DYNAMICS OF TEMPORAL AND SPATIAL MERCURY CONTAMINATION IN AN URBAN WATERSHED

by

MATTHEW ROBERT MURARO

B.A., University of North Carolina at Wilmington, 1996

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Abstract

Mercury is a concern in aquatic environments because it can lead to accumulations of methylmercury in fish, which is the primary source of mercury exposure to humans. The Brunette Watershed is a highly urbanized watershed in metropolitan Vancouver with a rich record of monitoring (1973-2003) trace metal distribution and dynamics. This study was conducted to investigate the 294% increase in Brunette Watershed stream sediment mercury concentrations from 1973-1996. The project conducted analysis of field samples, laboratory experiments and examined previous data to determine if methylcyclopentadienyl manganese tricarbonyl (MMT) may play a role in the increase of mercury in the watershed. Little evidence compiled in this study supported the hypothesis that manganese, iron, sulfur or DOC is associated with mercury throughout the watershed. Thus, it is difficult to conclude or rule out that MMT or manganese oxides play a major role in the transport of total mercury. Laboratory experiments creating summer anoxic conditions released a significant amount of mercury from lake sediment into overlying waters. It seems that this release of mercury may be controlled by sulfate reducing bacteria.

The study also found an analysis method used in the study caused 66.8% mean loss of mercury in stream sediment samples when the samples were dried. Temporal and spatial analysis of sediment data revealed that mercury concentrations have started to decrease since 1993. When sediment concentrations were adjusted for the 66.8% loss in stream sediment, 1993 mercury concentrations exceeded the Federal Interm Sediment Quality Guidelines at 12 locations; but in 2003, only 1 site exceeded the same guideline. The decrease in mercury concentrations may be linked to the increased public awareness and a large reduction of emissions from a nearby refuse incinerator. Effective imperviousness and mercury levels in stream sediment are significantly correlated throughout the period of high mercury releases from the incinerator. This may indicate that atmospheric mercury deposited on impervious surfaces connected to waterways may contribute to increases in stream sediment concentrations.

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1. INTRODUCTION

Mercury is intriguing to study because its toxicology, transformation and transport mechanisms are complex and not currently well understood. The U.S. Environmental Protection Agency is allocating 40-50% of its mercury budget over the next 5 years to be spent on transport, fate, and transformation, because it considers it a high priority for research (EPA 2003). Mercury is the most common contaminant in aquatic ecosystems worldwide, however, its sources and pathways and toxicity controlling processes are very complex (Krabbenhoft 1997). It's behavior in the environment is considerably different than other metals. Physically, it is unique because it is a liquid at room temperature and pressure. It and some of its compounds, have a high vapor pressure compared with other metals. Various complex processes affect mercury in atmospheric and aquatic systems that are not fully understood. Generally, it is very reactive in the environment and readily undergoes phase and reduction-oxidation (redox) changes. It will undergo many environmental processes, photochemical reactions, chemical oxidation and redox reactions, microbial transformations, and physiological fractionation.

Mercury pollution is a complex problem in the world today and an incident in the 1950's mercury poisoning drew worldwide attention when approximately 200 people died in the Japanese Fishing village of Minamata. Later in the 1980's, researchers found elevated levels of mercury in remote, isolated lakes where no sources could immediately be identified. This lead to the discovery that mercury contamination of aquatic systems is generally caused by atmospheric transport and deposition. Once in an aquatic system it bioaccumulates in organisms to levels much higher then the surrounding atmosphere, water or lake sediment.

In the past, analytical instrument technology was not able to reach a low enough mercury detection limit to study it effectively. Fish in the remote lakes would have levels of detectable mercury but a source could not be detected in water or air. Over the last fifteen years, improvements in analytical techniques and technology have increased the capability of researchers. Recently, advances in technology have made it possible to study levels as low as 0.005 ng/m^3 of mercury, which is low enough for ambient atmospheric testing (Meyers 1998).

Mercury is a concern in aquatic environments because it can lead to accumulations of methylmercury in fish. Seafood consumption is the only significant bio-accumulation pathway for humans and animals to become contaminated (EPA 2003; UNEP 2003). Interestingly, due to the complex processes that control mercury cycling, total mercury concentrations in air, water or soil can not be an indicator of methylmercury concentrations in water, sediment or biota. Thus, it is necessary to understand the cycling of mercury in aquatic systems.

1.1 Study goal

The Brunette Watershed, a highly urbanized watershed in metropolitan Vancouver, British Columbia which has been intensely studied over the last thirty years (Figure 1.1 and 1.2). A wealth of information regarding the watershed has been created in this time span and knowledge of watershed conditions and its processes has increased with each study. McCallum (1996) noted a 294% increase in mercury and a 131% increase in manganese

Figure 1.1 Location of the Brunette Watershed in Lower British Columbia
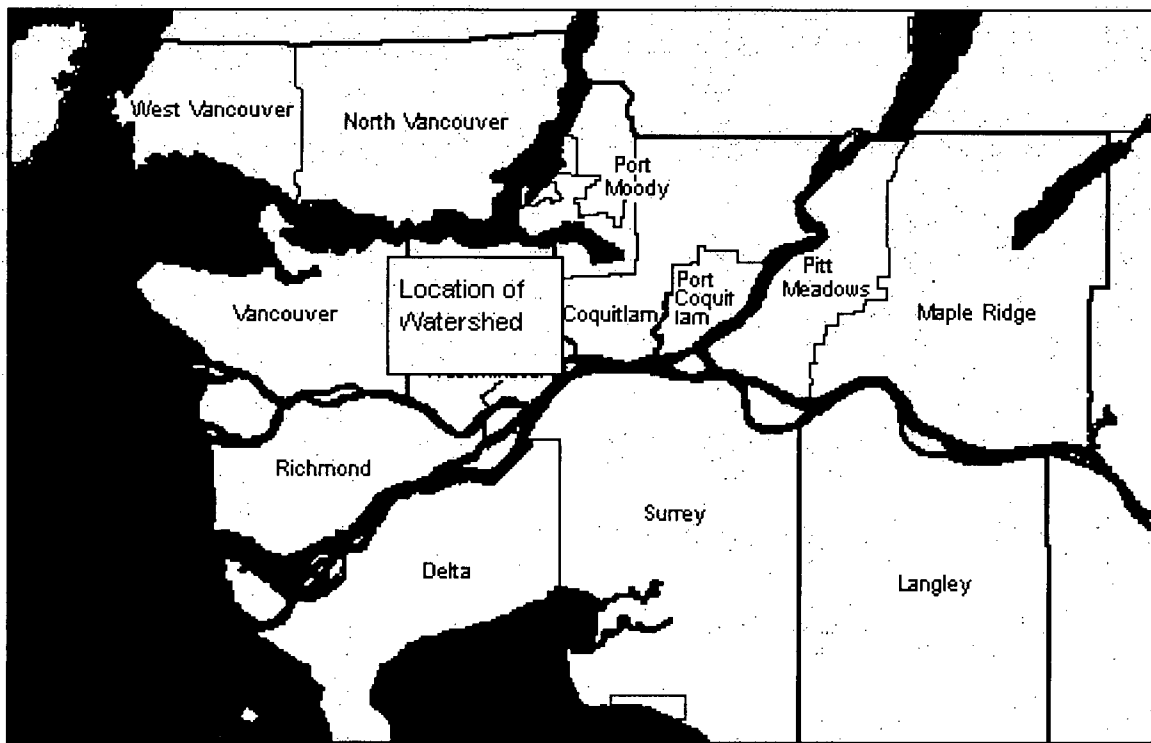
Figure 1.2 Map of Brunette Watershed (McCallum 1995)
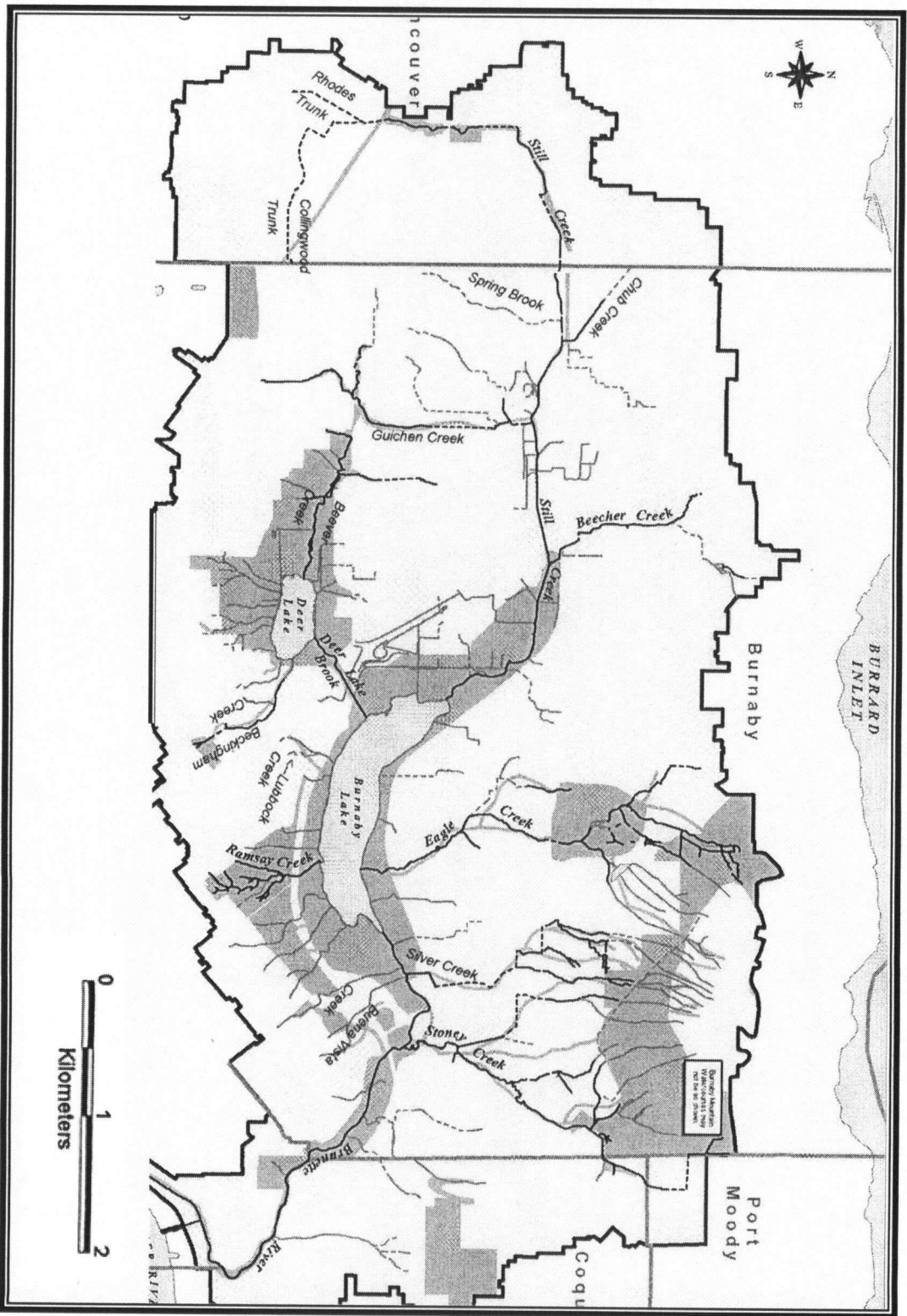
concentrations in stream sediment from 1973-1996 throughout the watershed. It was presumed by McCallum (1995) the increase in manganese concentrations was due to the addition of methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline after 1986, as a replacement for lead additives. This concept was reinforced by a 2600% increase in dilute acid extractable manganese from stream sediment, which is thought to be representative of the manganese oxide fraction (Bendell-Young and Harvey 1991).

One possible explanation used by McCallum (1995) for the increase in mercury concentrations was its adsorption by manganese oxides (Thabalasingam and Pickering 1985). Manganese, released from the exhaust of an automobile will oxidize and then absorb or bind with various materials, including mercury. Mercury and manganese could then be flushed into aquatic systems by stormwater events.

$$2Mn^{+2} + O_2 = (MnO_2)^{-2}$$
$$(MnO_2)^{-2} + Hg^{+2} = Hg\,(MnO)_2$$
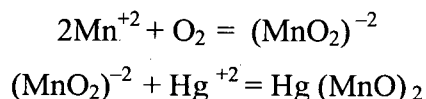
The geochemical processes for controlling mercury's associations in an aquatic environment are different than other metals, due to its unique physical and chemical properties. Mercury forms strong bonds with complexing agents or ligands. Ligands are molecules or ions that surround a metal ion in a complex. This project is intended to investigate the possibility that manganese oxides could be leaching mercury out of the soil and transporting it through the watershed; with the hope of expanding the current knowledge of mercury dynamics in the Brunette Watershed. It is suspected that these complexes transport mercury in the "flashy" Still Creek system as particulate matter.

Particulates eventually reach Burnaby Lake and settle out. In the summer, Burnaby Lake becomes anoxic. Reducing conditions may release mercury and methylmercury bound to iron and manganese oxides back into interstitial porewater and the overlying water column. This project was intended to determine if metals, including mercury, bound to these iron oxides (FeOx) and manganese oxides (MnOx) are released under anoxic conditions in sediment, interstitial water and overlying water. On a larger scale, it will investigate various processes to improve the understanding of mercury transport in the Brunette Watershed.

1.2 Objectives

1. Quantify current levels of mercury and other trace metal contamination in Brunette Watershed stream sediment to identify temporal and spatial changes in mercury contamination since 1973.

2. Identify if mercury correlates with organic carbon, iron oxyhydroxides, manganese oxyhydroxides, sulfur and other trace metals in stream sediment, lake sediment, stormwater and laboratory controlled redox conditions.

3. Identify if mercury, iron, manganese and organic carbon are released from lake sediment to overlying water under anoxic conditions.

4. Investigate if MMT could be responsible for the increase of mercury concentrations in the Brunette Watershed stream sediment by examining correlation's between manganese and mercury.

This project used a combination of field and laboratory data along with historical data. Laboratory microcosm experiments was designed to identify mercury's reactions to various environmental conditions in an effort to identify geochemical associations. Stream and lake sediment throughout the watershed was analyzed to determine temporal and spatial trends over the last thirty years in an attempt to locate sources and transport mechanisms. Stormwater was studied to identify features involved in contaminant transport.

1.3 Mercury sources and environmental contamination

Total releases of mercury to the environment in Canada is estimated at 20 tonnes per year (Hagreen et al. 2004). Releases of mercury are classified into two broad categories, natural and anthropocentric. According to EPA documents, the amount of mercury in the atmosphere is estimated to have increased by 200 % to 500 % since the beginning of the industrial revolution (Obenauf and Skavroneck 1997). Recent estimates calculated that anthropocentric emissions have tripled the concentration of mercury in the ocean over the

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last century (Mason *et al.* 1994). Other reports indicate that there is 3 to 6 times more mercury today vs. pre-industrial times in Atlantic Ocean water, Atlantic bird feathers, peat bogs, soils and lake sediments (Obenauf and Skavroneck 1997). Currently, atmospheric mercury originates from 25-40% natural sources and 60-75% anthropocentric (Mason *et al.* 1994). Natural sources of atmospheric mercury are mainly in the gaseous elemental form (Porcella *et al.* 1996). These sources include volcanoes, forest fires and off gassing of soils, vegetation and the ocean. Mercury is mined and used because its unique physical and chemical properties make it very useful for industrial processes. Its release into the environment is often unintended, accidental or a by-product of industrial processes. Anthropocentric sources to the atmosphere include incineration, chloro-alkali plants, metal extraction processes, cement production, coal, oil and gas incineration, (Table 1.1 and 1.2). Incineration of refuse is considered the second largest global source of atmospheric mercury, [Table 1.1] (Pacyna 1996).

A recent report indicated that 1 in 12 or 5 million people in the United States contain levels of mercury above levels considered safe by the U. S. Environmental Protection Agency [EPA] (UNEP 2003). The United States Research Council estimated that about 60,000

Table 1.1 Estimate of annual releases of mercury from purposeful uses in Milwaukee, Wisconsin. The area is 420 square miles with population just over 2 million. [Adapted from (Obenauf *et al.* 1997).

Sector	Amount (kg/yr)	Percent of Total	Releases to Media		
			Air (kg/yr)	Solid Waste (kg/yr)	Wastewater (kg/yr)
Refuse Incinerators	149	35%	149	0	0
Fluorescent Lamps	57	13%	0	57	0
General Industry	46	11%	0	0	46
Dental Facilities	45	11%	0	18	27
Switches - Automotive	32	8%	3	23	6
Thermostats	32	8%	0	32	0
Batteries	23	6%	0	24	0
Households	18	4%	0	0	18
Switches - Lighting	7	2%	0	7	0
Hospitals and Medical Facilities	3	1%	0	0	3
Switches - Appliances	2	<1%	0	1	<1
Crematories	1	<1%	1	0	0
Landfills	1	<1%	0	0	<1
Veterinary Facilities	1	<1%	0	<1	0
Septic	0	0%	0	0	0
Total for Purposeful Uses (lb/yr)	418	0	152	163	102
Total for Purposeful Uses (percent)	0	100%	37%	39%	24%

Table 1.2 Estimate of annual releases of mercury from processes that release trace impurities in Milwaukee, Wisconsin. The area is 420 square miles with population just over 2 million. [Adapted from (Obenauf *et al.* 1997).]

			Releases to Media		
Sector	Amount (kg/yr)	Percent of Total	Air (kg/yr)	Solid Waste (kg/yr)	Wastewater (kg/yr)
Coal Combustion Utilities	157	65%	125	31	0
Secondary Metal Smelting	31	13%	31	0	0
Motor Vehicle Combustion	22	9%	22	0	0
Oil Combustion Industry	16	7%	16	0	0
Oil Combustion Residential	14	6%	14	0	0
Coal Combustion Industry	0	0%	0	0	0
Lime Production	0	0%	0	0	0
Total for Trace Impurities (pounds)	329	0	207	31	0
Total for Trace Impurities (percent)	0	100%	87%	13%	0%

babies born each year in the U.S. could be at risk of brain damage with possible impacts ranging from learning difficulties to impaired nervous systems (UNEP 2003). Human mercury contamination has also been linked to cardiovascular problems including raised blood pressure, palpitations and heart disease (UNEP 2003). Effects on the brain can include irritability, tremors, disturbances to vision, memory loss, impaired coordination and other adverse effects (UNEP 2003). Fetuses, the newborn and young children are particularly vulnerable because of the sensitivity of their developing nervous system

(UNEP 2003). Other effects have been found on the thyroid gland, which regulates growth, the digestive system, the liver and the skin including peeling on hands and feet, itching and rashes (UNEP 2003).

As of December 2000, mercury was the contaminant responsible, at least in part, for the issuance of 2,242 fish consumption advisories by 41 US states (Bigler 2003). Furthermore, 79% of all fish and wildlife advisories issued in the United States are at least partly due to mercury contamination in fish and shellfish (Bigler 2003). EPA advisories for mercury have increased 149% in 7 years, from 899 advisories in 1993 to 2,242 advisories in 2000 (Bigler 2003).

On January 12, 2001, the EPA and U.S. Federal Drug Administration (FDA) jointly issued a press release notifying the public of a national fish consumption advisory due to mercury contamination (Bigler 2003). EPA's guideline recommends if a person is pregnant, could become pregnant, nursing a baby, or feeding a young child; consumption of freshwater fish caught by family and friends should be limited to one meal per week (Bigler 2003). For adults, one meal is six ounces of cooked fish or eight ounces of uncooked fish; for a young child, one meal is two ounces of cooked fish or three ounces uncooked fish (Bigler 2003).

The FDA has also released a consumer advisory recommending children and women, with or planning to have children, should avoid eating shark, swordfish, king mackerel, tuna steaks and tile fish. Safeway, Kroegers, Trader Joe's and Whole Foods, (large grocery store chains in California) have voluntarily agreed to post FDA warnings about mercury contamination of the previously listed fish at seafood counters.

1.4   Atmospheric processes and transport

Atmospheric deposition is considered the dominant pathway for mercury contamination of aquatic systems, without a point source (Fitzgerald *et al.* 1991; Watras *et al.* 1996; EPA 1999). Forms of deposition include direct wet/dry deposition and indirect sources like terrestrial runoff. Uncertainty exists about how the cycling of atmospheric mercury has changed with the addition of anthropocentric sources. The majority of uncertainty lies in assessing historic levels and processes (Fitzgerald *et al.* 1991; Guentzel 2001).

Currently in the atmosphere, 97-99% of mercury is in the zero oxidation state as gaseous elemental Hg (Hg^0) (Fitzgerald *et al.* 1991; Lindqvist *et al.* 1991; Nater *et al.* 1992). The remaining 1-3% is comprised of particulate Hg (Hg_p) or reactive gaseous Hg(ll)) (Lindqvist *et al.* 1991; Nater *et al.* 1992). Gaseous elemental Hg has a residence time in the atmosphere of up to 1 year (Fitzgerald *et al.* 1991; Lindqvist *et al.* 1991; Nater *et al.* 1992). Hg(ll) and Hg_p can reside for days or weeks in the atmosphere (Lindqvist *et al.* 1991; Nater *et al.* 1992). Hg^0 can enter the global mercury cycle and travel up to 10,000 km (Porcella *et al.* 1996). Hg_p or Hg(ll) are deposited near the emission source (50 km) (Porcella *et al.* 1996). When deposited mercury is almost exclusively in the Hg_p form (Porcella *et al.* 1996).

It is difficult to predict residence time and distance transported due to local variability in weather and the atmosphere (Porcella *et al.* 1996). Of the estimated 158 tons of mercury emitted annually into the atmosphere by human activities in the United States, approximately 87 percent is from combustion point sources, 10 percent from manufacturing, and 3 percent is from all other sources (Obenauf *et al.* 1997). Speciation, climate and meteorology of anthropocentric mercury determine the distance traveled (Guentzel 2001).

1.5 Aquatic processes and transport

The intent of this study is to analyze mercury transport in an aquatic, urban environment(Babirz *et al.* 1998). Urban watersheds have shown higher yields of mercury than forested and rural areas (Hurley *et al.* 1995; Mason *et al.* 1997). This is due to a lack of soil for binding, high stormwater fluxes and runoff due to impervious surfaces. Stormwater has been implicated in the movement of particulate mercury in aquatic systems due to the resuspension of sediment, increased runoff and disturbance of lake's hypolimnion (Jackson 1982; Mason *et al.* 1997; Benoit *et al.* 1998a).

Inorganic mercury will typically enter a freshwater system bound to various inorganic and organic particles. There is some uncertainty as to what conditions govern binding distribution. These particulates are predominately moved under high-flow or stormwater conditions until particulates settle to the bottom of the system. Studies have concluded that high-flow events lead to increased mercury transport (Hurley *et al.* 1995; Mason *et al.* 1997; Babirz *et al.* 1998; Benoit *et al.* 1998b). Aquatic mercury transport

generally occurs through a combination of two separate processes; mercury bound to suspended particulate matter (SPM) or bound to dissolved organic carbon (DOC).

A large body of research exists suggesting mercury in an aquatic environment predominately bonds to organic carbon (Watras *et al.* 1994; Mason *et al.* 1997; Benoit *et al.* 1998a; Meyers 1998). Organic matter has a strong affinity for mercury so it typically correlates well in transport and sediment (Meili 1997). Inorganic ligands, (iron and manganese oxyhydroxides, reduced sulfur compounds and clay minerals) generally correlate in systems with low levels of organic matter (Meili 1997). Furthermore, some research indicates that in eutrophic, circumneutral waters, mercury will predominately bind with iron and manganese oxides (Jackson 1982; Jacobs *et al.* 1995; Quemerais *et al.* 1998; Reggnell *et al.* 2001). The role of these different inorganic ligands in dissolved and particulate mercury transport is important but not well understood.

Hurley *et al.* (1995) monitored river sites in Wisconsin which exhibited strong seasonal variations. They observed a strong correlation between filtered Hg_t and DOC ($r^2 = 0.61$) during fall base flow but the relationship was reduced in the spring ($r^2 = 0.14$). This reduced relationship is most likely due to higher spring flows and increased SPM in the spring. Hurley *et al.* (1995) also compared land-use to mercury concentrations in 39 Wisconsin rivers and found urban areas had the highest spring and overall concentrations.

