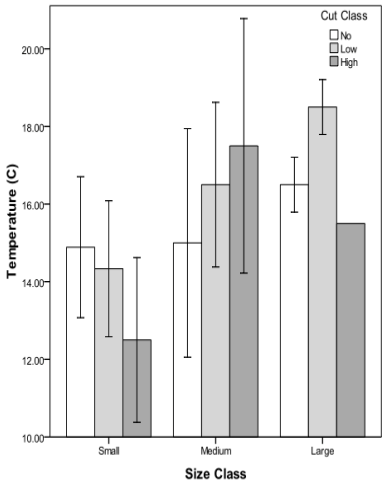


Appendix 1 Bar graphs of mean values of local variables grouped by size class and labelled by cut class. (a) pH, (b) conductivity, (c) wood debris and (d) stream gradient. The open bars represent the no cut streams, light grey bars represent the low cut and dark grey bars represent the high cut streams.

a)



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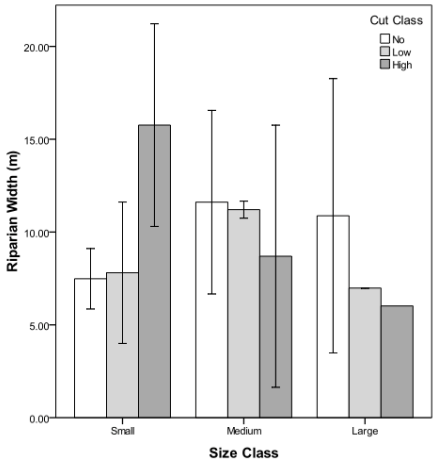

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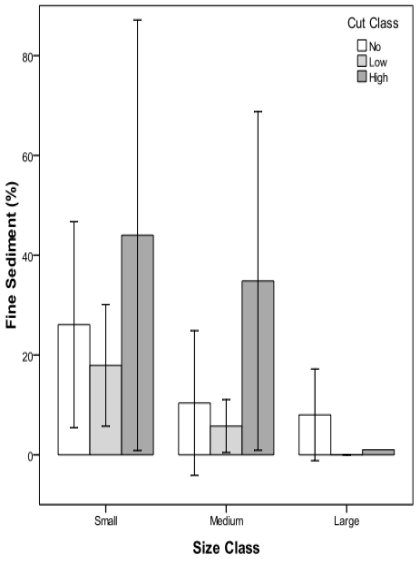

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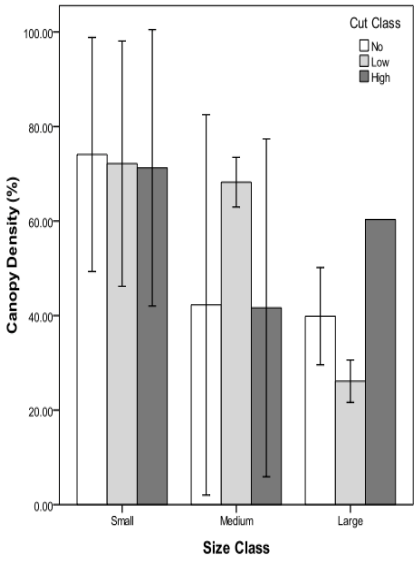
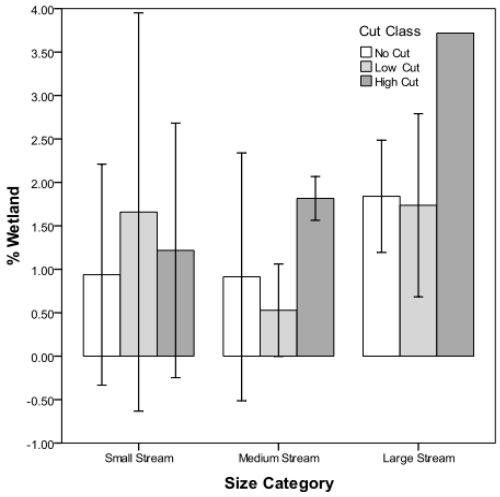


Appendix 2 Bar graphs of mean local variables grouped by size class of streams and labelled by cut class of streams. (a) temperature, (b) riparian width, (c) percent fine sediment and (d) in stream canopy density. The open bars represent the no cut streams, light grey bars represent the low cut and dark grey bars represent the high cut streams.

a)



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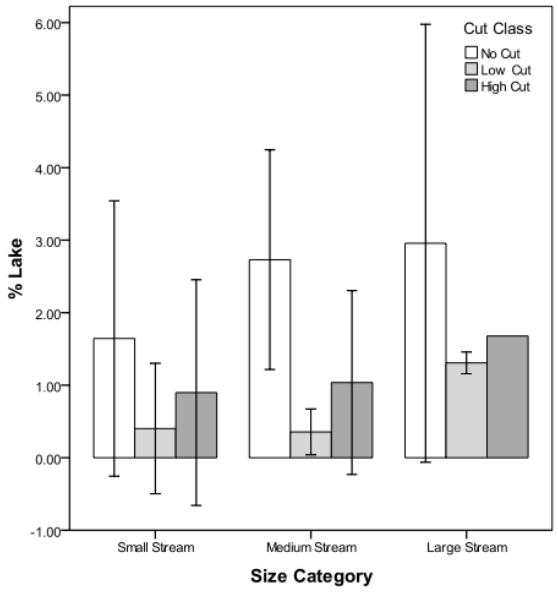

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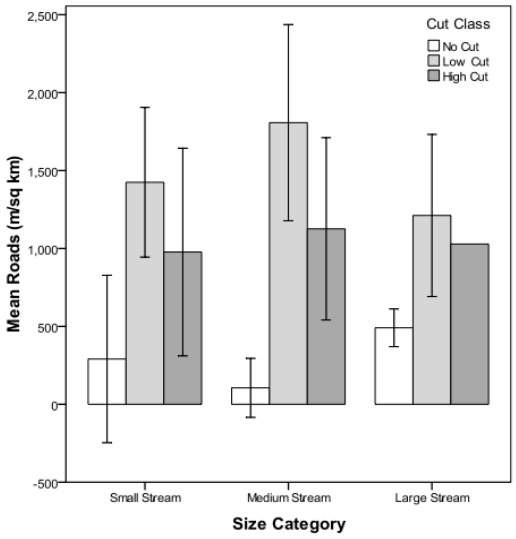
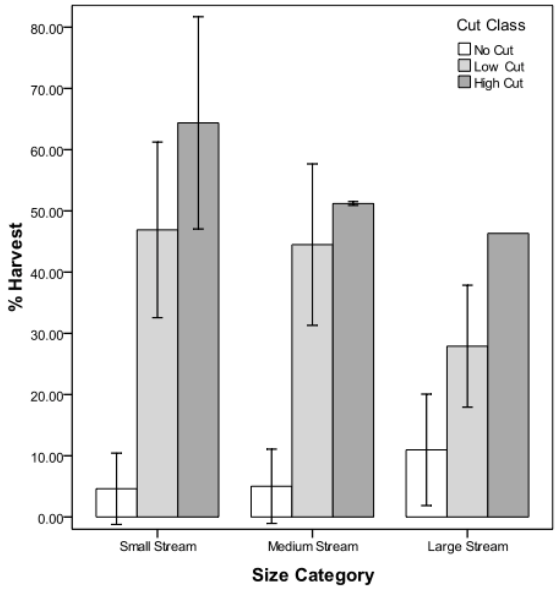


Appendix 3 Bar graph of mean catchment variables grouped by size category and labelled by stream cut class.(a) percent wetland in the catchment, (b) percent lake in the watershed and (c) roads in the catchment m/km^2. The open bars represent the no cut streams, light grey bars represent the low cut and dark grey bars represent the high cut streams.

a)



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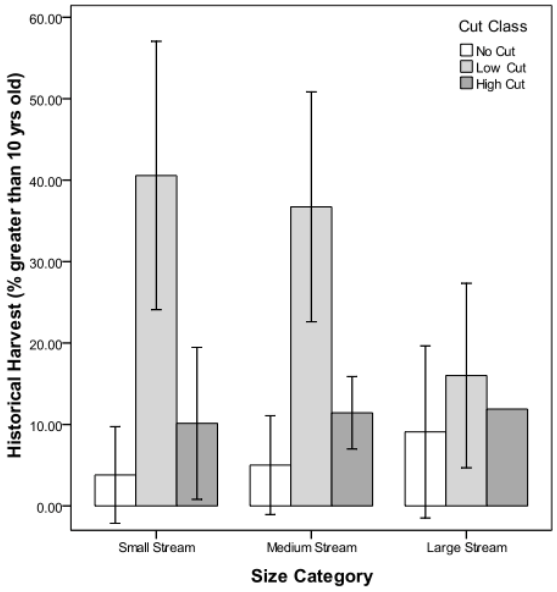

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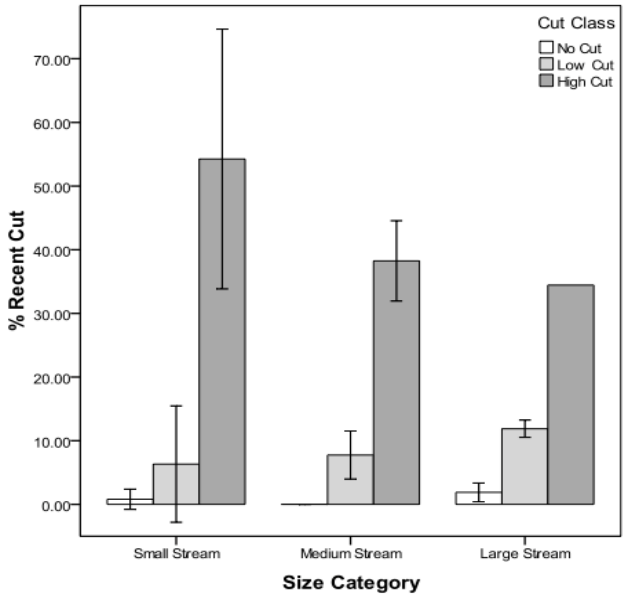

Appendix 4 Cut information for the sites sampled. (a) historical harvest percent in the catchment, (b) old harvest percent (greater than 10 years) and (c) recent cut percent (within the last 10 years). The open bars represent the no cut streams, light grey bars represent the low cut and dark grey bars the high cut streams.