Mercury bound to DOC is derived from porewater in "marsh like" areas (Hurley *et al.* 1995; Babirz *et al.* 1998; Benoit *et al.* 1998b). In urban watersheds, it seems that mercury transport is typically associated with SPM (Gill *et al.* 1990; Mason *et al.* 1997). SPM originates from run-off, suspended sediments and bank erosion (Hurley *et al.* 1995; Babirz *et al.* 1998). Spring flows are generally higher, which would increase the amount of suspended particulate matter.

Vasiliev *et al.* (1996), analyzed mercury transport by different fractions of suspended sediments in the spring and summer. They found that particles in the <0.45 um fraction had the highest concentration of mercury while the >50 um had the highest overall contribution to transport. The middle fractions mimicked these overall relative trends.

It is difficult to deduce the mobilization of mercury by examining the Brunette Watershed as a whole. This is due to the various mechanisms that can control transport. The upper catchments of the Brunette Watershed can be characterized by having a short

residence time. In these areas, it is likely that mercury transport is typical of other urban waters.

1.6   Geochemical processes of mercury in aquatic sediment

Sediment plays an important role in mercury transport and biogeochemical cycling. The biogeochemical cycling of mercury in sediment can be controlled by ligands. Ligands are polar molecules or anions that surround a metal ion in a complex (Brown *et al.* 1991). It is important to differentiate between mercury bound to ligands and other forms because ligands can determine sedimentation rates and bioaccumulation rates in animals. Metal oxides, including hydroxides and oxyhydroxides are ligands that may directly or indirectly control the mobility and transport of mercury in oxic and anoxic environments.

Iron and manganese oxides form labile complexes in particulate, colloidal and dissolved forms. The stability of these oxides are highly dependent on pH and redox potential (Meili 1997). Reducing conditions can create an increase of mercury (Hg) and possibly methylmercury (MHg) in anoxic waters (Regnell *et al.* 1996). Released ionic iron and manganese may also compete with mercury for sulfur binding sites, increasing the quantity of dissolved mercury available for methylation. Therefore, under oxic conditions sediment acts as a sink for mercury and methylmercury. While under anoxic conditions, mercury could be released from the sediment or converted to HgS.

In an oxic environment, MnOx and FeOx form strong bonds with Hg and organic matter. Porcella *et al,* (1995) suggest that FeOx have a mass related affinity for Hg ten times higher than organic matter alone. Quemerais *et al,* (1998) research indicates that organic carbon only attracts mercury when metal hydroxides are present, when they are removed, no relationship can be found. Also, FeOx and MnOx can be the main mercury complexing agent when their relative abundance is high (Meili 1997). This is indicated by coenrichment in dissolved and anoxic waters and as solid precipitates in a variety of boreal, temperate and tropical sediments.

Iron and manganese oxides may also regulate the potential for methylation by scavenging organic and sulfur binding sites (Reggnell *et al.* 2001). Regnell *et al* (2001) have identified a correlation between Fe, Mn and MHg in water of seasonally stratified lakes. Jacobs *et al,* (1995) studied an urban, eutrophic lake near Syracuse, New York, that experiences summer stratification, similar conditions to Burnaby Lake and found a strong

relationship between MHg and manganese. This is explained by "The reduction of Fe (III) requires a lower redox potential (or pe) than Mn. In addition, the oxidation of Fe (II) in the presence of oxygen is typically very rapid; thus, Fe diffusing across the redoxocline is rapidly converted to the particulate form [Fe (III)]. Mn oxidation kinetics are slower, and Mn oxidation has been attributed to Mn-oxidizing bacteria that are present at the redoxocline" (Jacobs *et al.* 1995).

1.7   Mercury and methylmercury in aquatic systems

Aquatic cycling of mercury is a complicated process that involves many pathways (Figure 1.2). Inorganic mercury and organic mercury (forms of methylmercury) are distributed and behave very differently in various aquatic systems (discussed in section 1.5). Inorganic mercury in a freshwater lake will also bond with a variety of substances and take many forms. The majority of inorganic mercury in a freshwater system is bound to sediment. Within a lake system, it is possible for the top 3 millimeters of sediment to hold the equivalent mass of mercury as the entire overlying body of water (Meili 1997). Within water, mercury is bound by sulfur, dissolved organic carbon (DOC) and inorganic complexes, such as MnOx and FeOx. Only a small fraction of mercury is found in biota (typically around 1%), relative to the rest of an aquatic system (Porcella 1994; Meili 1997). Conversely, methylmercury does bioaccumulate in biota by biomagnification and bioconcentration (Meili 1997). This can create up to a 10^4 fold increase in concentrations between upper and lower biota in the food chain (Meili 1997).

Methylmercury (MHg) is generally a high percentage (95-99%) of the total mercury found in fish (Porcella 1994; Meili 1997). Fish accumulate MHg through gills and food; therefore, foraging habits and proximity to sediment regulates uptake (Porcella 1994). It is eliminated very slowly from the liver, kidney and spleen (Meili 1997). The concentration of methymercury in biota is thought to depend on the rate of methylation and demethylation within the system and the substrate to which the ingested mercury is bound (Meili 1997). Mercury methylation rates are the highest in the presence of steep redox gradients and high microbial activity (Krabbenhoft 1996). The combination of steep redox gradients and high

Figure 1.3 Conceptual model of mercury cycling and pathways for a typical freshwater lake (Krabbenhoft *et al.* 1997).
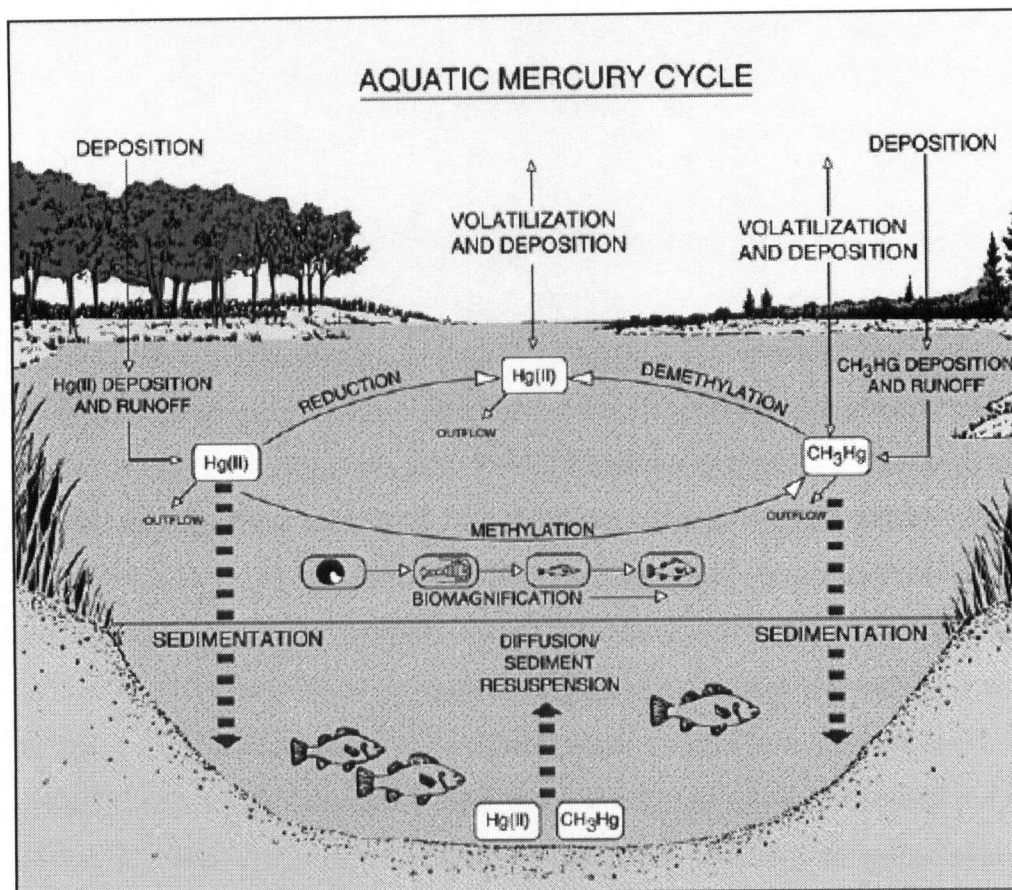
microbial activity are generally located at the hypolimnion or in sediment with anoxic and oxic layers (Krabbenhoft 1996; Meili 1997).

Methylation seems to be a fairly consistent process while demethylation is variable (Meili 1997). Demethylation tends to be highest in oxic waters (Watras *et al.* 1994). It has two pathways, irradiation from sunlight and breakdown by microorganisms (Krabbenhoft 1996). Although, it is theorized that methylmercury production in the oxic zone is important to mercury cycling because overall levels may be masked by demethylation, the location of production may increase bioavailability. This could lead to an increase of MHg bioavailability in the oxic zone.

The current paradigm of aquatic contamination is the location and level of MHg in the water governs the level of biota contamination, not inorganic mercury. Therefore, lakes with the highest net production of MHg have higher contamination in piscivorous fish. Typical water quality characteristics of these lakes include low pH, alkalinity, hardness and low overall biota productivity.

High productivity, eutrophic lakes typically have low levels of contamination in biota because mercury binds to organic matter and sediments out of the system. Overall, eutrophic lakes generally contain more mercury in sediments than oligotrophic. In eutrophic lakes, organic matter binds mercury and sediments it out of the system. Large quantities of plankton and algae biomass also dilute mercury concentrations.

2. CHARACTERISTICS OF THE BRUNETTE WATERSHED

2.1 Site Description

The Brunette Watershed is a 73 square kilometer urban area that flows into the Fraser River in New Westminster (GVRD 2001). At least a portion of the watershed is within the municipalities of Vancouver, Burnaby, New Westminster, Coquitlam, and Port Moody. Centralized in the watershed is Burnaby Lake, a receiving area for the upper catchments. Five main streams Still Creek, Eagle Creek, Deer Lake Brook, Ramsay Creek and Stoney Creek feed the lake (Figure 2.1 and Table 2.1). Sub-basins were delineated for Still Creek and the Brunette River with the Brunette Watershed. The Still Creek sub-basin includes catchments 1,2,3 and 7 in Figure 2.1. Brunette River sub-basin includes catchments 5, 6 and 10 in Figure 2.1. Still Creek carries approximately 58% of the flow to Burnaby Lake (Hall *et al.* 1976). The upper reaches of Still Creek and most other streams have a steep slope, along with its channelized banks and culverted stretches and produces quick stream velocities (Table 2.2). The lower portion of Still Creek (below Gilmore Street) has a decreased slope, increased channel width and backwater effects from the lake that contribute to low stream velocities. Stormwater drainage systems and groundwater contribute to the bulk of the watershed flow. The stormwater flow is considered flashy and carries a large particulate load in stormwater events.

Figure 2.1 Map of the Brunette Watershed and tributaries and catchments (GVRD 2000a).
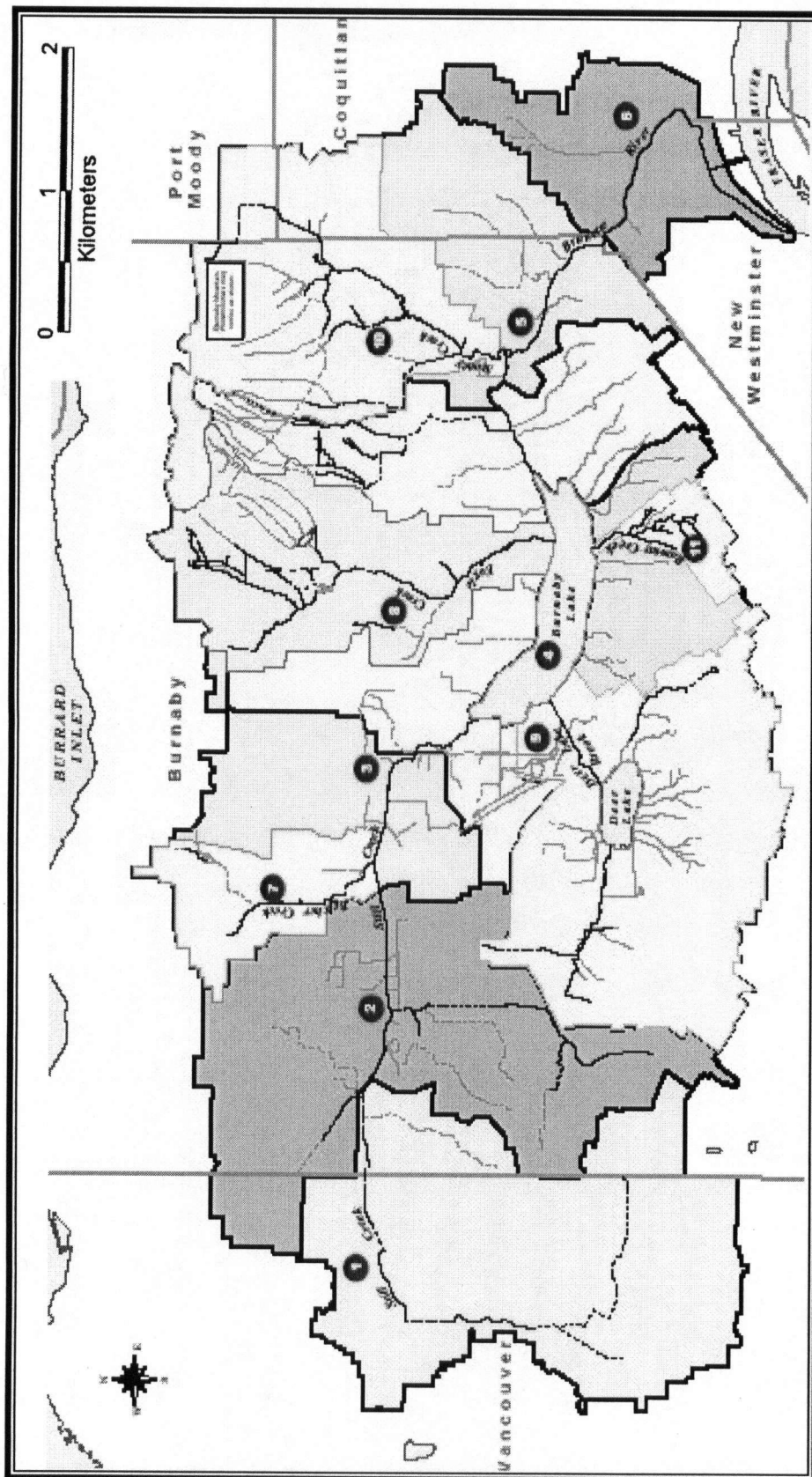
Table 2.1 Catchment name, number and imperviousness from Figure 2.1 (GVRD 2000a)

Catchment	Catchment number	Imperviousness (%)
Upper Still Creek	1	68
Middle Still Creek	2	58
Lower Still Creek	3	52
North Burnaby Lake	4	0
Upper Brunette River	5	37
Lower Brunette River	6	54
Beecher Creek	7	55
Eagle Creek	8	36
Deer Brook Lake	9	38
Stoney Creek	10	33
Ramsey Creek	11	33

Table 2.2 Average slope of catchments within the watershed (Hall *et al.* 1976)

Upper Still Creek Still Creek to Gilmore St.	15 m/km slope
Burnaby Lake Gilmore St. to Cariboo Dam	0.5 m/km slope
Brunette River Cariboo Dam to Fraser River	2.5 m/km slope

Burnaby Lake is 140 hectare in area, shallow and eutrophic, with a large amount of surrounding marsh (Fitzgerald *et al.* 1991). Bottom waters and sediments turn anoxic in the summer, which has resulted in fish kills (GVRD 2001). Mean water depth in 2001 was 0.97 meters (Enkon 2002). The sediments are a mix of silt, clay and amorphous peat in marsh areas (Enkon 2002). Four out of five of the larger catchments within the watershed flow into

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Burnaby Lake. The water level in the lake and flow in the Brunette River are controlled by the Greater Vancouver Regional District (GVRD) lake outlet at Caribou Dam. Water leaving Caribou Dam flows into the Brunette River, then into the Fraser River. The Brunette River slope and flow is initially moderate, but decreases as it nears the Fraser River (Figure 2.2). This is due to a decrease in slope and tidal effects from the Fraser River.

Surrounding Burnaby Lake is a small "green space" called the Burnaby Regional Nature Park. A medium density residential and commercial/industrial land-use encompass the park. The watershed has a history of trace metals contamination (Hall *et al.* 1976; Duynstee 1990; Macdonald *et al.* 1996a). This is attributed to large sediment loads, stormwater runoff and a high percentage of impervious surfaces within the watershed. Land-use and imperviousness can be useful indicators of pollution sources. Land-use changes over the last thirty years have been moderately increasing (Table 2.3). Impermeable cover has increased 7% from 1973-1993 (Table 2.4). Since 1993, the density of development has undoubtedly increased, but it has not been quanitfied.

Table 2.3 Land use in the Brunette Watershed in proportion to the total area in 1973 and 1993 (McCallum 1995).

Land Use	% 1973	% 1993	% Change
Residential	40.8	45.7	+ 4.9
Industrial	11.9	13.2	+ 1.3
Commercial	3.6	4.1	+ 0.5
Institutional	6.6	6.4	- 0.3
Agricultural	1.4	0	- 1.4
Open Space	32.9	28	- 5

Table 2.4 Land cover in the Brunette Watershed in 1973 and 1993. (McCallum 1995)

Land Cover	% 1973	% 1993
Permeable	66	59
Impermeable	34	41

Figure 2.2 Cross section view of Brunette Watershed indicating slope (McCallum 1995).
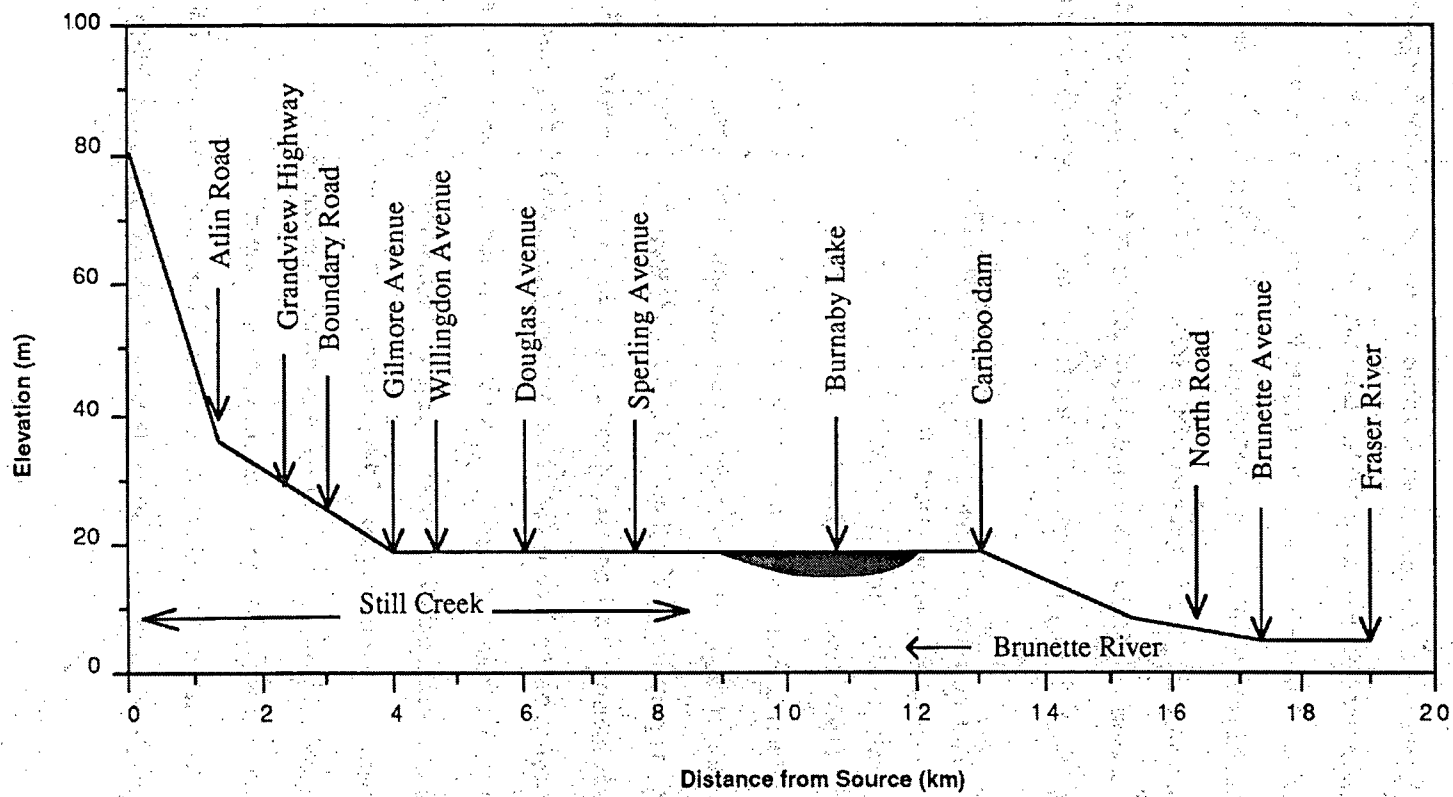
2.2 Historic contamination in the Brunette Watershed

The Brunette Watershed has become highly contaminated with a wide range of pollutants due to its urban environment. Stormwater loading calculations for nutrients, organic matter and a few trace metals (Cu and Zn) were the highest when compared to 22 other extensively studied locations in the United States (Hall *et al.* 1998). A variety of organizations have collected information about the microbial, organic and trace metal contamination over the last 35 years. The University of British Columbia (UBC), Simon Fraser University (SFU) and the British Columbia Institute of Technology (BCIT) have compiled valuable research about the watershed. These groups have worked together to share information and find solutions to various environmental problems. Federal, provincial, regional and city government agencies have also monitored the area and provided funding.

These studies indicate the high levels of contaminants have negatively impacted the watershed ecology. Toxicity bioassays demonstrated that stormwater runoff were periodically toxic to *Daphnia* (Hall *et al.* 1988). Later, chironomid (*Chironomus tentans*) bioassays indicated that elevated contaminants in Still Creek impacted their survival rate and weight, relative to an unimpacted site (Smith 1994).

2.2.1 Trace Metal Contaminants

Baseline trace metal contamination throughout the watershed was first quantified by Hall *et al.* (1976). McCallum (1995) analyzed Burnaby Lake and Deer Lake core samples for trace metals and found a steady increase in Cu, Cr, Cd, and Ni from 1950-1970. This increase is attributed to land-use changes and industrial discharges throughout that time frame. Since monitoring began, surface water and sediment criteria intended to protect aquatic life have often been exceeded for Pb, Cu, Zn and Cr (Swain 1989; McCallum 1995). Comparison studies by Duynstee (1990) and McCallum (1995) identified many variables that contribute to the increase in stream sediment concentrations. These variables include land-use, automotive traffic and imperviousness. Spatial analysis of stream and street sediment indicates traffic contributes a large proportion of the Pb, Cu, Mn and Zn to the watershed. Also, impervious surfaces create a pathway for trace metals and other contaminants to be transported into waterways.

Hall *et al.* (1976), Duynstee (1990) and McCallum (1995) all indicated that Still Creek is the largest source of contaminants into Burnaby Lake. Duynstee (1990) and McCallum (1995) attributed contamination levels to high levels of industry, automotive traffic and impervious surfaces. UBC conducted mesocosm flow-through experiments with benthic invertebrates in the Brunette River (Richardson *et al.* 1998). This study found that benthic invertebrates most sensitive to heavy metals exposure were largely absent from the Brunette River watershed and concluded that heavy metal contamination throughout the watershed contributes to the degradation of the watersheds aquatic ecosystems.

Mercury contamination data in the Brunette Watershed dates back to Hall *et al.* (1976), when the first comprehensive survey of stream sediments was conducted. Concentrations of mercury increased 294 percent from 1973-1993 in streambed sediments (McCallum 1995). Correspondingly, Mn increased 131% in total and 2600% in extractable forms respectively. McCallum (1995) suspects this large increase in manganese oxides is a result of automobile combustion of the gasoline additive methylcyclopentadienyl manganese tricarbonyl (MMT). In 1992, analysis of mercury in three carp livers from Burnaby Lake resulted in the following concentrations 114, 99 and 128 ug/kg dry weight (BCIT 1992).

2.2.2 Organic contaminants

Organic compounds can have a strong effect on mercury transport and distribution due to there large size and binding strength. High levels of polychlorinated biphenyls (PCB's), 1,1-bis (4-chlorophenyl)-2,2,2-trichloroethane (DDT) and chlorinate phenols have been found in Still Creek and detected throughout the watershed (Hall *et al.* 1974; Hall *et al.* 1976). These are a group of synthetic chemicals that are highly stable and were commonly used in industrial and commercial processes. These chemical compounds have been proven to cause negative effects on animals and humans, including cancer, immune system, reproductive system, nervous system, endocrine system and other health effects. Chlorinated hydrocarbon (DDE, DDT and PCB's) levels in stream sediment have been decreasing from peak concentrations between 1940–1970 (McCallum 1995). This indicates that increased regulation has been effective in reducing chlorinated hydrocarbon levels in the aquatic environment.

Polycyclic aromatic hydrocarbons (PAH's) are known carcinogens which can be derived from coal, tar and petroleum and are emitted by combustion related activities. Morton (1983) presented evidence of PAH bio-accumulation in fish and attributes the stream contamination to automotive sources, street deposition and runoff.

Larkin (1995) used core samples to determine that total petroleum hydrocarbon (TPH) concentrations have increased tenfold over the last 200 years. Analysis of streambed sediments indicated industrialized regions had the highest hydrocarbon levels. Transport mechanisms were also identified from catchment land-use (automotive activities), dilution of street runoff by stream volume and traffic intensity on mean hydrocarbon concentration in stormwater.

Overall, public awareness and pollution prevention practices have been implemented to reduce the overall levels of trace metals and hydrocarbons. Although, PAH's are likely still increasing due to rising automotive use.

2.2.3   Microbial Contaminants

Fecal coliform is a classification of bacteria used to identify the presence of human waste contamination. High levels of fecal coliform have been detected in the watershed for sometime. This is due to a combination of urban runoff and leaking or illegal stormwater cross-connections to sewer lines. Monitoring has identified high levels in Still Creek and contamination throughout the watershed. This has caused the closure of waterways throughout the watershed to primary contact recreational activities for sometime (Hall *et al.* 1998).

3. METHODS

Laboratory analysis methods will be described in sub-section 3.3 (Laboratory analysis).

3.1 Streambed sediment sampling and analysis

Aquatic sediments bind trace metals, govern aquatic toxicity and affect transport processes. The historic variation of trace metal contamination in streambed sediment's were determined in this urbanized watershed through streambed sampling, analysis and then comparison to historic data (1973-1993). Thirty streambed sediment samples were collected and analyzed for a comparison with historic data collected over the last 30 years. Sampling locations and analytical methods used in Hall *et al.* (1976) were also used in this study for data compatability (Figure 3.1). Statistical analysis was then used to look for historic trends and associations. Statistical analysis was also used to identify correlations between metals and sediment quality. These correlations could improve knowledge of aquatic geochemistry within the watershed.

Figure 3.1 Brunette Basin stream sediment sampling sites. Adapted from Hall *et al.* (1976)
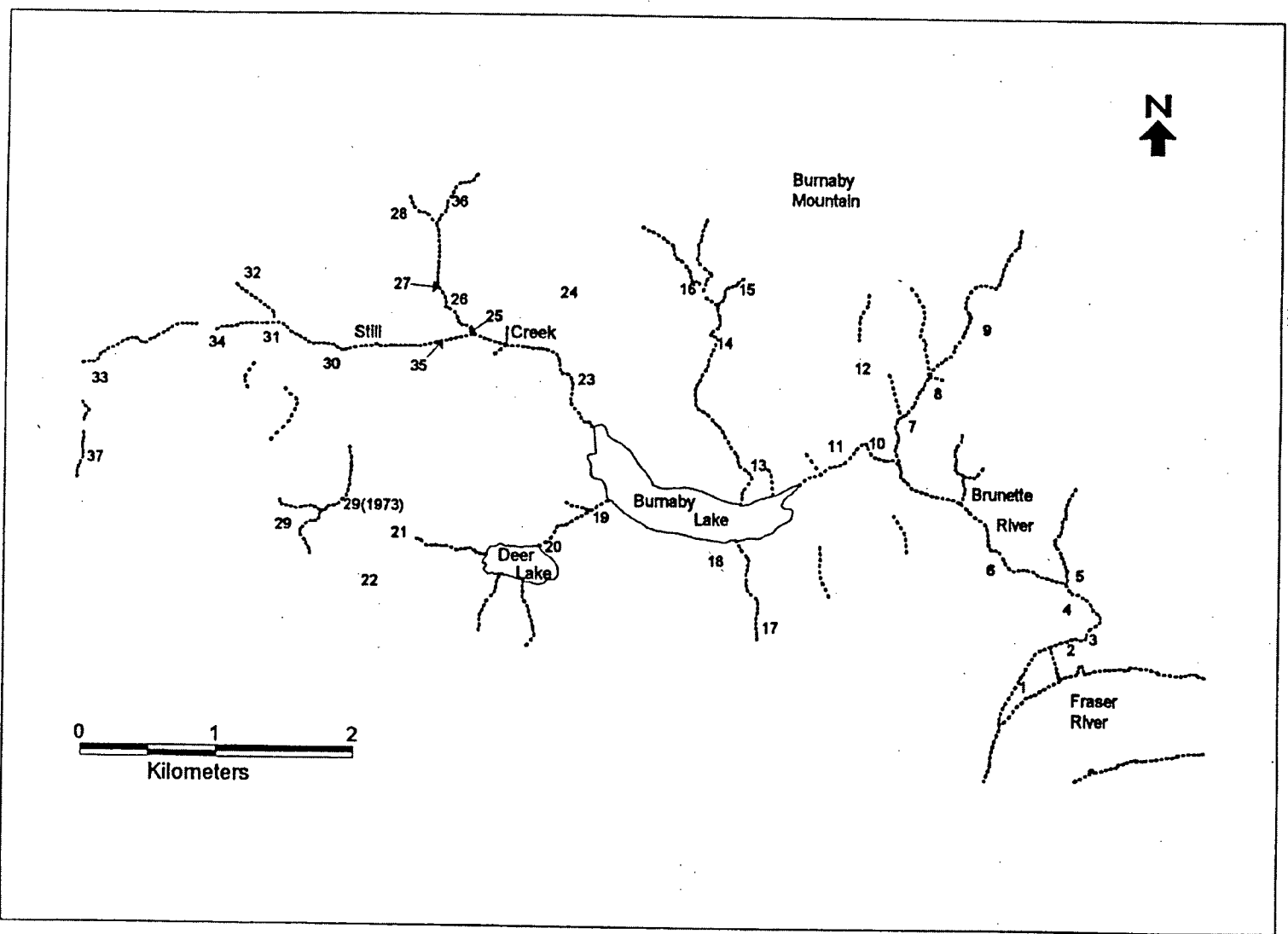
3.1.1 Streambed sediment locations

Thirty sampling locations were used to replicate previous work by (Hall *et al.* 1976; Duynstee 1990; McCallum 1995) by using the same site locations and identification numbers.   Some sites had to be excluded due to urban development (Table 3.1).

Table 3.1 Locations excluded due to urban development

Site number	Description of location
#5	Small stream north of Trans-Canada Highway. West of Hart St. between Roderick and Henderson St. Feeds Brunette River directly above site #4. Appears to have been culverted for new housing.
#23	Still Creek at Sperling Avenue. Located after the confluence of Beecher Creek and Still Creek. Inaccessible from the road.
#28	Beecher Cr at Westlawn Dr. Appears to have been culverted for new housing.
#12, 18, 22 and 36	Excluded from (McCallum 1995) due to culverting between 1973 and 1994.

3.1.2 Sediment sample collection

Sediment samples were collected with an aluminum pot attached to a three meter wooden pole from a minimum of five composite locations within the site, (Hall *et al.* 1976). Except for site #1, in which replicate samples were obtained with an Ekman Dredge. Samples were screened with a 2 mm plastic sieve to remove larger material and sealed in double layer, high-strength plastic bags for storage. Samples were stored in <4° C refrigerator prior to sample preparation. Sampling occurred on April 26, 27 and 30, 2003.

3.1.3 Sediment sample preparation and analysis

Sediment samples were removed from the refrigerator and allowed to warm to room temperature before analysis preparation. Then, the samples were sub-divided, with a portion of sediment removed for a wet vs dry comparison. The other portion was used in the metals analysis. Samples were analyzed wet, then dried at 105 ° C for 24 hours and reanalyzed to determine the percentage of mercury lost in the drying process.

Sample preparation for metals analysis was the same as previous studies (Hall *et al.* 1976; McCallum 1995) to allow for a consistent comparison of data. This portion was wet-sieved with a stainless steel 180 *u*m sieve; distilled water was used to increase particulate recovery. Sieving was intended to reduce spatial bias created by varying particle sizes at different locations when a composite sample is taken. The ≤180 *u*m sediment fraction was dried in a 105° C oven for a minimum of 24 hours. Sub-samples of the dried sediment were prepared for various analyses.

3.2 Lake sediment microcosm experiment

3.2.1 Microcosm sample collection

Sediment and water samples were collected from the Burnaby Lake rowing center on November 17, 2002. Water samples were taken with a large, acid-washed plastic container. Sediment samples were taken off the northwest corner of the Burnaby Lake Rowing Center's floating dock with an aluminum pot on the end of a 3-meter wooden pole. Sediment was then placed into double plastic bags and frozen within 6 hours of sampling.

3.2.2 Microcosm Laboratory Experiment

Laboratory experimentation was intended to replicate seasonal redox conditions within the lake. It allowed for a controlled, contained setting with limited variables. The experiment attempted to identify the reactions of metal hydroxides by comparing releases in anoxic and oxic conditions within sediment and the overlying water. There was a three-week trial experiment from November 17 to December 9, 2002 with 4 separate microcosms (Experiment 1), followed by a 6 microcosm study from February 9 to March 25, 2003 (Experiment 2), [Figure 3.2].

Figure 3.2 Diagram of a single microcosm with traps.
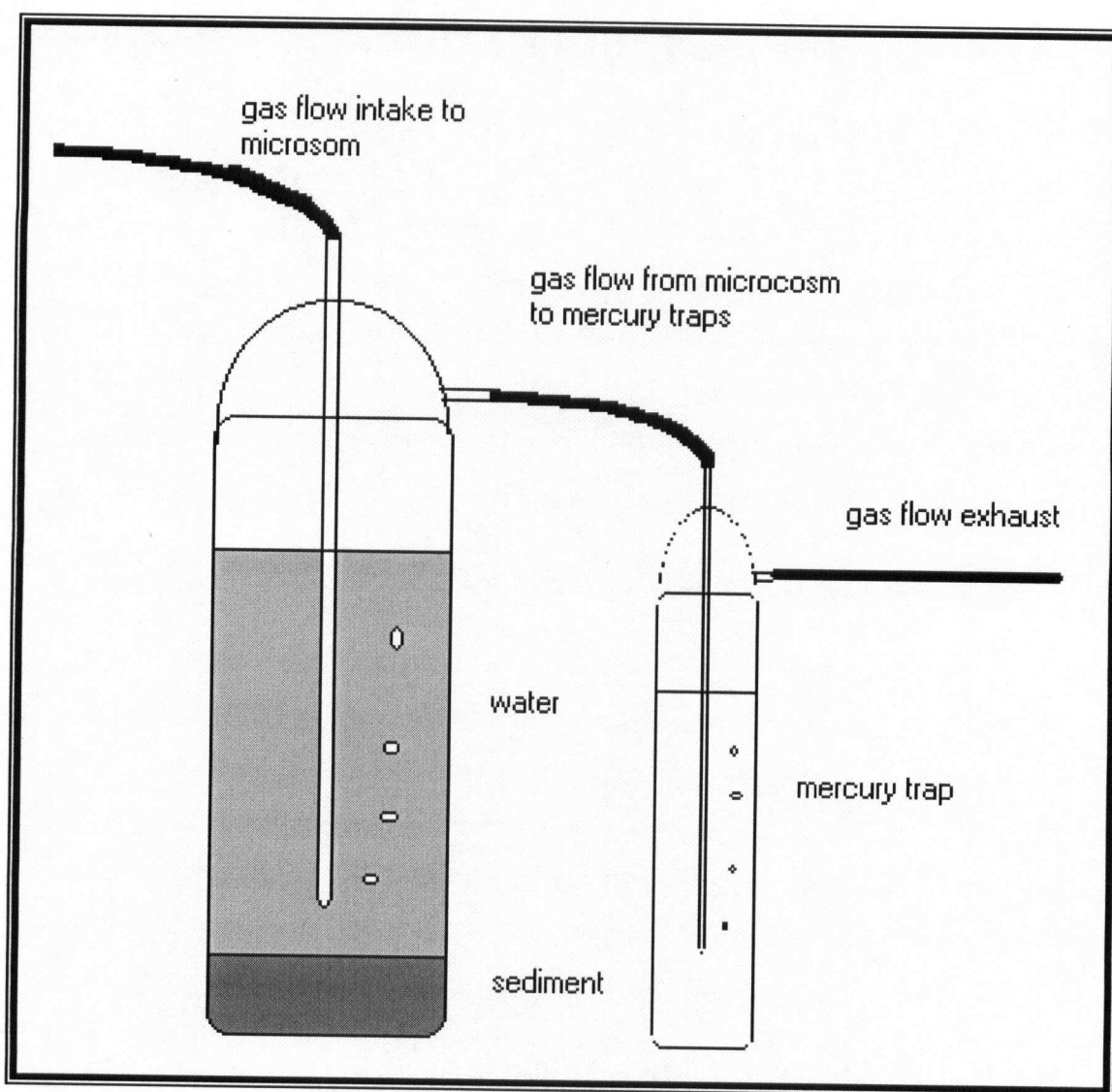
The microcosm setup process was similar for both Experiment 1 and Experiment 2. The glass microcosms and traps had a respective 1.5 and 0.1 liter volume. The soil was sieved with a 2 mm plastic screen to remove large particulates, then centrifuged at 4000 rpm for 30 minutes to remove most of the interstitial porewater. A 100 grams of wet sediment was placed in each microcosm. The average concentration of mercury in the sediment was 550.7 ppb. 1.2 L of 20 um filtered lake water was gently poured into microcosms 1, 3 and 4. De-ionized water was added to #2. Mercury traps were filled with 90 mL of potassium permanganate solution (0.5M $KMnO_4$ in 10% nitric acid) to capture any volatilized mercury. Microcosm 4 had 20 mmol/L molybdate ions (4.84g @ 241.95 g/mol) added to inhibit mercury methylating bacteria (Regnell 1994). The glass containers were wrapped in black plastic to prevent light induced volatilization of mercury.

The microcosms were allowed to settle for one day before sampling and the gas flows were started. Air was pumped at a slow rate into the aerobic microcosm 1. Nitrogen gas was bled into microcosms 2, 3, and 4 at a similar rate to create anoxic conditions in the microcosm. The microcosms were operated at ambient laboratory temperature ($\approx 20°C$). Individual microcosm conditions for Experiment One and Two displayed respectively in Figure 3.3 and Figure 3.4.

Figure 3.3 Experiment I, four different microcosms were set-up for the initial three-week trial run.

> 100 grams of homogenized sediment and 1.2 liters of water was placed in each microcosm.

(1)	(2)	(3)	(4)
-Lake sediment	-Lake sediment	-Lake sediment	-Lake sediment
-Lake water	-D.I. water	–Lake water	-Lake water
-Anoxic (N_2 gas)	-Anoxic (N_2 gas)	-Oxic (air gas)	-Anoxic (N_2 gas)
			-Molybdate ions added.
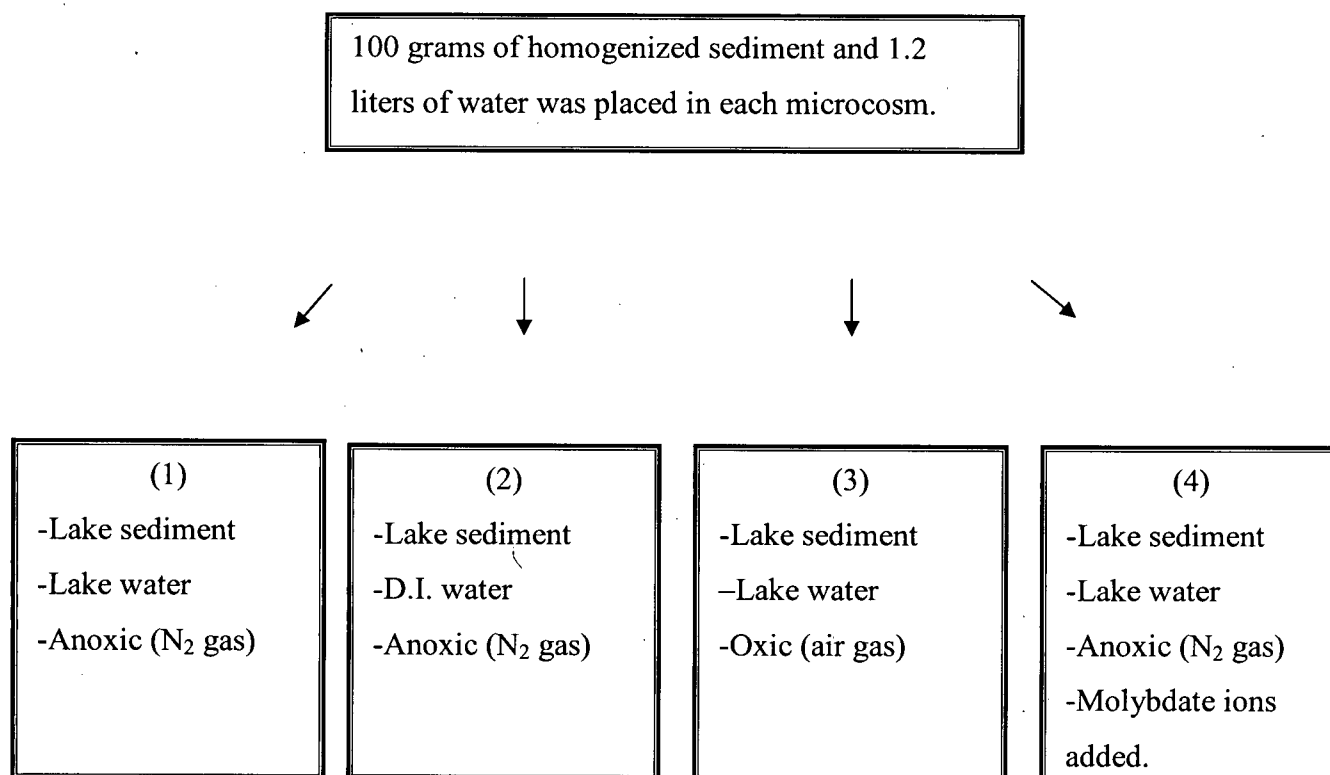
Figure 3.4 Experiment II, six microcosms were set-up with the same parameters as the first run for the six week analysis. Each contained 100 g of sediment and 1.2 L lake water. The following variables were in each microcosm:

2) Burnaby Lake
   sediment
   Burnaby Lake water
   Anoxic (N_2 gas)

1) Still Creek Sediment
   Still Creek Water
   Anoxic (N_2 gas)

4) Still Creek Sediment
   Still Creek Water
   Oxic (Air gas)

3) Still Creek Sediment
   Still Creek Water
   Molybdate ions added
   Anoxic (N_2 gas)

6) Burnaby Lake
   sediment
   Burnaby Lake water
   Anoxic (N_2 gas)
   Molybdate ions added

5) Burnaby Lake
   sediment
   Burnaby Lake water
   Oxic (Air gas)

3.2.3 Microcosm sampling

Sampling was performed weekly by using acid washed plastic syringe and tubing to withdraw 120 mL of water from the middle of each microcosm. Half of each sample was filtered with a 0.45 um hydrophobic filter and then subdivided for metals, mercury and DOC analyses. Each mercury sample was preserved with 2 mL/L HCl in acid washed bottles, metals with 2 mL/L HNO_3 and DOC with 2 mL/L H_3PO_4 (Phosphoric Acid). Water quality measurements were performed on the DOC sample to avoid contamination of the metals or mercury sample.

Although the U.S. Environmental Protection Agency (1999) requires "ultra-clean" procedures for sampling and storage of mercury samples in water; recent studies have indicated that storage in PET and HDPE plastic bottles is acceptable for mercury samples at or above 0.5 ng/l (Fadini *et al.* 2000; Hall *et al.* 2002). Therefore, PET and HDPE plastic bottles were used in this study.

3.2.4 Microcosm analysis methods

Specific conductance, pH, dissolved oxygen and DOC were analyzed according to methods in section 3.3.7, mercury in waters 3.3.3 and mercury in soil 3.3.4. All samples were analyzed within 7 days of the microcosm completion.

3.3 Laboratory Analysis
3.3.1 Aqua-Regia digest

To prepare stream sediment for trace metal analysis, a 1.0 ± 0.01 gram, homogeneous dry weight sample was digested with and 4 mL of (1+1) nitric acid and 10 mL of (1+1) hydrochloric acid. The sample was refluxed on an 85° C hot plate for 30 minutes. After cooling, the sample was brought to volume in a 100 mL volumetric flask. The sample was given time to settle before analysis on the ICP (refer to 3.3.2).

3.3.2 Trace Metals

Soil samples were *aqua regia* digested and analyzed with an ICP-AES (UBC Soil Science Lab). Iron and manganese concentrations were determined by analyzing undigested microcosm water samples with a Varian SpectrAA 220 flame AA (UBC Civil Engineering

Laboratory). A four-point curve was used for calibration. The detection level for iron and manganese was 50 ppb.

3.3.3 Mercury in Waters

Cold BrCl digestions of water samples were analyzed with a Millennium Merlin PSA 10.025 by cold vapor atomic fluorescence spectroscopy (CVAFS) (Analytical 2001). The method detection limit of the instrument (4.1 ng/L) was calculated as (n-1_@ 99% confidence) multiplied by the standard deviation of 10 samples. A 30 mL sample was digested by adding 7.5 mL of 33% HCl and 1 mL of 0.1N potassium bromate/potassuim bromide then brought to a 50 mL total volume with deionized water. This solution was capped and allowed to stand for no less than 30 minutes. Immediately prior to analysis, 30 uL of 45% hydroxylamine hydrochloride was added to remove any remaining bromine. The instrument was calibrated with a five point curve with a minimum linear regression of 0.995. A blank and check sample, of known concentration, was run after every 20 samples to ensure data quality and reduce instrument drift.

3.3.4 Mercury in sediments

Sediment samples were analyzed with a Lumex RA-915 Mercury Analyzer with a Zeeman processor used for interference and background correction (Lumex 2001). A 900° C pyrolysis oven ionizes the undigested sediment sample before it was vacuum pumped into the AA cell. The instrument was calibrated with various concentrations of Hg^{+2} mercury standard in methyl alcohol. The methyl alcohol solution was allowed to evaporate at room temperature, leaving a mercury residue on the sample boat, which was then inserted into the instrument. A four-point curve was used for calibration with a minimum linear regression of 0.995. Instrument accuracy was measured by the analysis of certified reference soils and surrogate check samples. Precision was measured by relative percent deviation (RPD) of replicate samples. After calibration, 0.050-0.200 grams of dry sediment was analyzed. A blank and check sample (of known concentration) were analyzed after every 20 samples to ensure data quality.

3.3.5 Percent Total Carbon in sediment

A Leco induction furnace analyzer (model no. 572-200) in the UBC Soils Laboratory was used to measure total organic carbon, using a sample size range of 0.1-0.5 grams (APHA 1989).

3.3.6 Total Sediment Solids

One gram of wet sediment was weighed and dried for a minimum of 24 hours at 105°C (APHA 1989). The sample was then re-weighted to calculate the loss of moisture.

3.3.7 Water Quality Measurements

Table 3.2 The following parameters were analyzed in the UBC Civil Engineering Laboratory

pH	Measured with a Beckman 44 pH meter using "Standard Methods" (APHA 1989)
Dissolved Oxygen	Measured with a YSI model 54A using "Standard Methods" (APHA 1989)
Specific Conductivity	Measured with a Radiometer CDM3 using "Standard Methods" (APHA 1989)
Dissolved Organic Carbon	Samples were filtered with a 0.45 *u*m hydrophilic Millipore filter membrane and analyzed with a Shimadzu model TOC-500 using "Standard Methods" 1030 (APHA 1989).

3.4 Statistical analysis

Non-parametric statistical methods of analysis were used in this project because the majority of sample sets were not normally distributed. Also in the case of sediments, the interaction between metals is very complex therefore sediments cannot be considered independent variables.

Summary statistics (mean, median, etc.) Kruskal-Wallis rank test and Mann-Whitney U test determined with S-Plus 6.1 Student Edition. Normality tests were performed on

35

JMPIN version 3.2.6. Box-whisker plots and Spearman rank correlation coefficients were determined with SPSS version 11.5.

Box-Whisker plots were used to display distributions of analytical values (Figure 3.5). The box contains 50 percent of the values with a line in the box representing the median. The absolute difference of the box ends are labeled Hspreads. The "whiskers" extend 1.5 Hspreads from either direction of the box. An asterisk designates samples between 1.5 and 3 Hspreads, with values greater than 3 Hspreads plotted with an open circle. The Mann-Whitney U test compares two non-parametric samples to determine if they are from the same population. The Kruskal-Wallis test is a non-parametric method of comparing means/medians of more than two populations. Spearman rank correlation coefficients aid in the identification of relationships between variables. Bonferroni's Correction was used to calculate the significance of more than two correlations for Spearman's rank correlation coefficients. Any data point below the detection limit of the instrument was given a value of half the instrument detection limit. Although there are more sophisticated and time-consuming methods that provide a better estimate of the true value (El-Shaarawi 1989, Gilbert 1987), this is also a standard method for addressing censored ("less-than" or "below detection limit") data. The mean was used for small populations (n<20) and the median was used for large populations (n>20) to limit the influence of outlying data points (Zar 1996).

Figure 3.5 Box-whisker diagram. Adapted from McCallum (1995)
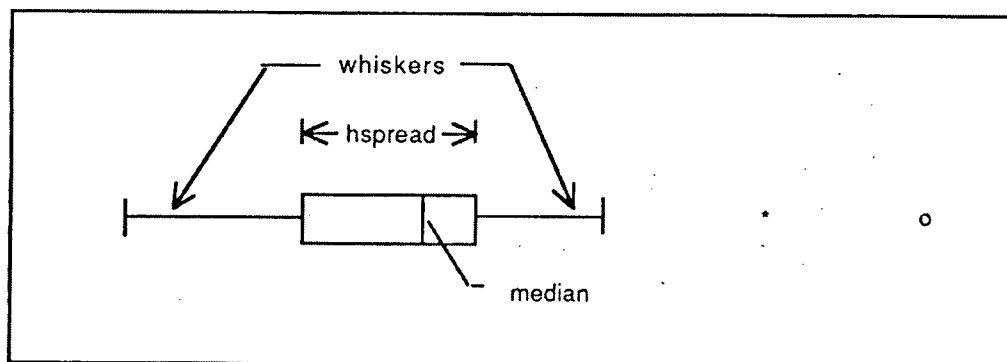
4. RESULTS AND DISCUSSION

4.1 Data quality

An attempt was made to avoid deviations in previous methods to allow for valid comparisons between data sets. In some cases, newer methods, instruments or technology were used to improve data quality (Table 4.1). Depending on the method or analyst, various data quality control methods were used to ensure accuracy and precision.

Blanks, sample spikes and check samples (of known concentration) were used every 20 samples to ensure data quality for mercury, water and soil samples (Appendix J). Sample spikes were used to check accuracy and determine the amount of matrix interference within mercury samples. If mercury data quality objectives were not met, the instrument was re-calibrated and the samples were reanalyzed. (*i.e.* <20% relative percent difference (RPD) or between 75-125% surrogate spike recovery). Certified reference sediments were analyzed for trace metals sediment analysis (Table 4.2). Antimony and potassium were out of range for sediment QC reference samples but these are not elements of primary concern in this study. It should be noted that potassium is known to be a difficult metal to analyze on an ICP. Checks and blanks were used to minimize instrument drift and maximize precision for all samples.

Table 4.1 Comparison of methods used in stream and lake sediment analysis in 1973, 1989, 1993 and 2003 (Hall, 1976; McCallum, 1995)

Measurement	Digest and Analysis Technique			
	1973	1989	1993	2003
Fe, Mn, Mg, Cd, Pb, Cu, Zn, Ni	HNO_3-$HClO_4$/ Flame AA	HNO_3-$HClO_4$/ ICP	HNO_3 / Flame AA	*Aqua-Regia* digest / ICP
Cr	Direct analysis / DC-arc Spectrography	HNO_3-$HClO_4$/ ICP	HNO_3 / Flame AA	*Aqua-Regia* digest / ICP
Hg	H_2SO_4-H_2O_2-$KMnO_4$ Hydroxylamine / Cold vapour	H_2SO_4-H_2O_2-$KMnO_4$ Hydroxylamine / Cold vapour	H_2SO_4-HNO_3-$KMnO_4$ Hydroxylamine / Cold vapour	Lumex AA with Zeeman processor and pyrolysis attachment

Table 4.2 Quality control data for sediment metals analysis. Results in ug/kg, dry wieght. Environmental Resource Associates: Reference Sample Catalog #540 Lot # D035-540.

Element/ Method	Limits mg/kg (from website)	5-Aug-03	7-Aug-03	10-Aug-03	Ave	Within limits
Al[1]	1000-50000	2614	3322	3593	3176	Y
As[1]	50-400	174.8	190.3	167.3	178	Y
B[1]	80-200	127.3	140.5	128.2	132	Y
Ba[1]	80-3000	361.9	414.5	371.1	383	Y
Ca[1]	1500-25000	3036	3334	2986	3119	Y
Cd[1]	40-300	125.3	136.1	119.8	127	Y
Co[1]	30-200	53.11	57.75	52.46	54	Y
Cr[1]	40-300	117.7	129.6	118.2	122	Y
Cu[1]	40-200	85.53	93.88	85.18	88	Y
Fe[1]	1000-22000	5069	6378	7292	6246	Y
K[1]	1400-25000	1070	1387	1469	1308	N
Mg[1]	1200-25000	1260	1501	1509	1423	Y
Mn[1]	150-2000	282.9	314.9	287.3	295	Y
Mo[1]	5-250	56.70	62.19	57.89	59	Y
Na[1]	150-15000	248.8	282.1	296.0	276	Y
Ni[1]	40-250	168.1	183.7	161.3	171	Y
P[1]	N/A	391.6	424.9	411.1	409	Y
Pb[1]	50-250	155.6	170.1	153.9	160	Y
Se[1]	50-250	86.95	96.99	89.33	91	Y
Si[1]	N/A	560.9	594.8	884.8	680	Y
Sb[1]	200-2000	144.0	161.3	144.7	150	N
S[1]	N/A	1.7	N/A	N/A	1.7	N/A
Zn[1]	70-1500	223.1	245.6	220.1	230	Y
Hg[2]	21.6-26.5	23.5	N/A	N/A	23.5	Y

Methods:
1. Aqua-Regia digestion analyzed with ICP
2. Lumex AA with pyrolysis oven

4.1.1 Variability between sample and methods: Determining the effects of drying samples

Mercury and some of its complexes are volatile at room temperature and pressure. Therefore, a portion of mercury would be lost when dried in a 105° C oven, as described in Section 3.1.3. The effects of drying 2 mm sieved sediment samples were determined in a small experiment with 27 samples. Wet samples were analyzed before drying then there concentrations were adjusted based the percent of moisture in the soil. This was performed to estimate the amount mercury lost by drying the <180 um samples.

The Wilcoxon Paired Sample Signed Rank Test was used to determine that wet and dry sample sets are significantly independent. The wet samples lost a mean 66.8% of their mercury content when dried (Figure 4.1). The high variability in the wet samples is not seen in the dry samples. Drying samples seems to normalize the distribution by lowering the highest wet levels considerably. A comparison of ≤180 um and 2 mm fractions is difficult because of the high variability of the wet samples relative to the dry. Using smaller fractions of sediment samples typically increases the metal concentration of the sediment (Wilber and Hunter 1979). It is not logical to assume the ≤180 um sediment fraction would have lost at least an equal percentage of mercury as the 2 mm fraction. Due to its higher concentrations, the ≤180 um fraction is likely to have a higher bonding strength than the larger fraction. Smaller particles have a higher surface area, therefore a higher bonding strength.

Figure 4.1 Box-whisker plots comparing mercury concentrations in 2 mm wet vs dried
stream sediment at 105°C (n=27)
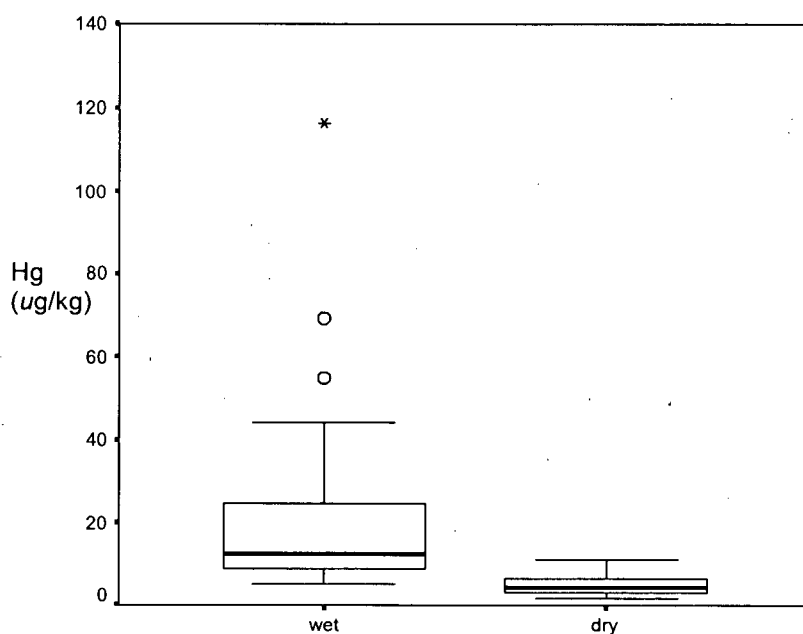
4.2   Microcosm Experiments

The intent of the microcosm experiments was to create controlled reduction and
oxidation (redox) conditions to mimic seasonal changes within Burnaby Lake. Oxygen
levels, bacterial activity and water chemistry were controlled throughout the experiment.
The dissolved oxygen (DO)in the oxic microcosm was never recorded below 5.35 mg/L. In
the microcosms filled with nitrogen gas, the DO was never recorded above 0.50 mg/L after
the first week. Regardless of the type of water or gas in the microcosm, mercury was
released from the sediment into the water Figure (4.2-4.5).

Figure 4.2 Microcosm 1 containing lake sediment, lake water under anoxic conditions, for
Experiment 1
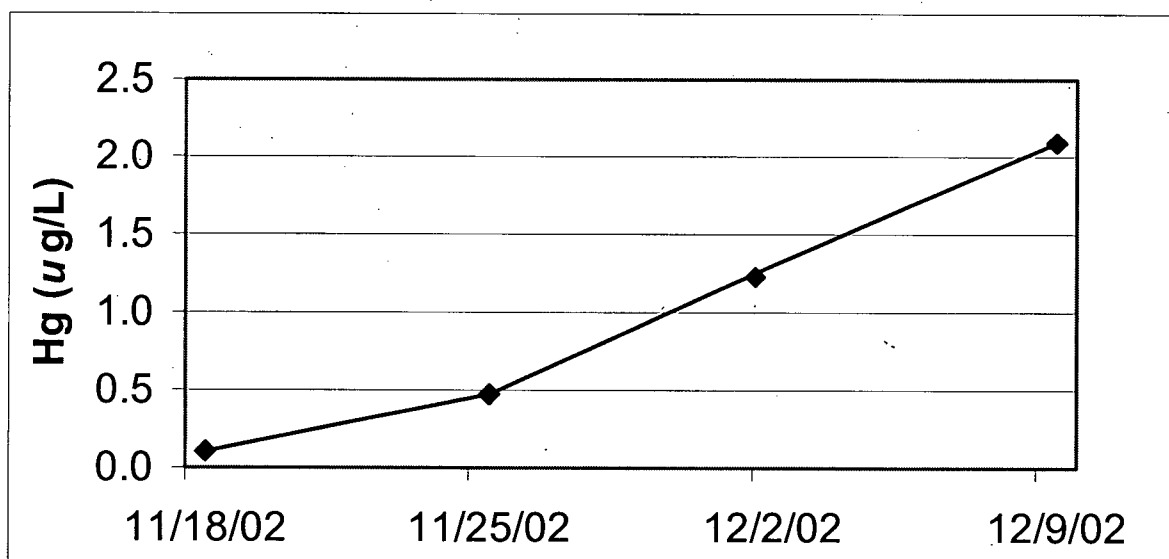
Figure 4.3 Microcosm 2 containing lake sediment, de-ionized water and under anoxic
conditions, for Experiment 1
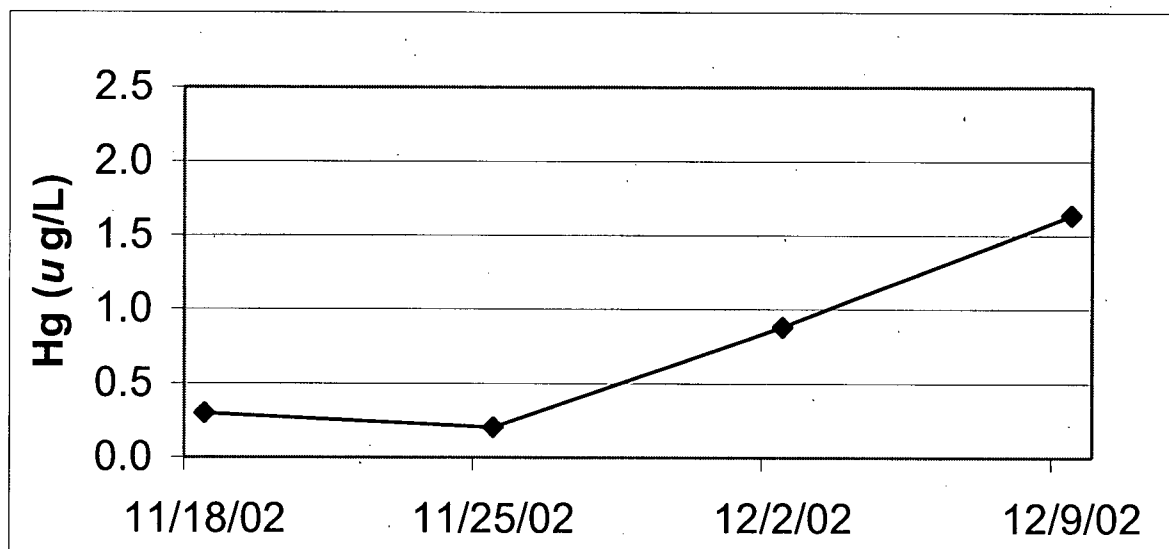
Figure 4.4 Microcosm 3 containing lake sediment, lake water under oxic conditions, for Experiment 1
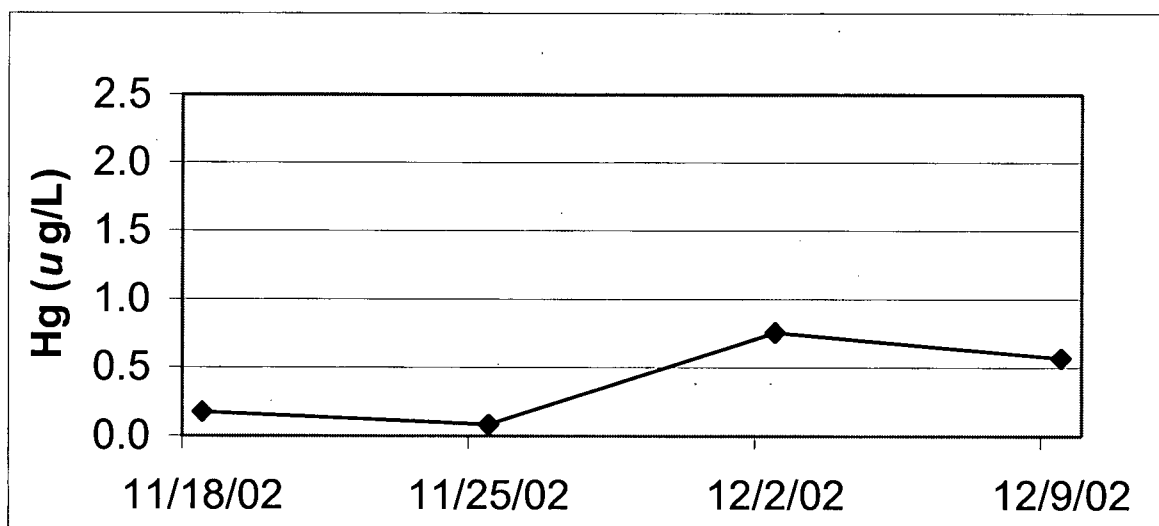
Figure 4.5 Microcosm 4 containing lake sediment, lake water with molybdate ions added under anoxic conditions, for Experiment 1
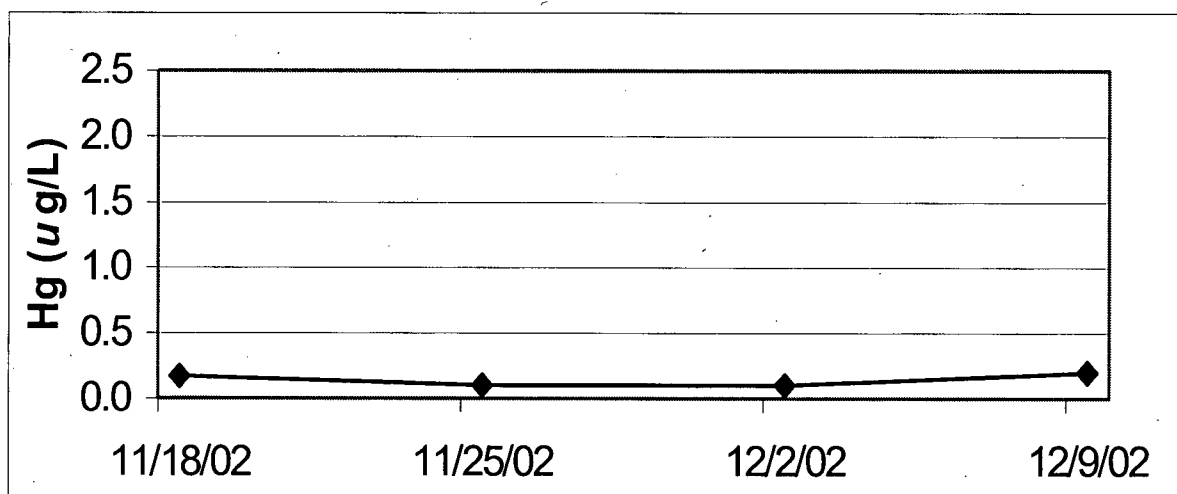
Levels of mercury within the microcosms were quite high (Table 4.3). They ranged from 0.100-2.092 ug/L. The highest release of mercury and iron was in Microcosm 1. The second chamber released less mercury than microcosm 1 indicating the deionized water may have slightly inhibited the release of mercury possibly due to the lack of complexing substrate indicated by is slightly lower DOC concentrations (Appendix E-4). The oxic microcosm (3) increased 229% over four weeks. It is difficult to determine the sediments remained oxic or anoxic throughout because only the water was tested. Respiration of bacteria in the sediment may have lowered the oxygen content inducing the release of the metals. The anoxic microcosm (4) with molybdate ions added had an increase of 16%. Molybdate ions inhibit bacterial growth and have been shown to eliminate production of methylmercury by sulfate reducing bacteria (Regnell et al. 2001). Therefore, only geochemical releases of mercury would be observed in the microcosm. This could indicate the increases in the other microcosms were due to reduction of mercury bound to sulfate by methylmercury producing bacteria.

Table 4.3 Percent increase of mercury and iron in four microcosms over four weeks in experiment 1. Manganese concentrations were all below the 50 ug/L detection limit.

Microcosm	Hg increase over 4 weeks (%)	Hg increase over 4 weeks (ug/L)	Fe increase over 4 weeks (%)	Fe increase over 4 weeks (ug/L)
1. Anoxic with lake water	1912%	1.99	1974%	2.13
2. Anoxic w/ DI water	444%	1.33	29%	0.18
3. Oxic	229%	0.40	59%	0.27
4. Anoxic with bacteria inhibited	16%	0.03	8%	0.13

Data analysis reveals that iron and mercury had a correlation coefficient of 0.599 but it was not statistically significant due to the small sample size. DOC and pH had a statistically insignificant positive correlation coefficient of 0.745, $\alpha = 0.031$. DO and pH had a statically significant inverse correlation of -0.649, $\alpha = 0.006$. The data for the microcosm experiments is located in Appendix E.

Refer to Appendix E for microcosm data. In all of the microcosms, mercury was predominately associated with the dissolved phase. Particulate concentrations ranged from 6.6%- 14.2%. Iron was associated with the particulate phase from 54.2%- 96.3%. This does not exclude mercury from binding with iron because dissolved iron concentrations are still around 100 times greater than the dissolved mercury concentration.

Manganese concentrations were all below the detection limit of 50 ug/L, indicating that very little, if any was released into the overlying water. Either manganese oxides were not at high concentrations in the sediment or they released then re-sorbed by sulfur before they could be dispersed into the water column. Manganese has a higher reduction potential than iron, therefore it would reduce first, allowing it to fill up any of the available complexing sites in the soil, probably with sulfur (Jacobs *et al.* 1995).

In addition, the oxidation of iron is typically very rapid (Laima *et al.* 1998). Therefore, iron diffusing across the redoxcline is rapidly converted to the particulate form. Manganese oxidation kinetics are slower compared to iron, and manganese oxidation has been attributed to Mn-oxidizing bacteria that are present at the redoxcline (Jacobs *et al.* 1995; Laima *et al.* 1998).

Regnell *et al.* performed similar microcosm studies but also added radiolabeled [203]HgCl (Regnell *et al.* 1991; Regnell 1994; Regnell *et al.* 1996; Regnell *et al.* 2001). In 1991, they found significantly more mercury in the water for the anaerobic columns. On average, 69% of mercury was in the dissolved form. They concluded that the oxic sediment was able to bind four times more mercury than anoxic sediment, most likely due to the presence of hydrous ferric oxides. In 1996, they found an average 43% increase in mercury in the anoxic water over the oxic, compared to an average 69.4% increase in this experiment. Radiolabled [203]Hg was found to constitute 80-90% of the total methylmercury in anoxic water, but only 40-60% of the extractable. This may indicate that the production of methylmercury was occurring within the microcosms 1-3 in this experiment.

Methylmercury analysis was planned for Microcosm Experiment 2 samples but was not performed due to contamination problems in the experiment.

Figure 4.6 indicates that mercury in the microcosms under slightly acidic or neutral and oxic conditions associate predominantly with oxide/hydroxides. Under reducing conditions, conversion to metallic mercury increases as pH decreases. Therefore, it seems that in the oxic microcosms, mercury may have been converted from oxide/hydroxide to mercury (II) as the pH dropped on December 2, 2002. In the anoxic microcosms, mercury was probably converted from oxide/hydroxide to metallic mercury.

Figure 4.6 Diagram of E_h-pH for mercury in aquatic systems. Adapted from (Veiga and Meech 1998).
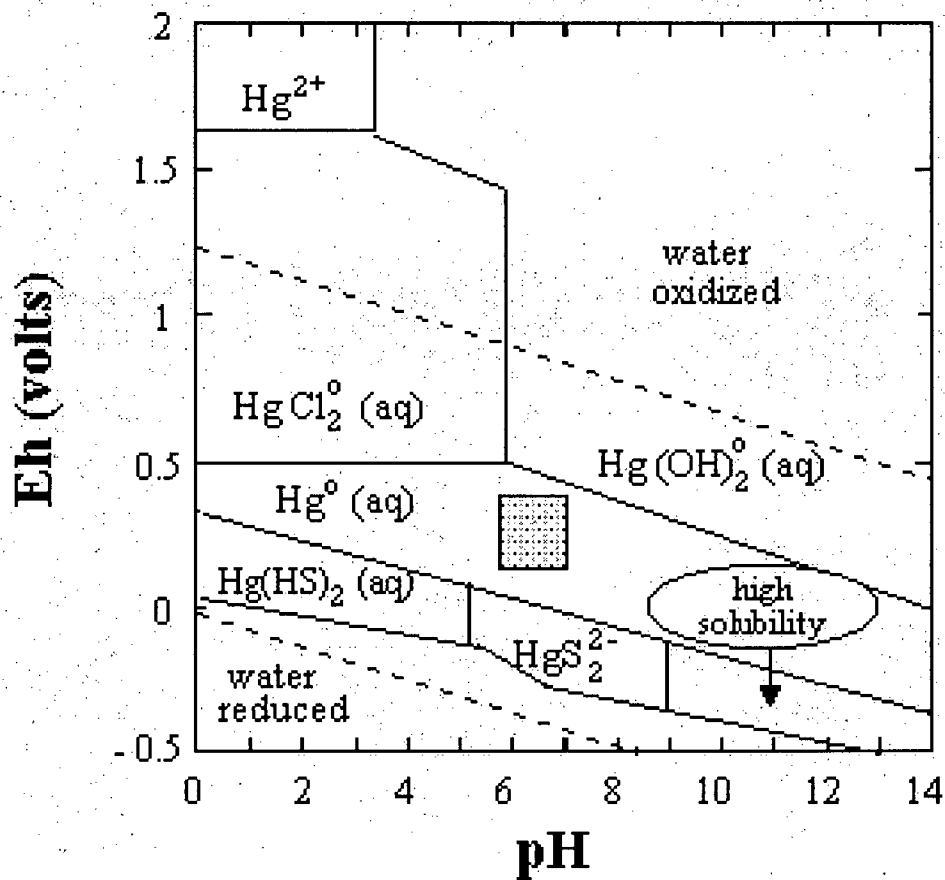
: results from Poconé after Silva et al. (1991)

Mercury was volatilized in all of the anoxic systems. The first two traps contained 242 and 311 *ug*/L respectively. The fourth contained 104 *ug*/L, indicating that bacteria inhibited by molybdate may have reduced mercury volatilization. The oxic trap became clogged and overflowed which may have resulted in contamination of the trap.

In microcosm experiment two, the six-week microcosm was completed. However the mercury samples were randomly contaminated before analysis. The mostly likely source of contamination was leaching from reused plastic bottles. It is likely that although the HDPE bottles were acid washed and rinsed thoroughly, contamination still leached from or permeated into the plastic bottles.

4.3   Suspended sediments in Still Creek and the Brunette River

Historical information from a February 28, 1997 stormwater event was used in this analysis. Six stormwater samples were taken every two hours, along with sediment collected by a Westfalia Separator model KA-2-06-175 continuous flow centrifuge. An attempt was made to collect stormwater samples for this study to compare with historical data but was unsuccessful. In January 2003, stormwater samples were collected from Still Creek and the Brunette River. The samples were not analyzed due to an in-operational flow meter and contamination problems within the trace mercury laboratory. Other stormwater sampling events were planned but never occurred due to insufficient precipitation throughout the 2003 summer.

Sekela *et al* (1998) results of the stormwater event indicated that the Brunette River had higher mercury concentrations in suspended sediments than Still Creek (Table 4.4). This trend is not seen in any of the other metals tested except for manganese. This is unusual because Still Creek is known to have higher levels of sediment contamination than the Brunette River (Hall *et al.* 1976; McCallum 1995). It is also unusual because Burnaby Lake is thought to act as a sediment and contaminant sink for the watershed, as shown in lower turbidity levels in the Brunette River. Furthermore, in the same storm event, Still Creek's total mercury concentrations in water were higher than the Brunette River's (Figure 4.7).

Table 4.4 Total metal concentrations in suspended solids collected with a continuous flow centrifuge during a February stormwater event on the Brunette River system, concentrations in mg/kg, dry weight. [Data from Sekela *et al.* (1998)]

Parameter	Brunette River	Still Creek
Suspended solids	34.3	47.6
Hg	0.615	0.146
Fe	54800	80800
Mn	2900	1260
Pb	175	254
Zn	557	772

Figure 4.7 A Box-whisker plot of total mercury concentrations in stormwater over a stormwater event, units in ng/L [Data from Sekela *et al* (1998)]
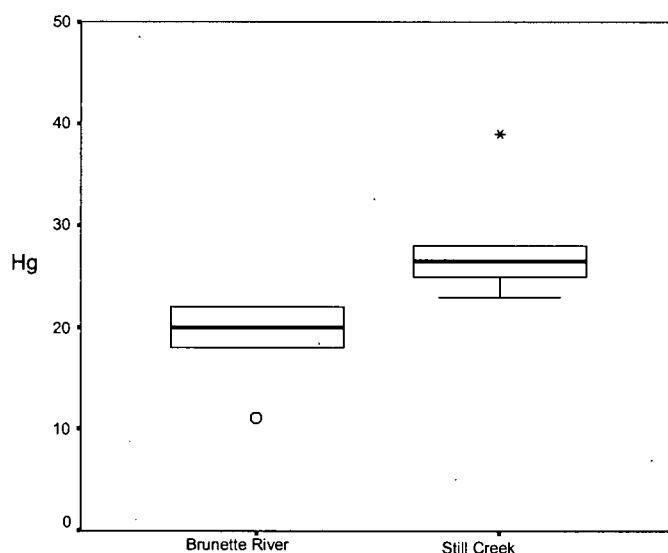
There are a few possible explanations for this anomaly. Burnaby Lake acts as a settling basin as indicated by the lower concentration of suspended sediments in the Brunette

River (Table 4.4). The first possible explanation is a natural or anthropocentric source of mercury either in the Brunette River or Stoney Creek. The second possibility could be contamination samples, which is always a possibility when working with trace metals analysis. Clean methods were not specified in the report.

Finally, it is also possible that the sediment is desorbing mercury and manganese into the overlying water when anoxic conditions exist. This would explain the increase in mercury and manganese concentrations in Brunette River suspended sediments. The oxides that bond manganese and mercury in the sediment would breakdown under anoxic conditions, thus releasing oxidized metals into the interstitial pore water and overlying water where they would re-associate with suspended particulate matter or DOC (Regnell et al. 2001). Increased flow through the lake could mobilize mercury reduced in the lake's water, similar to the releases seen in the microcosm experiments. Studies have shown that lakes with marshes have higher mercury concentrations then those without (Hurley et al. 1995; Babirz et al. 1998; Sonesten 2002).

The mean mercury concentration of stream sediments in the Still Creek sub-basin is 61.3 ug/kg. Burnaby Lake has an average concentration of 142 ug/kg (Enkon 2002). Although the lake sediment is less likely to be suspended in a stormwater event, it would likely have an impact on downstream concentrations. The higher lake concentrations may be due to vertical movement of reduced ionic mercury.

It seems that Still Creek is behaving like a typical urban stream while the Brunette River may be showing the downstream effects of a wetland environment in Burnaby Lake. The lake is very shallow, eutrophic and surrounded by marsh. The Brunette River had 72% less suspended solids and 109% more total organic carbon than Still Creek (Sekela et al. 1998). It is possible that mercury deposited in the lake may alter bonding associations under the lake's anoxic conditions. Mercury transported into the lake bound to oxides would be released under anoxic conditions. Then, it could associate with dissolved organic carbon (DOC) in the sediment pore water or the overlying water, were it would be resuspended under high flow conditions. Regnell et al. (2001) found an increase of total mercury, methylmercury, iron and manganese simultaneously during a lake's summer stratification. They believe that these processes may be mediated by biological processes, due to the positive relationship of the metal oxides and methylmercury.

Data for each stormwater sampling site is located in Appendix D. Spearman Rank correlation was performed on the data from each stormwater sampling site but the small sample size (n=8) limits detailed statistical analysis (Appendix I). Iron and mercury in stormwater were significant at 95% with a coefficient of 0.829, α=0.042 for Still Creek, but was not significantly correlated in the Brunette River. Contrary to the total values, mercury was not significantly related to manganese at Still Creek and negatively correlated with 95% significance in the Brunette River. Iron, lead and manganese are correlated with 95% significance in the Brunette River. It is difficult to explain why mercury has an inverse relationship to all other metals at the Brunette River site but it may be due to lake sediments releasing mercury from disturbed, anoxic porewater (Benoit *et al.* 1998b; Hall *et al.* 1998).

Flow for both systems increased over the eight-hour sampling period. Still Creek had consistent concentrations, except for one spike at 4:33 (Figure 4.8). Brunette River exhibits a first flush of high contaminants at the onset of increased flow (Figure 4.9). The Brunette River had little variability in concentrations except for a drop of 50% after the first hour. It is possible that the first hour concentrations are from the first flush of Stoney Creek and storm sewers below the dam, while the increase in flow and mercury is a result of higher flow from the lake.

Figure 4.8 Mercury concentrations in stormwater grab samples collected by Environment Canada in Still Creek on February 28, 1997 (Sekela *et al.* 1998). Bars indicate mercury concentrations and squares indicate flow.

Still Creek
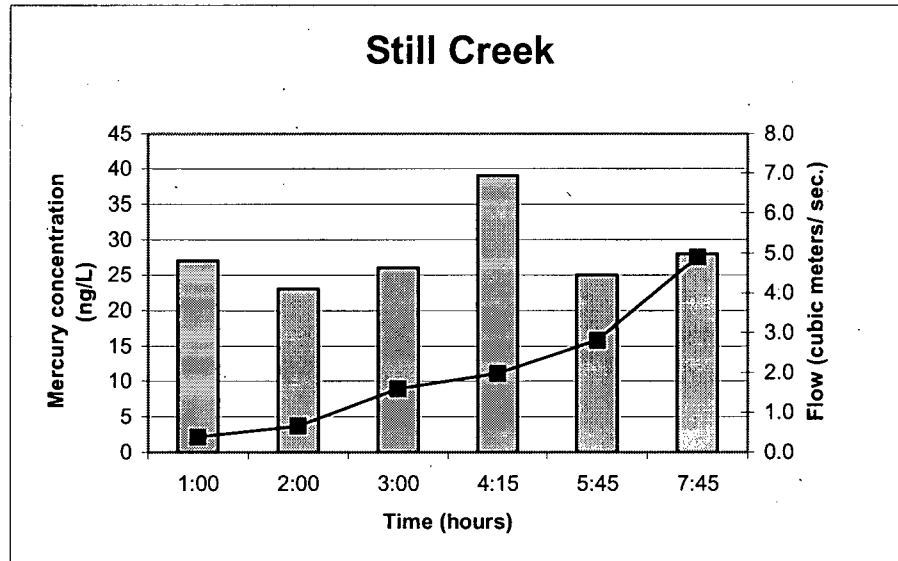
Figure 4.9 Mercury concentrations in stormwater grab samples collected by Environment Canada in the Brunette River on February 28, 1997 (Sekela *et al.* 1998) Bars indicate mercury concentrations and squares indicate flow.

Brunette River
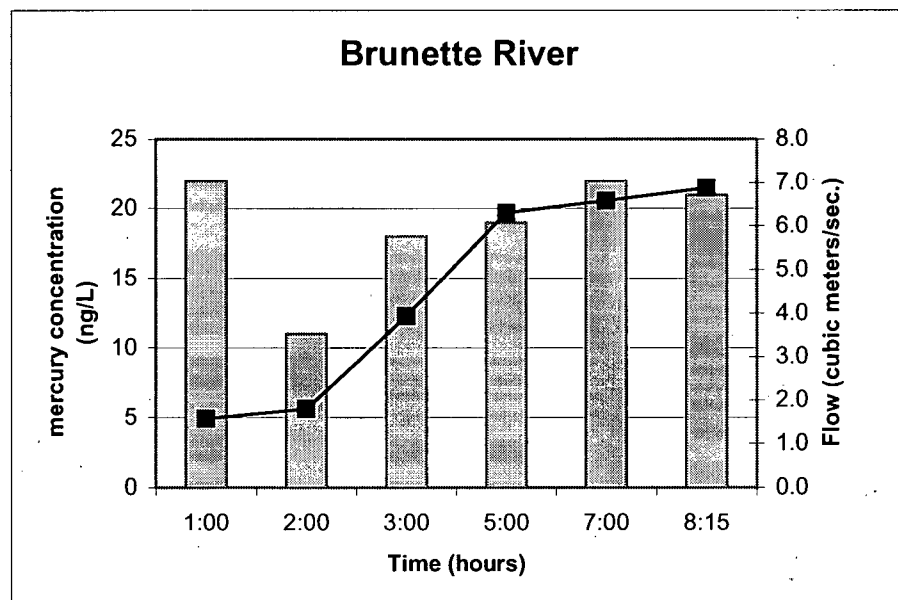
4.4   Burnaby Lake sediment

Recent studies have been performed examining sediment quality or contamination levels in Burnaby Lake. Lake coring has been used extensively as an effective method of sampling for temporal and spatial trends.   Historical data was analyzed to examine trends within the lake sediment. McCullum (1995) collected three cores in the lake, two at the mouth of Still Creek and one on the north shore of the lake to determine the impacts of urbanization. As a follow up, Hall and Mattu (1998) collected 7 sediment cores around the mouth of Still Creek and Eagle Creek and on the north side of Burnaby Lake. These cores were analyzed for lead, copper, nickel, manganese, zinc and iron to determine temporal trends although both studies did not determine mercury concentrations.   In 1999, Enkon collected and analyzed eighteen sediment cores from Burnaby Lake for trace metal concentrations as part of a pilot dredging program (Appendix C). The core sediments had a maximum depth of ≤ 1.2 cm and were a composite samples. Cores had a mean mercury concentration of 0.15 mg/kg (Figure 4.10) and most of the cores at the mouth of Still Creek had a metal concentration that exceeded Environment Canada's ISQG guideline (0.174 mg/kg) (Enkon 2002).

Figure 4.10 Box-whisker plot of mercury concentrations in Burnaby Lake core samples, concentrations in mg/kg dry weight [n=18] (Enkon 2002) [Environment Canada's ISQG guideline is 0.174 mg/kg]
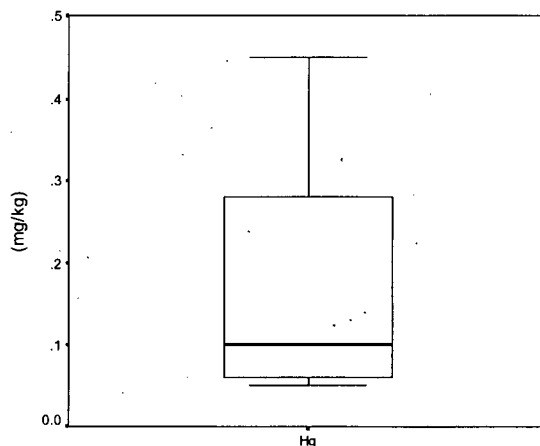
In general, studies have found that lake sediment is made up of clay-silt material mixed with amorphous peat in wetland areas (McCallum 1995; Enkon 2002). Sediment levels of total organic carbon (TOC) ranges from 7-14% throughout lake sediment (Enkon 2002). High TOC levels is thought to be a combination of anthropocentric loading and naturally occurring peat and plant material. Historic sampling has shown that most metal concentrations typically decrease with depth. The exception was lead, which is expected to decrease since it was phased-out from gasoline in 1974.

Gwendoline Lake is unimpacted by development and was used as a reference site in the McCullum (1995) study. The mean mercury concentration of two cores taken by (McCallum 1995) in 1993 at Gwendoline Lake were 0.191 mg/kg and 0.231 mg/kg. This is 0.084 mg/kg higher than the mean concentration found in Burnaby Lake. Therefore, its level of mercury contamination should not be above background (Table 4.5). The mean concentration in two cores from Deer Creek Lake's was 0.233 mg/kg and 0.219 mg/kg. All samples are composite core data; similar to the method used in the Enkon study for Burnaby Lake. Cores all exhibited little variation with depth. Both Gwendoline and Deer Creek Lake

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average concentrations are over Environment Canada's Interm Sediment Quality Guideline (ISQG) of 0.174 mg/kg. This may be due to inputs of atmospheric mercury without the

Table 4.5 Comparison of mercury concentrations in sediment from various locations. The Environment Canada guideline ISQC is 174 ug/kg. All concentrations in dry weight.

Location	Description of area	Range of mercury concentrations (ug/kg)
Gwendoline Lake	Unimpacted, forested	181-224
Deer Lake	Urban	221-238
Burnaby Lake	Urban	60-440
Sweden *	Remote lakes	13-300
Finland*	Stratified, forest	134-277
Wisconsin*	Pristine, seepage lakes	1-140
Wabigoon River, Canada *	Wood treatment plant	1500-3000

* (Suchanek *et al.* 1996)

dilution of sediment found in Burnaby Lake due to its high sedimentation rates (McCallum 1995).

Mercury was detected in all of the fifteen lake core sites from Enkon (2002), with the exception of two. The highest observed concentration was 0.44 mg/kg, which is more than double the ISQG of 0.174 mg/kg. High mercury levels appear to be due to stormwater flow into the lake from Still Creek, due to spatial distribution.

Statistical analysis indicated that mercury, manganese, iron and lead were all correlated with each other at 95% significance in Burnaby Lake sediments (Appendix G). Mercury was significantly correlated with all of the parameters. Sulfur and TOC also had a significant, positive relationship with each other. Mercury's correlation was positive and significant with TOC but not sulfur. The positive relationship of mercury and lead is most likely due to loading from streets and drainage systems. High lead and mercury concentrations are assumed to be from anthropocentric sources. Although lead concentrations have been decreasing over the last 30 years throughout the watershed, it has

been linked to deposition of automotive exhaust (McCallum 1995). Mercury's strongest correlation is with lead, (r^2=0.876). Similar transport processes from impervious surfaces are a likely explanation for this relationship.

4.5   Stream sediment

Historic data from Hall (1975) Duynstee (1990) and McCallum (1995) was compared to current data from this study for this analysis of trace metal concentrations in stream sediment (Appendix A and B). The methods from previous studies were replicated to ensure data compatibility. The median mercury stream sediment value in 1973, 1989, 1993 and 2003 was 22.0, 90.0, 93.0 and 57.6 mg/kg respectively (Figure 4.11).

Mann-Whitney U tests were run to determine that the levels each year were significantly different from the previous, except for 1989 and 1993 (Appendix K). Therefore, the mercury sediment increased significantly from 1973-1989, then levels remained statistically unchanged from 1989-1993. Mercury levels from 1993-2003 have significantly decreased by 35.4 mg/kg.

A comparison of stream sediment mercury concentrations and Canadian Guidelines and U.S. regulations was made to determine if contaminant levels in stream sediment exceeded guidelines (Table 4.6). It should be noted that these concentrations do not accurately represent environmental conditions for two reasons and therefore can not accurately be compared to any guidelines or regulations. First, only the <180um sediment fraction was analyzed and this is not representative of environmental conditions. Second, as part of the method used in this study, sediments were dried which has been shown to volitalize some metals like mercury. However, since a mean of 67% of mercury was lost from dried samples in this study, these data can be considered "minimum" values (refer to section 4.1.1). There were three samples above the Interm Sediment Quality Guideline (ISQG) level of 174 ug/kg, all measured in 1993 (Table 4.6). The highest overall site was 870.0 ug/kg in 1993, was the only sample tested over Environments Canada's probable effects level (PEL) of 486 ug/kg (Table 4.6). Even if the 2003 screened sediment was adjusted for the estimated 66.8% loss from drying the screened sediment, the lake mean concentrations are still 155% more than Still Creeks concentration.

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Figure 4.11 Box-whisker plot of mercury concentrations (*u*g/kg dry weight) in Brunette
Watershed stream sediment from 1973-2003. One outlier excluded from 1993 at 870
*u*g/kg.
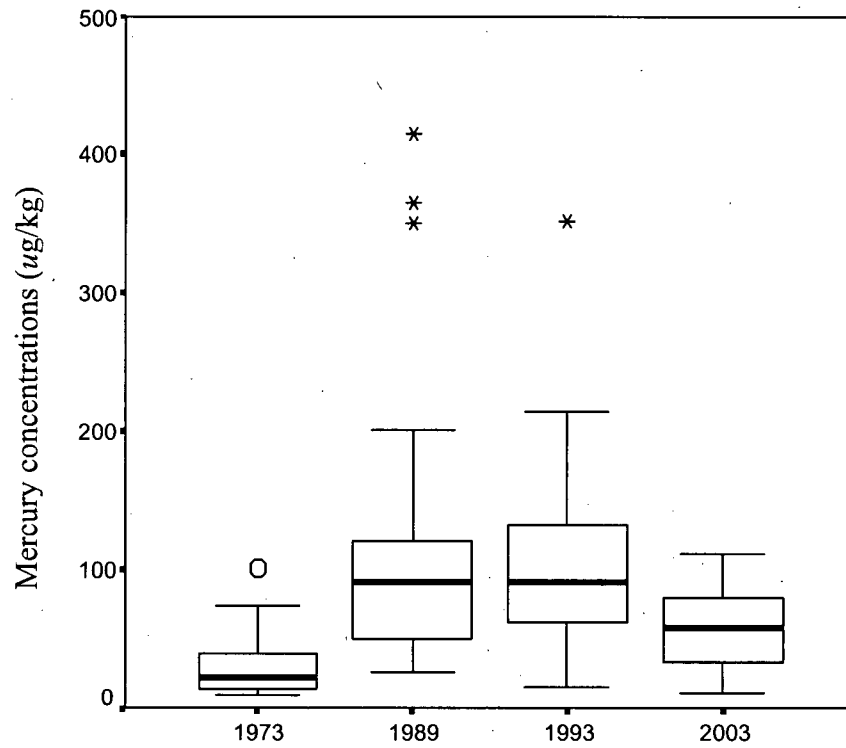
Table 4.6 Various federal guidelines, regulations and objectives for mercury for different water uses

Organization	Criteria	Fresh water	Sediment/Solids
US EPA Regulations (U.S. E.P.A. 2003)	Ambient water	0.144 *ug*/L	
	Freshwater- acute exposure	2.4 *ug*/L	
	Fish consumption (FDA)		1 ng/L methyl mercury (wet weight)
	Sludge/ public lands		17 ppm
Environment Canada Guidelines (Canada 2002)	Aquatic life	0.1 *ug*/L	
	ISQG		174 *ug*/L
	PEL		486 *ug*/L
	Fish Contamination		33 *ug*/L methyl mercury (wet weight)
BC Guidelines (Nagpal 2001)	Drinking water	0.1 *ug*/L	
	Aquatic Life (30 day Ave.)	20 ng/L w/ MeHg $\leq$0.5% THg	
		10 ng/L w/ MeHg $\leq$1.0% THg	
		4 ng/L w/ MeHg $\leq$2.5% THg	
		2 ng/L w/ MeHg $\leq$5.0% THg	

ISQG- Interm Sediment Quality Guideline
PEL- Probable Effect Level

When the 1989 sediment concentrations are adjusted for the loss of mercury associated with drying, concentrations were over Environment Canada Interm Sediment Quality Guidelines (174 *ug*/kg) at 9 sites, and Environment Canada Probable Effect Level

(486 ug/kg) at 3 sites (Table 4.7). The 1993 sediment concentrations adjusted for the loss of mercury associated with drying had concentrations in had 10 sites over Environment Canada's Interm Sediment Quality Guidelines (174 ug/kg) and 2 sites over Environment Canada's Probable Effect Level (486 ug/kg) (Table 4.7). Sediment from 1973 did not exceed any of Environment Canada's guidelines while 2003 had only one that exceeded the Interm Sediment Quality Guidelines (174 ug/kg) [Table 4.7].

Table 4.7 Adjusted mercury concentrations in stream sediment for a loss caused by drying that exceeded federal guidelines within the Brunette Watershed from 1973-2003 (Appendix L) [Concentrations in ug/kg, dry weight].

Year of sediment sampling	Environment Canada Interm Sediment Quality Guidelines (174 ug/kg)	Environment Canada Probable Effect Level (486 ug/kg)
1973 (n=26)	0	0
1989 (n=29)	9	3
1993 (n=29)	10	2
2003 (n=30)	1	0

Figure 4.12 and 4.13 are box-whisker plots of surface sediments mercury concentrations in Still Creek sub-basins and the Brunette River sub-basins; Table 4.8 is a ratio of mercury concentrations in Still Creek sub-basins and the Brunette River sub-basins. In 1973 and 1989 the levels of mercury in the Still Creek were double in the lower Brunette River sub-basin. This study seems to indicate that mercury levels have normalized throughout the sub-basins. This may be due to a decrease in point sources along Still Creek and/or the distribution of mercury from the upper to the lower basin. The latter is reinforced by the increased levels of mercury in Brunette River suspended sediment relative to Still Creek (Refer to section 4.63, Table 4.9).

Figure 4.12 Box-whisker plot of mercury concentrations in the Still Creek sub-basin stream
sediment from 1973 to 2003.
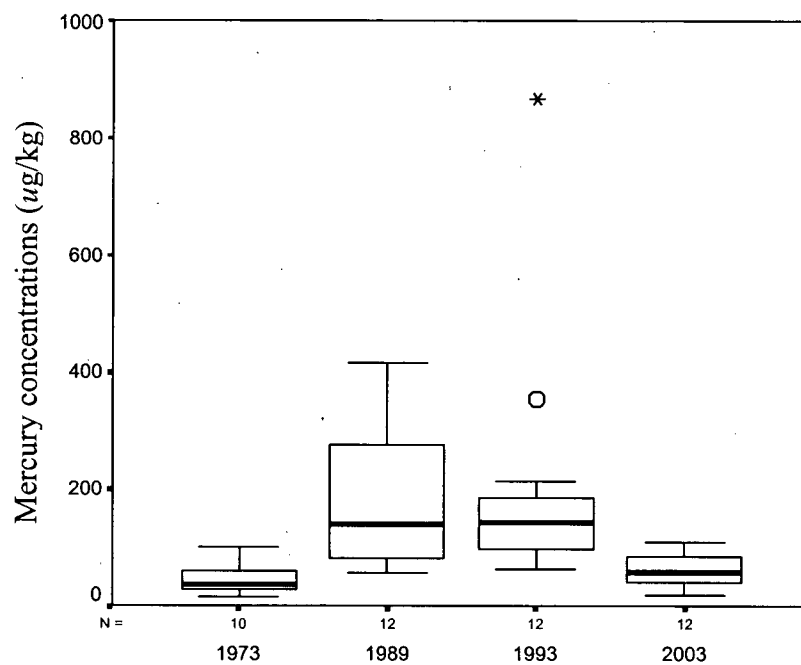
Figure 4.13 Box-whisker plot of mercury concentrations in the Brunette River sub-basin stream sediment from 1973 to 2003.
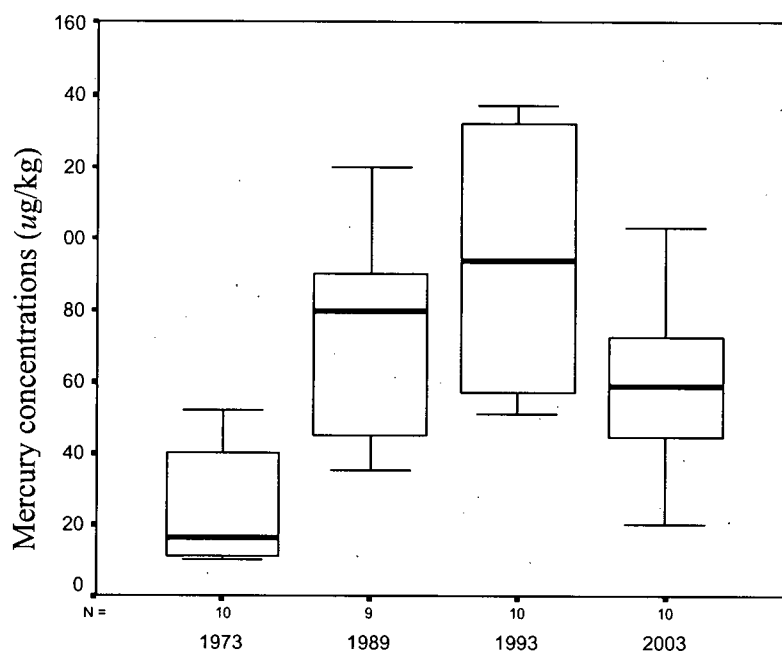
Table 4.8 Ratio of mercury concentrations in the Still Creek sub-basin and the Brunette River sub-basin in sediments and stormwater over a thirty-year period

Media and year sampled	Still Creek / Brunette River Sub basins
Stream sediment 1973	1.97
Stream sediment 1989	2.44
Stream sediment 1993	2.18
Stream sediment 2003	1.05

A Spearman rank correlation test with Bonferroni's correction was performed on trace metal data in stream sediment from each year to determine the extent of significant statistical correlation (Appendix F). Iron and manganese were significantly related with 95% confidence from 1974-2003. The highest mercury correlation was with percent sediment organic matter (0.208). Mercury exhibited a few trends over time. Mercury was correlated

to lead, copper, nickel and zinc with 99% significance from 1973-1993. It was correlated to chromium with 95% significance from 1989-1993. Figure 4.14 presents temporal relationships (1973-2003) of mercury to other trace metals found in stream surface sediments.

Figure 4.14 Spearman's correlation coefficients for mercury in 180 um stream sediment from 1973-2003. Data located in Appendix F.
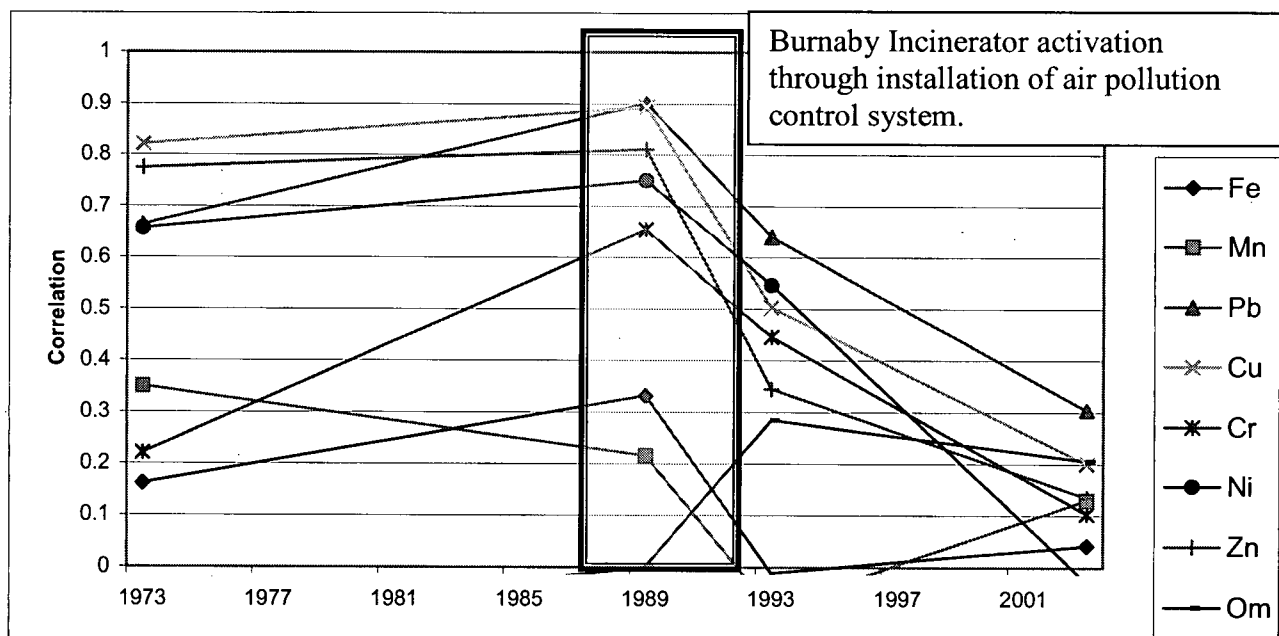
Lead, copper, nickel, zinc and chromium were all significantly related to each other from 1973-2003. McCallum (1995) found that Pb and Cr had a direct relationship with traffic volume in street sediment in 1993. A contaminant identification study identified vehicle exhaust emissions, tire wear and brake wear as the most significant non-point source of Pb, Cu and Zn in their study (Woodward-Clyde 1992; Armstrong 1994). McCallum (1995) also linked impervious area or traffic volume to Pb, Cu, Cr, Ni and Zn enrichment in 1993 stream sediment .

Consistently high correlations over time indicates that some type of relationship exists, possibly due to similar transport mechanisms. From 1974-1993 the levels of mercury

in sediments increased throughout the watershed. This coincides with mercury's correlation with Pb, Cu, Ni and Zn (Appendix F). Concentrations of mercury decreased from 1993-2003 along with its correlation to other metals. It seems that the processes that contributed to the increase of mercury in the watershed between 1993-2003, reduced the relationship to other trace metals. Although, the process that contributes these other metals to the watershed are still present.

4.6 Comparison of mercury in stream sediment and catchments imperviousness

Atmospheric transport is mercury's dominant pathway for non-point source contamination (Refer to section 1.3). Studies have shown that the catchment to lake ratio can be an indicator of mercury levels in fish and sediment. Swedish studies have discovered a significant correlation between the catchment to lake area ratio and the levels of mercury in fish (Bishop *et al.* 1997). A Canadian study used the same catchment/lake area ratio to significantly correlate mercury concentrations in sediment (French *et al.* 1999). Both of these studies examined remote lakes, and their watersheds where the only source of anthropocentric mercury was from the atmosphere.

Urban watersheds have been shown to have higher stormwater yields of mercury than other land-uses (Hurley *et al.* 1995; Mason *et al.* 1997; Babirz *et al.* 1998). Urban development has created impervious areas where precipitation is unable to penetrate ground cover and infiltrate into the soil. Examples of impervious areas include buildings, roads, compacted soil and parking lots. Impervious area (IA) has a negative affect on water and sediment quality due to the run off of trace metals and other contaminants (Zandbergen *et al.* 1997; Zandbergen *et al.* 2000). Mercury distribution in a watershed is affected by imperviousness due to its transport mechanisms. Mercury resides and is transported in the atmosphere before it is deposited on land. When mercury reaches the ground or a waterway by either dry deposition or rainwater, it is almost always in the particulate form (Pacyna 1996). Mercury has a strong affinity for metal-oxides and organic carbon. If mercury is deposited on a pervious surface, it is likely that it will bond with organic material in soil (Bishop *et al.* 1997). Impervious areas increase the amount of runoff and mercury carried by the runoff.

Catchments and there impervious area were delineated by the GVRD in 2001 using GIS and GPS systems. All of the streams in the catchments used in this analysis are first order; except for the Brunette River, which has the lake as a source. Imperviousness decreases the likelihood of mercury binding to soil and contributes mercury run-off into a streams or lakes. Therefore, impervious areas create a pathway for mercury to reach streams. Effective imperviousness area (EIA) is assessed by quantifying the impermeable area connected to or discharging into a catchment. For example, a roof is only considered EIA unless the gutter is connected to the stormdrain but if the gutter runs onto the lawn it is not considered EIA.

Impervious area and effective impervious area per catchment was calculated by McCallum (1995) in 1973 and 1993. The GVRD (2000a) calculated impervious area in 1996 (refer to Table 2.1). Average catchment concentrations was calculated with data from Appendix B and follow the trends of the overall watershed (Figure 4.15). McCallum (1995) divided up the watershed into two sub-basins, Still Creek and Brunette River, with respective impervious levels at 52% and 35%. The same sub-basins were also used in this study for comparison.

The sample range was at least three times larger for 1993 concentrations than 1973 and 2003. There are three times the number of samples per catchment in 1993 as the 1973, 1989 and 2003 since the samples were taken in triplicate. The large number of samples in 1993 allows for a more detailed statistical analysis. Individual mercury catchment concentrations are shown in Figure 4.15.

Figure 4.15 Box-whisker plot of mercury streambed sediment concentrations (ug/kg) from six catchments in 1993. One outlier was excluded from Still Creek with a value of 2115 *ug*/kg. In 1993, three independent samples were analyzed at each site.
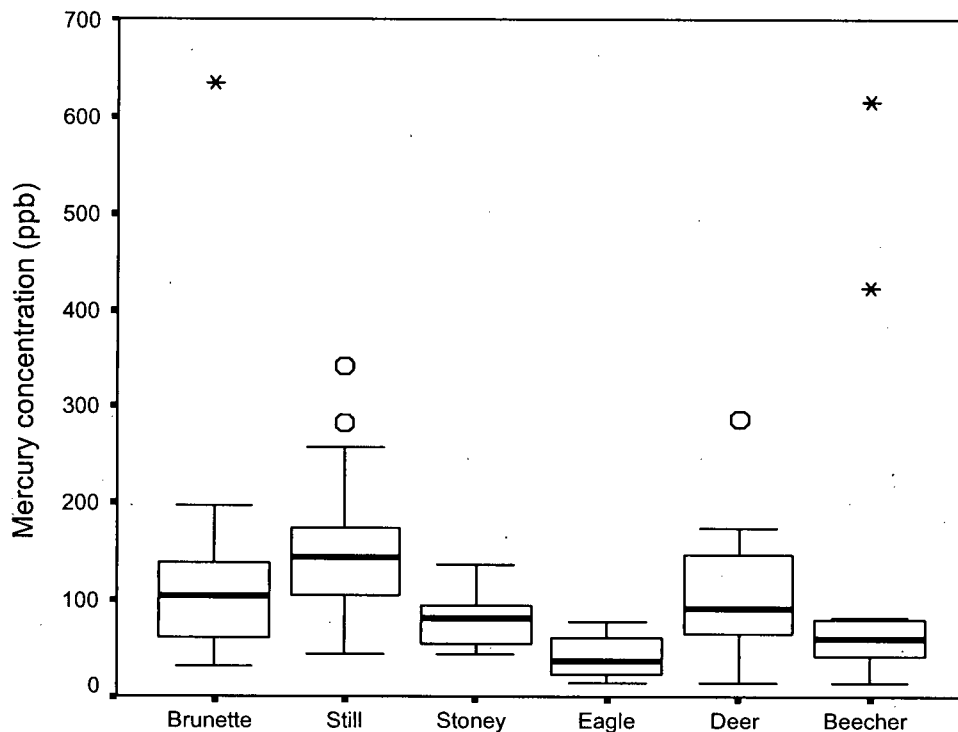
Sediment concentrations from 1973, 1993 and 2003 were compared with corresponding imperviousness and EIA data. The Kruskal-Wallis Test provided sufficient evidence to conclude that catchment means were statistically different in 1973, 1993 and 2003. The linear regression for the 1973 study year did not have a good fit with EIA data due to the scattered data points and relatively low mercury concentrations (Figure 4.16). This may indicate scattered point sources or natural background sources.

Figure 4.16 Scatter-plot of 1973 stream sediment mercury concentrations (ug/kg) vs
effective impervious area (hectares) from 1973. Line indicates the linear regression of
the six area's
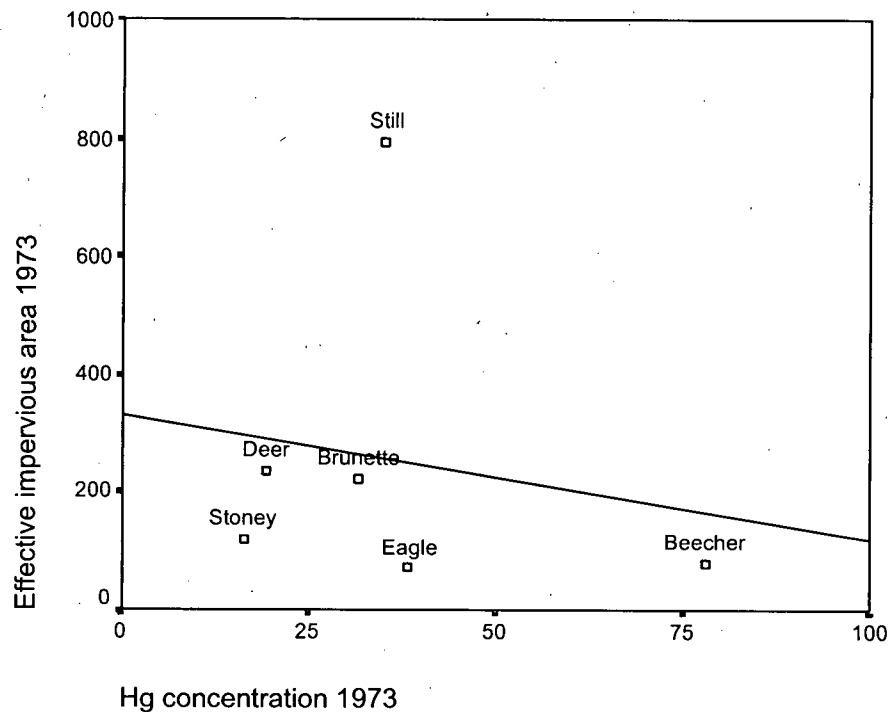
The average mercury content increased 294% in stream sediment and all catchment
concentrations increased substantially, between 1973-1993. A positive correlation was
found between the effective imperious area within catchments and mercury in 1993 stream
sediment (Figure 4.17). Spearman's correlation coefficient is 0.371 and 0.257 for EIA and
IA respectively. This seems to indicate that EIA is a better fit than IA, which is logical
considering mercury's run-off transport processes. Beecher Creek has the worst fit of all the
catchments in the watershed, due to its high historic mercury content in a low impervious
area. Beecher Creek is the most industrialized catchment and it is likely impacted by a
combination of atmospheric sources and point-source spills/releases. Spearman's
correlation coefficient is 0.900 (α=0.037) with the Beecher Creek point excluded. This
seems to suggest that the watershed is affected by a combination of point source releases and
runoff from impervious surfaces for a period before 1993.

Atmospheric mercury could disperse relatively evenly over a 7200-hectare
watershed. A possible high volume, localized source that fits into the 1973 to 1993 time

frame is the Burnaby Incinerator, which is located only four kilometers south of Burnaby Lake. Generally, westerly airflow from the Pacific Ocean prevents the watershed from having any high mercury concentration, long distance sources. High rainfall, typical in the coastal area would increase deposition of mercury released in the area, while atmospheric and particulate deposits of mercury should decrease in concentration away from the source (Nater *et al.* 1992).

Figure 4.17 Scatter-plot of 1993 stream sediment mercury concentrations (*ug*/kg) vs
effective impervious area (hectares) Line indicates the linear regression of the six area's
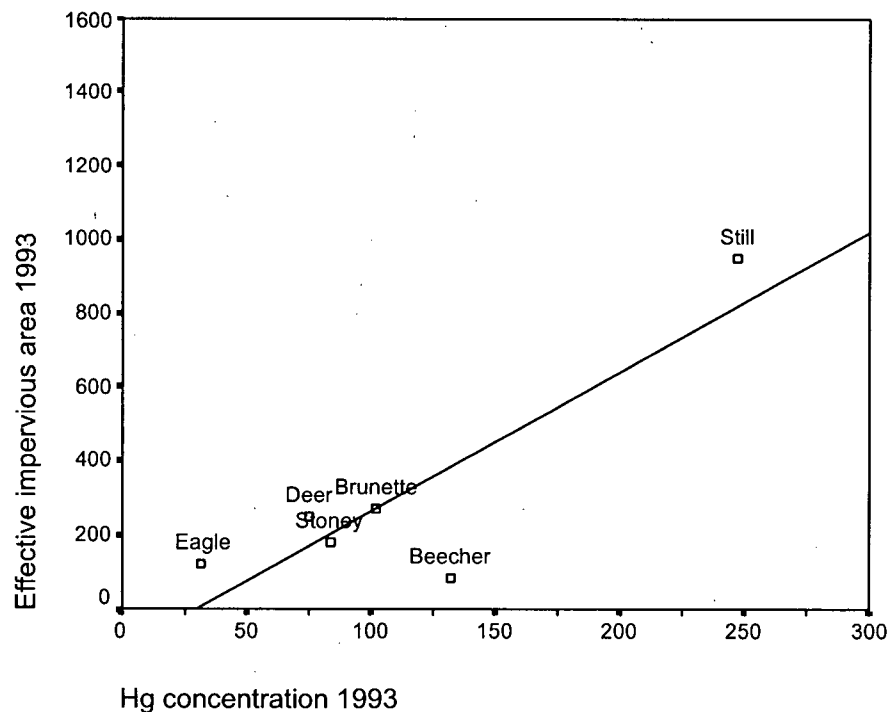
The Burnaby incinerator was fully operational on March 1, 1988 and mercury releases peaked in 1989 at 1.8 kg/day . Vegetation and soil samples monitored for mercury near the incinerator from 1987-1989 displayed an increasing trend over time (McCallum 1995). Mercury releases from the incinerator have significantly decreased since 1993 due to the installation of an activated carbon injection system (McCallum 1995). The average mercury discharge in 1993 was 0.079 ng/m^3 (Allen 2003). Estimates by Horvate (1996) of

global atmospheric concentrations of mercury are from 0.5-10 ng/m^3. Which is significantly more than currently discharged from the Burnaby Incinerator and since the system was installed, discharges have averaged 0.031 ng/m^3 (Allen 2003). This is over a 6 order of magnitude decrease in emissions since 1996. This state of the art system was the first to be installed in the North America and discharges are three times less than permits allow (Holt 2003).

An attempt was made to draw inferences from the best available data but due to insufficient data, the 2003 sediment data was compared to 1996 imperviousness. Although densification probably has occurred in the area, it is assumed for this study that impervious areas and land-use has not significantly changed over the last 10 years. McCallum (1995) noted that imperviousness in the area had only increased 7% from 1973-1993. It is even more difficult to assume that impervious levels have increased proportionately within each catchment but the correlation is worth noting for the purpose of making comparisons.

The 2003 sediment concentrations compared to the 1996 impervious area had a Spearman's correlation coefficient of 0.429, α=0.397 (Figure 4.18). Still Creek is an outlier with a high imperviousness relative to its mercury concentration. This could be due to a combination of factors like source abatement or effective use of Best Management Practices (BMP's) storm-sediment containment systems.

Figure 4.18 Scatter-plot of 2003 stream sediment mercury concentrations (*ug*/kg) vs total impervious area (hectares) from 1996. Effective impervious area data was unavailable for the period of 1994-2003. Line indicates the linear regression of the six area's
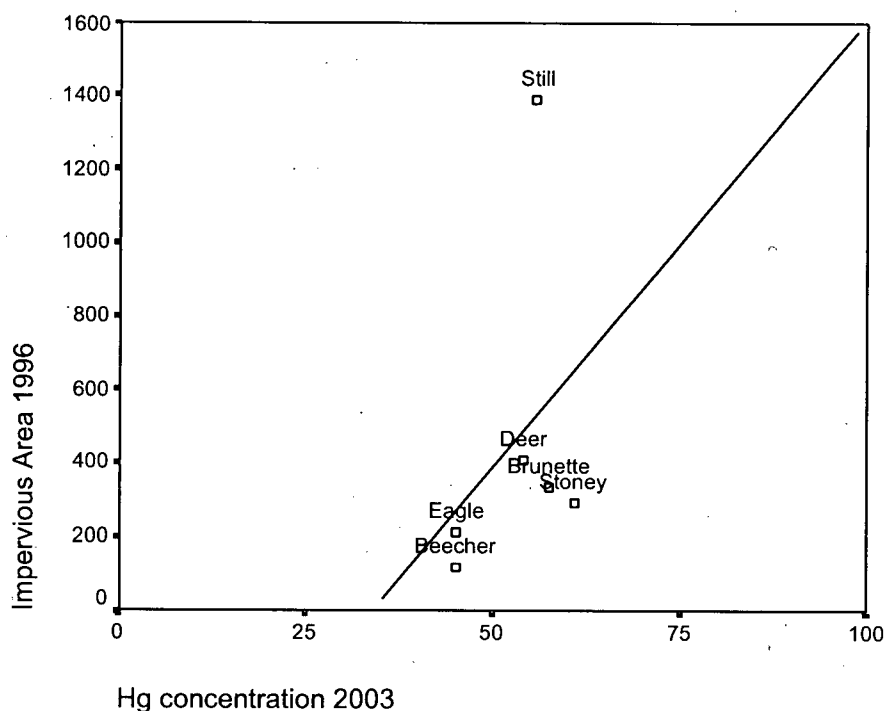
4.7 Comparison of various analysis

This project was an attempt to determine how the majority of inorganic mercury is being transported through the watershed, which includes ascertaining its forms and associations. This project examined various segments of the watershed independently, including suspended sediments, stream sediments, lake sediments and redox changes of Burnaby Lake sediment. The intent of this section is to compare and examine these segments together to determine if any significant trends exist.

Suspended sediment, Burnaby Lake sediment and stream sediment data was analyzed from the watershed with Spearman's Rank Correlation Test and Bonferroni's Correction to ascertain if statically significant relationships exist between variables. It is difficult to compare concentrations due to the various methods used in analysis, but it is

possible to discuss their relationships (Table 4.9 and 4.10). These relationships will be characterized as changes of transport mechanisms, geochemical associations or similar source locations. Characteristics will be differentiated by evaluating literature, chemical properties and watershed attributes.

Table 4.9 Comparison of sampling locations, matrix and methods for mercury determination in the Brunette Watershed.

Location	Matrix	Method
Lake	Sediment	Maximum depth of cores 1.2 cm
Stream	Sediment	<180 um surface stream sediment
Suspended Sediments	Sediment	Centrifuge of suspended stormwater sediments
Suspended Sediments	Water	Stormwater

Table 4.10 Mercury median or mean concentration in various media throughout the watershed. (Water concentrations in ug/L and sediment in ug/kg)

Median / Mean	Source	Still Creek Sub-basin	Burnaby Lake	Brunette River Sub-basin	Watershed Average
Suspended Sediment '98 (Mean, n=1)	(Sekela et al. 1998)	146	-	615	-
Stormwater '98 (Mean, n=12)	(Sekela et al. 1998)	18.8	-	28.0	-
Stream sediment '73 (≤180 um) (Median, n=27)	(Hall et al. 1976)	46.0	-	23.3	30.2
Stream sediment '89 (≤180 um) (Median, n=29)	(Duynstee 1990)	186.0	-	76.1	133.0
Stream sediment '93 (≤180 um) (Median, n=30)	(McCallum 1995)	205.6	-	94.2	132.9
Stream sediment '03 (≤180 um) (Median, n=30)	Current study	61.3	-	58.4	56.8
Enkon '02 Composite core (Median, n=15)	(Enkon 2002)	-	142.0	-	-

Iron and manganese did not have a statistically significant relationship to mercury in Burnaby Lake sediment. Also the relationship was not found in stream sediment throughout the watershed. Iron was correlated to mercury in Still Creek stormwater but was inversely

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related in the Brunette River stormwater (Spearman correlation coefficient 0.829 and –0.725 respectively). Manganese was inversely correlated with mercury in Brunette and Still Creek stormwater, (Spearman correlation coefficient –0.870 and –0.143 respectively).

Iron and manganese were correlated with each other in lake sediment and every year of stream sediment, the lowest significance of 0.041 occurred in 1973. Iron and manganese have similar physical properties due to their similar atomic weight and atomic charges, yet behave differently under redox conditions. This may indicate that correlation comparison of metals in various segments can be representative of geochemical associations due to similar transport mechanisms, even though kinetic redox rates differ.

Two elements that mercury typically has a high degree of correlation with are sulfur and dissolved organic carbon (Shafer et al. 1997; Benoit et al. 1998b; Regnell et al. 2001). In this study, different methods were used to quantify organic matter making it difficult to make comparisons between methods. The microcosm experiment with Burnaby Lake sediment resulted in a Spearman correlation coefficient of 0.651 and α= 0.081 for DOC and mercury (Appendix K). Burnaby Lake cores were analyzed for total organic carbon and correlation confidence to mercury, (Spearman correlation coefficient 0.634, α=0.011) [Appendix G]. In stream sediment, total carbon was used as an approximate indicator of total organic matter and the relationship with mercury was found to be very low. Organic matter was not analyzed in stormwater. Total sulfur was only quantified in lake and 2003 stream sediments. No statically significant correlation was found between mercury and sulfur concentrations.

Two separate environments exist within the Brunette Watershed. The western portion of the basin is highly urbanized with a steep elevation gradient. In these systems, mercury generally associates with suspended particulate matter (SPM). This section feeds Burnaby Lake, which is characterized as shallow and dystrophic, more comparable to a marsh. In these systems, mercury is typically found in the dissolved form or associated with colloidal particles (<0.45 um) (Hurley et al. 1995; Babirz et al. 1998; Benoit et al. 1998b).

Lead generally had the strongest relationship with mercury throughout the various segments of data. They both were significantly correlated with 99% confidence in Burnaby Lake sediment and every year of stream sediment except 2003 (α=0.071) [Appendix G and

F]. It has the strongest relationship with mercury out of all the Burnaby Lake core samples (Spearman correlation coefficient 0.876) [Appendix G]. No significant correlation was found in the stormwater event (Appendix I). This, combined with a decreasing relationship in 2003, could indicate that sources or transport mechanisms are changing. Lead will not form any strong chemical association with mercury but may associate with similar particles. Lead has a higher partitioning coefficient (K_d) for SPM / DOC in a variety of watersheds than Zn, Cd, Cr and Cu, but mercury's K_d will depend on the type environmental conditions (Shafer *et al.* 1997). From 1993-2003, it should be noted that concentrations of lead and mercury decline throughout the watershed. Lead concentrations in the environment have been steadily declining in North America since their phase out from gasoline in 1986.

Copper, chromium, nickel and zinc appear to have the same temporal trend in all media except for the stormwater study. It is possible that correlations in stormwater were not observed due to a low number of samples (n=8). In the watershed, copper, chromium, nickel and zinc all had a positive, significant statistical relationship to each other. Copper is significant with mercury at 0.001 in lake sediment and stream sediment in 1973 and 1989. Copper, chrome, nickel and zinc all have a significant relationship with iron in 2003.

Overall, mercury in sediments had the strongest relationships with Pb, Cu, Ni and Zn in relative order. Due to their varying chemistries and sources, it seems that this relationship is primarily due to similar sources and/or transport processes, in which all of these metals have been linked to automotive sources. It is difficult to explain why the mercury's relationship to other metals decreased in 2003 but the large reduction in point source mercury concentrations from the incinerator may be one explanation.

It seems very little can be determined about the geochemistry within the watershed with the current data. Mercury has only weak relationships that can be identified for iron, manganese, sulfur and organic carbon. These three parameters, based on literature, are typically found to geochemically associate with mercury.

4.8   Possible Sources

Mercury is found extensively throughout the world. Global studies analyzing sediment cores concluded that mercury concentrations have increased around 3-5 time's since pre-industrial times (Krabbenhoft *et al.* 1997). The intent of this section is to account

for the mercury source that led to an average 102.9 ug/kg increase in stream sediment over twenty years (Hagreen *et al.* 2004). Overall, concentrations in the Brunette Watershed range from low to moderately contaminated. Gwendoline Lake is an undisturbed, forested site and mercury sediment concentrations there are higher there than in Burnaby Lake. Although increased lead concentrations in core samples taken from Gwendoline Lake indicate that atmospheric processes have transported lead, the same scenario is possible for mercury.

Point-sources may have also increased the mercury concentration in localized areas. Mercury is commonly used in fluorescent lights, electrical switches, batteries, laboratory, medical facilities and general industry processes. Data from 1989 and 1993 studies indicates that Still Creek has the highest concentrations in the watershed and sediment cores at the mouth of the stream are also relatively high. Burnaby Lake core and stream sediment samples taken from the watershed strongly correlate high levels of Hg, Cu, Fe, Pb and Zn. Mercury is presumably released from a variety of industries along with Cu, Fe, Pb and Zn metals, although the 2003 distribution does not indicates any detectable point sources. It is possible that a pulse of mercury was released in Still Creek and/or Beecher Creek in the 1980's and 1990's and it is currently being distributed down-gradient. Sediment mercury concentrations have decreased since 1993 due to an increase in awareness of mercury's hazardous affects and controls on its use.

Mercury concentrations increased dramatically throughout the watershed between 1973 and 1993 and sources that could uniformly distribute mercury concentrations over the entire watershed are limited. Source transport processes including mercury leached from the soil by MMT or deposited from the atmosphere are both possibilities. In theory, both scenarios would run-off impervious areas and therefore should correlate well with effective impervious area. Mercury in street dirt has also increased significantly from 1973-93 (McCallum 1995). The source of mercury in street dirt is most likely a combination of atmospheric or automotive sources. But for the tentative assumption that MMT is leaching mercury out of soil to be true, there should be some type of correlation between mercury and manganese in sediment loading, geochemistry and transport, which was not observed anywhere in the watershed. Also, the microcosms experiment released very little, if any manganese. This also reinforces the idea that manganese oxides are not a dominant process in the transport of mercury.

McCallum (1995) suspects the nearby Burnaby incinerator is a contributing source of mercury to the watershed due to its proximity, which released up to 1.8 kg/day in 1989 (McCallum 1995). McCallum (1995) also found a significant correlation "that traffic density is responsible for a large part of Pb, Cu, and Zn contamination in urban streams". McCallum (1995) associates all of these metals with automotive deposition and runoff. Another study indicated that yields to aquatic sediment from atmospheric mercury of urban watersheds are 40-100% higher then forested, rural areas (<10%) (Mason *et al.* 1997). Increased imperviousness, surficial runoff and the lack of organic binding sites are suspected processes for higher levels of mercury in urban areas.

Mercury deposited from atmospheric sources is almost always bound to particulate; regardless of wet or dry deposition (Pacyna 1996). It is highly likely that particulates released from an incinerator would be associated with other metals like Ni, Cu, Pb and Zn. How long these associations would last through transport would depend on their bonding strength and environmental conditions.

If the incinerator were responsible for the large mercury increase in watershed concentrations, it would have to be a rapid process. The incinerator became operational in March 1988 and stream sediment sampling was next performed in May 1989. It is feasible that mercury could be released, deposited and washed into streams leading to a 68.0 *ug*/kg median increase in concentrations from 1973-1989, especially with the regions high level of precipitation (Figure 4.19 and 4.20). The decrease of mercury from the incinerator could also be related to the decreased level of mercury observed throughout the watershed sediment in 2003.

Mercury follows a similar trend of most other metals in the watershed from 1973 to 1989. It is highly correlated with lead, copper, nickel and zinc through this time (Figure 4.20). This may indicate similar transport mechanisms because these other metals have been linked to automotive sources and they do not react geochemically with mercury.

Figure 4.19 and 4.20 indicate that mercury is the only metal that increases from 1989 and 1993. All other metal concentrations decrease from 1989. This is probably due to an overall increased awareness of the presence of toxic metals in urban sediments and implementation of sediment control best management practices by the GVRD. After 1989, mercury's correlation to most other metals drops and this trend continues until 2003.

Mercury concentrations peaked in 1993, the same year that air scrubbers were installed at the Burnaby Incinerator.

Figure 4.19 Metal median concentrations in ≤180 um stream sediment from 1973-2003. Mercury in ug/kg. Iron in mg/kg. Manganese in ug/kg x 0.1
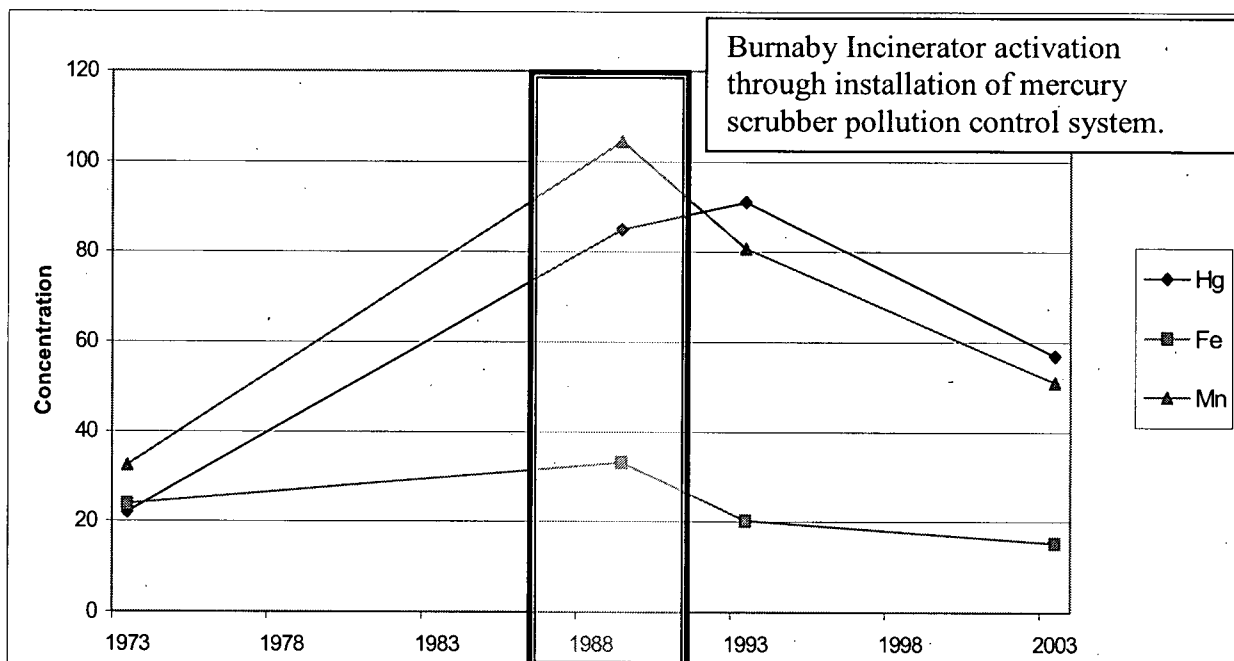
Figure 4.20 Metal median concentrations in ≤180 um stream sediment from 1973-2003.
(All metals in ug/kg)
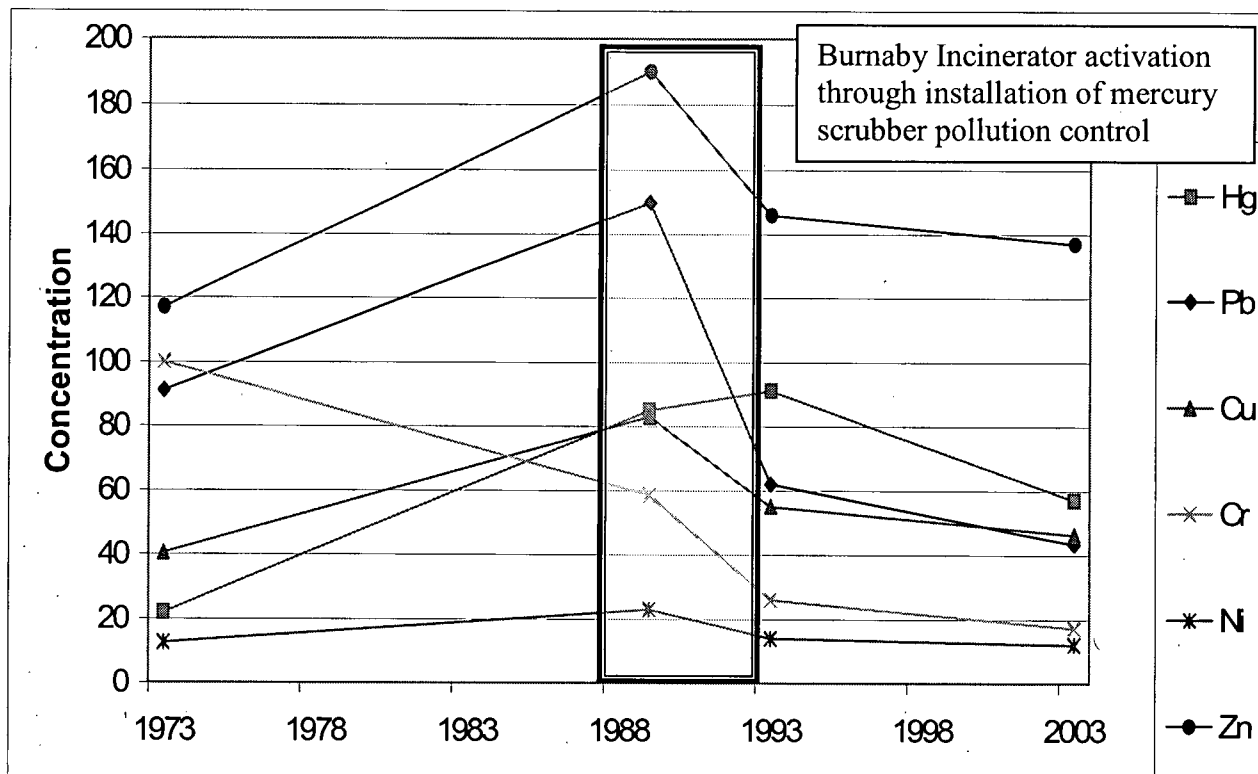
5. SUMMARY AND CONCLUSIONS

The results of this project are summarized in the following sections. Contaminant levels from different media and time frames were compared and evaluated for trends. Temporal changes are representative of historical trends in watershed.

Due to problems with laboratory results in microcosm Experiment II, water quality parameters could not be compared to sediment concentrations and other parameters. Therefore, focus was shifted to examine the temporal relationship between trace metals within stream sediment. These conclusions are discussed in the following, Section 5.3.

5.1 Temporal and spatial changes in mercury and trace metal contamination since 1973

One important temporal trend identified in this study is the overall level of mercury in stream sediment has started to decline in the watershed. This decrease is probably due a combination of increased public awareness and a decrease of releases. Overall, the level of contamination in Burnaby Lake is similar to other nearby lakes, Deer Lake and Gwendoline Lake, both of which are not connected to stormwater drainage systems. Due to its remote location, contamination in Gwendoline Lake is primarily from atmospheric deposition.

Mercury concentrations in Brunette Watershed stream sediment are actually higher than reported in this and other studies because it was found that an average of 66.8% of mercury was lost in the drying process. When sediment concentrations were adjusted for the loss 1973, 1989 1993 and 2003 sediments exceed n=0, n=12, n=12, and n=1 of the federal Interm Sediment Quality Guidelines, in respective order.

Previous studies from 1973-1993 have shown that mercury concentrations were highest in the Still Creek Sub-basin. Current 2003 data indicates that Still Creek Sub-basin mercury levels are approximately equal in the Brunette Sub-basin with at ratio of 1.05 (Still/Brunette). With an overall decrease in the watershed concentrations from 1993-2003, it is reasonable to conclude that source loadings are decreasing and mercury concentrations are being distributed downstream.

The trends in Section 4.8 indicated the Burnaby incinerator was a probable source of mercury to the watershed from 1988-1993. Mercury seems to follow a trend similar to other trace metals within the watershed, except in a small period from 1989-1993 when

every metal concentration decreased from 1989-1993, except for mercury. Consequently, the incinerator was releasing its highest concentration of mercury into the atmosphere for the same period.

It is well known that atmospheric mercury can lead to increased levels of mercury contamination in waterways. Mercury's transport mechanisms and geochemical associations after deposition are not as well known. Catchment effective impervious area may play an important role in determining the transport mechanism relative to mercury runoff. Although this needs to be examined further, when the Burnaby Incinerator provided a source, levels of mercury increased in stream sediment while all other metals decreased. Also, in that same time frame, mercury's correlation with the catchments effective impervious area was higher than without the incinerator releases.

5.2 Mercury's correlations with organic carbon, iron oxyhydroxides, manganese oxyhydroxides, sulfur and other trace metals in stream sediment, lake sediment, stormwater and laboratory controlled redox conditions

From 1973-2003, mercury's correlations in stream sediment and Burnaby Lake sediment were highest with lead, copper, nickel and zinc. These four metals and chromium were all significantly related to each other from 1973-2003. This may be due to their similar anthropocentric sources and transport mechanisms, more than their geochemical associations. No consistent correlations were observed between mercury and organic carbon, iron oxyhydroxides, manganese oxyhydroxides and sulfur in stream sediment, lake sediment, stormwater and laboratory controlled redox conditions .

5.3 Levels of mercury, iron, manganese and organic carbon released from lake sediment to overlying water due to sediment anoxia

Two separate microcosm experiments were performed to determine if anoxic conditions would lead to increased levels of mercury in overlying water. The first trial microcosm, from November 17 to December 9, 2002, displayed a release of mercury in all four microcosm chambers. This release coincided with a release of iron. The anoxic microcosm with lake water released 398% (1.59 ug/L) more mercury and 688% (1.86 ug/L) more iron than the oxic microcosm with lake water. It is suspected that methylmercury may have been

produced in the microcosms due to lower levels of mercury released when microbial activity was suppressed. Since the microcosms were intended to replicate seasonal redox conditions within Burnaby Lake, it is likely that similar releases of mercury and iron occur in the lake. (The second experiment ran from February 9 to March 25, 2003 without any results due to mercury contamination.)

5.4 MMT's responsibility for the increase of mercury concentrations in the Brunette Watershed stream sediment

Little evidence compiled in this study supported the hypothesis that manganese, iron, sulfur or DOC is associated with mercury throughout the watershed. Thus, it is difficult to conclude or rule out that MMT or manganese oxides play a major role in the transport of total mercury. Overall, evidence that would lead to conclusions about mercury's geochemical association within the watershed from this study was inconclusive. In this study, mercury does not correlate with any substances typically found in the literature to have geochemical associations with mercury. Therefore, correlation' s in stream sediment, lake sediment, stormwater and laboratory controlled redox conditions may not be the optimum method to examine a watershed's geochemical associations. Since a relationship between mercury and manganese was not observed in field data, microcosm experiments, stream sediment, and other studies were examined to determine other potential sources of mercury to the Brunette Watershed.

6. RECOMMENDATIONS

The conclusions drawn from this study can be used to make better management decisions concerning the remediation and conservation in the Brunette Watershed and urban watersheds in general. Further research would enable improved understanding of the source, transport and fate of mercury and other trace metals in urban environments.

6.1 Implications for further research

This project indicates source and transport processes to a waterway may be important to the distribution of mercury in stream sediments. Further research into effective imperviousness effect on mercury distribution in waterways and stream sediments is recommended. It may be an important component in modeling mercury's intermediary fluxes between air to aquatic transport. Other projects should examine the relationship between mercury in waterways and point-source releases, including a detailed examination of mercury concentrations in core samples from 1988- 1996 to identify temporal fluxes.

Future work should investigate the levels of mercury and methylmercury within various media throughout the watershed. Due to methodological errors, historic concentrations of mercury in sediment and waters are suspect. More research is needed, using current methods, to determine levels of contamination throughout the watershed. Methylmercury is a highly toxic compound and the microcosm Experiment I indicated anoxic sediments might release methylmercury. Laboratory analysis should examine the relationship between MMT and mercury to reduce variables present in the environment. Further research is needed to identify levels of methylmercury in fish and other biota within the watershed. Then, if necessary, investigate levels of contamination in water and sediment.

Further research is needed into mercury's geochemical associations and the release of mercury from anoxic sediments in the Burnaby Lake and other urban watersheds, possibly Gwendoline Lake could be used for a comparison. Burnaby Lake has the environmental conditions/cycling that would make it possible for sediment releases of stored mercury into the overlying sediment and thus downstream. For this investigation, methodologies involving microcosms to study mercury's geochemical relationships and stormwater sampling to study mercury's aquatic transport are recommended.

Also, it is important to determine if the biological and ecological health of the watershed has improved with decreased trace metal contamination. An ecological assessment conducted in 1998 by the UBC could be used to provide background information on contamination (Richardson *et al.* 1988) There has been a focus on improving the physical and chemical indicators within the watershed for sometime. It would be interesting to determine if improvements in physical and chemical indicators resulted in biological indicator improvements.

6.2   Management implications

The GVRD is considering dredging Burnaby Lake to improve the recreational and environmental conditions. To prevent the need for further dredging, the GVRD and the Brunette Basin Task Group (BBTG) should continue implementing sediment control measures to reduce the influx of contaminated sediment into the lake.

Environmental impacts of dredging would be dependent on the level of freshly exposed sediment. Enkron(2002) recommends the use sediment control devices to minimize the impact of suspended solids over a large area within the lake. Small mercury releases are possible from anoxic sediment due to sediment exposed by dredging; although mercury would have already had the opportunity for release when it was originally deposited. The planned sediment controls proposed by the GVRD should reduce the release of mercury and the transport of mercury and other contaminants.

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APPENDIX A Stream Sediment Sampling Locations

Table A-1 Stream sediment sampling locations

Station Number	Station Description	General Remarks
1.	Brunette R. at Spruce Ave. (bridge)	At river mouth, wood products industries
2.	Brunette R. at Camphor Ave., near railway bridge.	Wood products industry nearby.
3.	Brunette R. at Braid St. (bridge)	Wood products industry nearby.
4.	Brunette R. at Brunette Rd.	Potentially affected by high traffic volumes
6.	Brunette R. at North Rd. (east side)	Sampled within Hume Park.
7.	Stoney Creek at Grandview Hwy., 100m west of intersection of Hunter and Keswick Streets	
8.	Stoney Cr. at Beaverbrook Dr. and Noel Dr., samples obtained upstream and downstream of bridge.	Residential area.
9.	Stoney Creek at East Broadway, 50m west of Norcrest Rd.	Residential area.
10.	Brunette R. at Cariboo Rd., samples obtained upstream and downstream of bridge.	Potentially affected by high traffic volumes.
11.	Small stream arising from a storm sewer, south side of Winston St., east of Brighton St.	Light industrial and residential area.
13.	Eagle Creek on Piper Avenue, south of Winston St.	Located in Werner Boat Park.
14.	Eagle Creek at East Broadway (south side), bgetween Lake City Way and Lawrence Drive.	Below golf course.
15.	Tributary of Eagle Creek at Shellmont St. (north side), east of Arden Drive.	Downstream of petroleum tank farm runoff detention facility.
16.	Tributary of Eagle Creek at Woodbrook Place, east of Phillips Ave.	Upstream of golf course, wooded stream buffer.
17.	Robert Burnaby Creek, near park entrance at 4th St.	Located within Robert Burnaby Park.
19.	Deer Lake Brook at Glencairn Dr. (north side)	North of freeway south of Burnaby Lake.
20.	Deer Lake Brook at Deer Lake Ave., south of Canada Way, upstream and downstream of bridge.	Downstream of Deer Lake.
21.	Small stream at Moscrop St. (south side),	Residential area downstream of

	between Royal Oak Ave and Oaktree Ct.	cemetery.
24.	Small creek at intersection of Sperling Ave. and Jordan Dr.	Residential area.
25.	Beecher Cr. near Goring Ace., sampled on south side of railroad tracks	Small tributary of Still Creek
26.	Beecher Cr. at Lougheed Hwy. (south side)	Upstream of station 25.
27.	Beecher Cr. at Springer Ave. (east side).	Upstream of station 26.
29.	Small stream in Westburn Park along Gilpin Cr.	400m upstream of 1973 location.
30.	Still Creek on Still Creek Dr., west of Willingdon Ave.	Industrial area, heavy traffic.
31.	Still Creek at Gilmore Ave. (east side).	Industrial area.
32.	North branch of Still Creek at Lougheed Hwy. (south side)	Affected by heavy traffic.
33.	Still Creek at Grandview Hwy. (south side) and Rndfew St. (east side)	Residential area.
34.	Still Creek at Myrtle St., east of Boundary Rd.	Industrial area
35.	Still Creek at Douglas Ave.	Industrial area.
37.	Still Creek at Atilin St. and 27th Ave.	Wooded ravine.

APPENDIX B Concentration of trace metals in Brunette Watershed stream sediment from 1973-2003

Table B-1 Streambed sediment, ≤180um fraction in the Brunette Watershed, total concentration in 1973 (Hall *et al.* 1976). Values in dry weight. Nitric acid digest for all metals except Hg. Mercury analyzed with potassium permanganate digestion and cold vapor analysis.

1973 Stations	Fe (mg/kg)	Hg (ug/kg)	Mn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	OM %
1	41600	44	716	104	52.3	175	41.1	136	6.4
2	36000	40	684	108	46.3	100	23.6	128	5.3
3	20800	52	652	134	44.4	50	15	117	6.3
4	25200	11	460	50	16.1	75	10	52	2.3
6	14000	11	165	50	12.3	100	7.4	47	2
7	22600	19	248	45	16.7	50	8.4	46	52.2
8	23000	14	444	63	18.2	75	9	67	5
9	26000	20	275	39	17	100	9	60	2.3
10	19400	12	655	24	14.5	100	12.4	60	2.4
11	10800	10	196	14.5	13.9	50	5	32	7.4
13	24000	27	315	91	42	200	12.6	126	2.1
14	15200	30	325	10	12.3	0	8.4	65	2.5
15	50000	9	250	5	11.6	75	10	47	7.9
16	14800	13	205	26	15.8	700	11	47	2.5
17	23800	14	436	118	16.5	75	9.4	47	4.6
19	15600	18	242	292	48.6	50	14.4	136	2.2
20	24000	22	682	324	40.3	50	13.4	167	7.3
21	31800	18	875	58	40.4	125	20.8	118	7.9
24	24000	53	415	470	72.8	100	18.8	168	7
25	30800	29	328	950	82.9	100	194	199	2.2
26	23200	15	225	66	19	125	12	51.5	4.6
27	22600	22	468	48	17.8	100	8	69	9.4
29	73000	73	398	276	50.7	125	29	121	5.9
30	23800	101	211	440	684	100	33.6	206	6.4
31	2500	60	308	400	1765	150	23	168	1.8
32	22600	37	200	359	62.8	150	54	130	2.2
33	19400	34	294	34	52.7	50	10	100	3.8
34	36200	NA	114	600	95.1	200	19.2	305	29.7
35	33400	NA	425	840	816	NA	85	408.00	NA

Table B-2 Streambed sediment, ≤180*um* fraction in the Brunette Watershed, total concentration in 1989 (Macdonald *et al.* 1996b). Values in dry weight. Nitric acid digest for all metals except Hg. Mercury analyzed with potassium permanganate digestion and cold vapor analysis.

1989 Stations	Fe (mg/kg)	Hg (ug/kg)	Mn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
1	379000	120	1108	169	91	75	35	263
2	381000	110	1203	180	77	73	33	218
3	325000	80	1187	155	77	53	25	177
4	385000	45	1123	142	58	57	17	148
6	333000	80	1398	245	91	50	23	211
7	297000	80	726	113	85	75	19	126
8	291000	35	727	85	61	48	18	106
9	330000	45	720	82	48	55	20	104
10	344000	90	2118	159	85	55	20	205
11	NA	NA	NA	NA	NA	NA	NA	NA
13	190000	40	506	36	53	34	16	83
14	540000	35	1090	48	53	55	17	130
15	455000	40	1007	60	72	50	18	306
16	277000	50	756	90	63	47	21	120
17	350000	25	757	47	50	65	28	95
19	266000	95	1093	247	151	55	22	227
20	324000	105	2513	132	69	58	25	178
21	261000	115	640	356	108	63	24	202
24	782000	350	4083	577	262	94	31	443
25	363000	55	1084	145	83	70	23	163
26	329000	65	1101	143	80	64	21	150
27	299000	70	899	93	61	54	21	138
29	332000	90	701	176	83	61	24	212
30	300000	160	1152	388	234	59	27	298
31	254000	90	649	140	102	46	18	155
32	530000	365	554	667	394	131	59	445
33	448000	415	8794	444	267	93	34	759
34	390000	200	845	267	157	81	40	252
35	282000	120	676	170	106	62	25	208
37	350000	175	767	479	155	76	24	285

Table B-3 Streambed sediment, ≤180*um* fraction in the Brunette Watershed, total concentration in 1993. (McCallum 1995). Values in dry weight. Nitric acid digest for all metals except Hg. Mercury analyzed with potassium permanganate digestion and cold vapor analysis.

1993 Stations	Fe (mg/kg)	Hg (*ug*/kg)	Mn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	OM %
1	32739	132	768	63	66	38	34	186	6.3
2	20929	132	534	62	51	41	24	134	5.4
3	26948	137	401	55	58	38	22	145	5.9
4	20199	51	1299	48	42	20	11	116	4.5
6	10437	57	561	48	31	15	7	111	3.2
7	20287	85	1009	37	32	24	13	87	4.6
8	13208	51	508	32	30	21	9	115	4.2
9	17474	115	807	96	51	26	12	95	4.7
10	30431	79	1435	407	141	35	19	310	8.1
11	22800	103	975	62	101	26	11	185	5.6
13	16994	45	1109	22	43	18	8	106	4.2
14	23872	50	791	39	34	18	9	93	3.7
15	44724	15	1553	24	45	19	6	163	7.8
16	28657	15	839	36	50	20	24	166	5.9
17	14822	60	474	40	97	40	14	161	4.8
19	9370	61	200	53	55	19	8	110	5.0
20	12923	69	1315	86	72	18	10	171	7.8
21	18421	95	906	60	52	30	17	146	6.3
24	27289	102	2004	190	119	45	21	391	5.0
25	13901	352	333	43	50	18	12	89	19.9
26	18178	64	869	72	55	24	11	128	4.2
27	21421	68	1273	73	56	29	16	196	6.5
29	11430	154	357	26	26	17	13	136	4.2
30	23219	121	346	127	195	34	28	262	4.6
31	23293	149	1334	141	279	33	16	341	7.1
32	12225	91	194	133	80	31	15	140	10.6
33	23115	870	1440	307	162	33	19	278	5.2
34	21054	214	366	190	142	35	17	255	3.7
35	18787	137	287	116	142	37	18	283	5.9
37	14651	NA	722	207	199	38	19	271	3.0

Table B-4 Streambed sediment, ≤180um fraction, in the Brunette Watershed, total concentration in 2003. Values in dry weight. Nitric acid digest for all metals except Hg. Mercury analyzed with pyrolysis digestion and AA detection.

2003 Stations	Fe (mg/kg)	Hg (ug/kg)	Mn (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Zn (mg/kg)	OM %	S (mg/kg)	Cd (mg/kg)
1	20163	72.4	461	43	32	12	12	140	1.57	268	2.6
2	4707	26.3	171	9	8	8	7	39	0.40	75	0.6
3	20539	65.1	210	7	29	27	29	60	0.60	66	1.9
4	22179	20.1	224	8	31	28	30	62	0.65	71	2.7
6	7571	102.9	294	22	14	7	4	49	0.36	105	0.7
7	12456	78.8	503	15	24	11	9	86	1.25	161	1.3
8	7805	59.6	373	33	15	7	6	57	1.45	157	0.8
9	11897	44.3	511	31	32	13	8	104	1.45	232	1.4
10	14695	56.1	1594	67	78	20	13	190	1.22	329	1.9
11	36853	58.4	1490	62	87	26	13	311	2.84	389	4.4
13	16189	10.9	1587	20	22	11	7	136	3.20	324	1.8
14	7990	32.7	402	3	8	4	3	45	0.55	112	0.8
15	17670	56.9	927	8	14	7	4	124	1.69	173	1.7
16	12575	79.4	790	50	50	17	8	143	4.24	352	1.6
17	10846	85.5	153	622	176	19	9	220	4.26	872	1.4
19	20831	101.2	1725	93	103	27	13	301	13.90	1773	2.8
20	11884	28.2	1438	50	48	10	18	126	5.74	619	1.4
21	8492	33.1	509	18	20	8	6	68	1.93	164	1.3
24	17187	99.6	990	157	99	22	17	181	3.44	345	2.3
25	21693	24.3	1076	60	53	18	13	181	3.38	360	2.6
26	9231	62.1	361	29	28	11	7	83	1.93	195	1.1
27	15006	48.7	633	44	49	18	13	129	1.82	243	1.8
29	23528	110.8	1662	33	41	16	13	160	3.09	312	2.7
30	15228	51.7	212	54	76	18	11	162	1.16	285	1.8
31	15516	69.1	306	102	107	19	18	152	1.46	261	1.8
32	38807	46.2	312	270	162	49	33	403	4.73	729	4.6
33	24247	71.1	1439	168	166	37	19	359	3.31	545	3.8
34	31769	17.8	1601	186	126	38	23	366	2.52	801	4.6
35	8609	32.2	160	27	46	11	9	96	1.32	205	1.0
37	11140	102.0	201	69	55	22	9	106	0.81	274	1.5

APPENDIX C Metal concentrations in sediment cores from Burnaby Lake

Table C-1 Metal concentrations in sediment cores (depth ≤ 2.0 cm) from Burnaby Lake (Enkon 2002) [mg/kg dry weight]. Refer to Figure C-1 for site locations. (C) indicates composite sample was analyzed.

Site	Hg	Mn	Fe	Pb	Cu	Ni	Zn	TOC	S
A-C	0.16	240	13300	153	80.9	17.6	177	14	2210
B-C	0.28	394	25100	514	189	26.9	476	8.3	2210
C-C	0.05	443	25700	4	35.3	16	55.2	0.24	234
D-C	0.06	180	10400	5	20	13.3	48.2	9.1	3290
E-C	0.1	243	15700	62	35.7	16.8	152	8	1870
F-C	0.08	232	1500	50	39.8	39.5	91.3	7.3	2170
G	0.07	252	9850	6	16.2	14.9	56.7	14	2580
H	0.06	233	15300	4	29.3	17.9	60.4	7.8	2690
I	0.05	219	14200	12	24.9	14.9	62.2	7.7	2400
J	0.1	201	9720	30	23.6	12.5	80.5	12	2970
K-C	0.26	420	16800	277	125	33.6	412	14	5430
L-C	0.25	323	20900	209	175	22.6	426	9.7	2700
M-C	0.2	291	17300	70	38.6	16.1	172	14	2470
N-C	0.05	218	10600	58	28.4	12.5	98	7.3	1030
OC	0.44	424	31500	533	254	36	571	12	4330

Figure C-1 Location of Burnaby Lake sediment core sampling stations. Photo adapted from (Enkon 2002).

○ Burnaby Lake sediment core locations.   ⇧ North
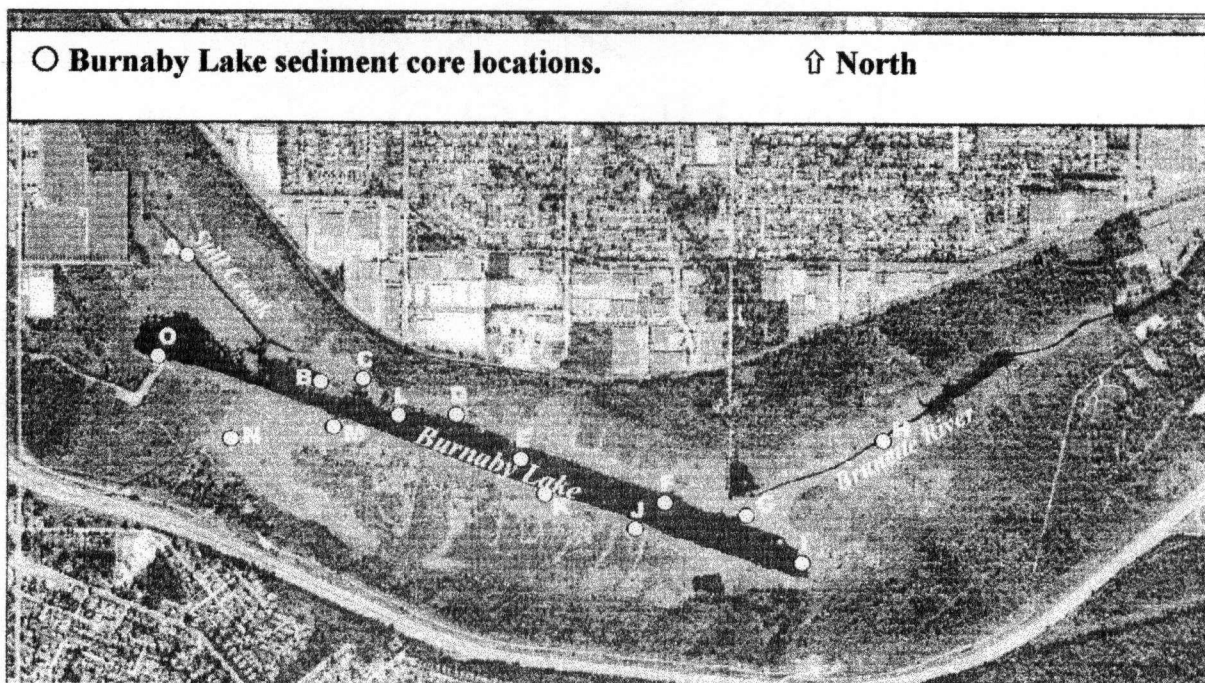
APPENDIX D Total metal concentrations within a Brunette Watershed stormwater event

Table D-1 Total metals within a stormwater event on the Brunette River, February 28, 1997 (Sekela *et al.* 1998)

Brunette River

Flow (cms)	time (hr)	Hg (ng/L)	Fe (mg/L)	Mn (mg/L)
1.57	1:00	22.0	0.882	0.075
1.80	2:00	11.0	1.600	0.087
3.92	3:00	18.0	1.830	0.117
6.30	5:00	19.0	0.983	0.085
6.58	7:00	22.0	0.986	0.083
6.88	8:15	21.0	1.120	0.086
	Ave	18.8	1.234	0.089
	Std Dev.	4.1	0.387	0.015

Table D-2 Total metals within a stormwater event on Still Creek, February 28, 1997 (Sekela *et al.* 1998)

Flow (cms)	Time (hr)	Hg (ng/L)	Fe (mg/L)	Mn (mg/L)
0.38	1:00	27.0	1.790	0.240
0.66	2:00	23.0	1.740	0.234
1.59	3:00	26.0	2.540	0.225
1.97	4:15	39.0	4.280	0.179
2.81	5:45	25.0	2.080	0.088
4.90	7:45	28.0	3.020	0.098
	Ave	28.0	2.575	0.177
	Std Dev	5.7	0.966	0.069

APPENDIX E Microcosm data from Experiment 1, November 17 to December 9, 2002

Table E-1 Microcosm pH data from Experiment 1, November 17 to December 9, 2002.
Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	20-Nov-02	2-Dec-02	9-Dec-02
1	5.73	6.44	5.60	6.54
2	5.38	6.02	4.03	6.44
3	5.80	5.32	4.80	5.73
4	5.73	6.68	6.48	6.70

Table E-2 Microcosm conductivity data (uS/cm) data from Experiment 1, November 17 to December 9, 2002. Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	25-Nov-02	02-Dec-02	09-Dec-02
1	70	126	112	620
2	12	38	54	34.7
3	73	108	112	75.0
4	70	2675	2525	1385

Table E-3 Microcosm dissolved oxygen data (mg/L) data from Experiment 1, November 17 to December 9, 2002. Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	20-Nov-02	02-Dec-02	09-Dec-02
1	2.0	0.45	0.35	0.20
2	3.4	0.55	0.5	0.20
3	2.1	5.2	5.1	5.8
4	1.5	0.5	0.45	0.15

Table E-4 Microcosm dissolved organic carbon data (mg/L) data from Experiment 1, November 17 to December 9, 2002. Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	09-Dec-02
1	13	37
2	13	33
3	13	34
4	13	17

Table E-5 Microcosm mercury data (ug/L) data from Experiment 1, November 17 to December 9, 2002. Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	25-Nov-02	02-Dec-02	09-Dec-02	09-Dec-02 Dis
1	0.104	0.47	1.3	2.092	1.953
2	0.300	0.204	0.88	1.631	1.400
3	0.173	0.081	0.758	0.570	0.524
4	0.173	0	0	0.201	0.450

Table E-6 Microcosm Iron data (ppm) data from Experiment 1, November 17 to December 9, 2002. Note: Microcosm variables (1. Control, 2. DI water, 3. Oxic and 4. Molybdate ions)

Microcosm	18-Nov-02	25-Nov-02	02-Dec-02	09-Dec-02	09-Dec-02 Dis
1	0.108	0.213	0.128	2.24	0.084
2	0.624	0.464	0.129	0.804	0.176
3	0.448	0.476	0.184	0.714	0.327
4	1.654	1.353	0.263	1.784	1.092

Table E-7 Mercury concentrations of Burnaby lake sediment used in Microcosm #1 analysis, November 1, 2002

Description	Concentration (ug/kg)	% Solids	Adjusted concentration (ug/kg)
Microcosm Sediment	21	9.97	210.63

APPENDIX F Correlations for 1973-2003 stream sediment in the Brunette Watershed

Table F-1 Spearman's rho Correlations with Bonferroni Correction- 1973 Stream Sediment in the Brunette Watershed

		Fe	Hg	Mn	Pb	Cu	Cr	Ni	Zn	OM%
Fe	Correlation Coefficient	1.000								
	N	35								
Hg	Correlation Coefficient	.162	1.000							
	N	33	33							
Mn	Correlation Coefficient	.347	.350	1.000						
	N	35	33	35						
Pb	Correlation Coefficient	.188	.664(**)	.127	1.000					
	N	35	33	35	35					
Cu	Correlation Coefficient	.281	.821(**)	.038	.850(**)	1.000				
	N	29	27	29	29	29				
Cr	Correlation Coefficient	.288	.221	-.115	.312	.377	1.000			
	N	28	27	28	28	28	28			
Ni	Correlation Coefficient	.483	.657(**)	.212	.772(**)	.815(**)	.500	1.000		
	N	29	27	29	29	29	28	29		
Zn	Correlation Coefficient	.362	.774(**)	.178	.843(**)	.894(**)	.320	.820(**)	1.000	
	N	29	27	29	29	29	28	29	29	
OM%	Correlation Coefficient	.209	-.105	.069	-.087	-.042	-.168	-.088	-.041	1.000
	N	33	32	33	33	28	28	28	28	34

* Correlation is significant at the 0.005 level (2-tailed).
** Correlation is significant at the 0.001 level (2-tailed).

Table F-2 Spearman's rho Correlations with Bonferroni Correction- 1989 stream sediment data in the Brunette Watershed

		Fe	Hg	Mn	Pb	Cu	Cr	Ni	Zn
Fe	Correlation Coefficient	1.000							
	N	29							
Hg	Correlation Coefficient	.190	1.000						
	N	29	29						
Mn	Correlation Coefficient	.450	.216	1.000					
	N	29	29	29					
Pb	Correlation Coefficient	.263	.901(**)	.264	1.000				
	N	29	29	29	29				
Cu	Correlation Coefficient	.150	.894(**)	.133	.902(**)	1.000			
	N	29	29	29	29	29			
Cr	Correlation Coefficient	.557(*)	.654(**)	.167	.630(**)	.571(**)	1.000		
	N	29	29	29	29	29	29		
Ni	Correlation Coefficient	.362	.750(**)	.262	.691(**)	.596(**)	.725(**)	1.000	
	N	29	29	29	29	29	29	29	
Zn	Correlation Coefficient	.490	.810(**)	.380	.825(**)	.818(**)	.541(**)	.641(**)	1.000
	N	29	29	29	29	29	29	29	29

* Correlation is significant at the 0.005 level (2-tailed).
** Correlation is significant at the 0.001 level (2-tailed).

Appendix F-3

Table F-3 Spearman's rho Correlations with Bonferroni Correction- 1993 stream sediment in the Brunette Watershed

		Fe	Hg	Mn	Pb	Cu	Cr	Ni	Zn	OM%
Fe	Correlation Coefficient	1.000								
	N	36								
Hg	Correlation Coefficient	-.012	1.000							
	N	35	35							
Mn	Correlation Coefficient	.427	-.080	1.000						
	N	36	35	36						
Pb	Correlation Coefficient	.134	.640(**)	.224	1.000					
	N	36	35	36	36					
Cu	Correlation Coefficient	.288	.502	.052	.848(**)	1.000				
	N	30	29	30	30	31				
Cr	Correlation Coefficient	.414(*)	.445	-.027	.619(**)	.706(**)	1.000			
	N	30	29	30	30	31	31			
Ni	Correlation Coefficient	.496(*)	.546(*)	-.076	.531(*)	.565(**)	.780(**)	1.000		
	N	30	29	30	30	31	31	31		
Zn	Correlation Coefficient	.485	.345	.293	.701(**)	.830(**)	.631(**)	.608(**)	1.000	
	N	30	29	30	30	31	31	31	31	
OM%	Correlation Coefficient	.302	.285	.343	.299	.261	.147	.227	.291	1.000
	N	36	35	36	36	30	30	30	30	36

** Correlation is significant at the 0.001 level (2-tailed).
* Correlation is significant at the 0.005 level (2-tailed).

Appendix F-4

Table F-4 Spearman's rho Correlations with Bonferroni Correction- 2003 Stream Sediment in the Brunette Watershed

		Fe	Hg	Mn	Pb	Cu	Cr	Ni	Zn	O%
Fe	Correlation Coefficient	1.000								
	N	36								
Hg	Correlation Coefficient	.041	1.000							
	N	36	36							
Mn	Correlation Coefficient	.398	.129	1.000						
	N	36	36	36						
Pb	Correlation Coefficient	.245	.304	.353	1.000					
	N	36	36	36	36					
Cu	Correlation Coefficient	.555(**)	.200	.215	.930(**)	1.000				
	N	30	30	30	30	30				
Cr	Correlation Coefficient	.748(**)	.103	.167	.635(**)	.800(**)	1.000			
	N	30	30	30	30	30	30			
Ni	Correlation Coefficient	.715(**)	-.030	.189	.493(**)	.667(**)	.825(**)	1.000		
	N	30	30	30	30	30	30	30		
Zn	Correlation Coefficient	.712(**)	.135	.514(*)	.864(**)	.890(**)	.685(**)	.553(*)	1.000	
	N	30	30	30	30	30	30	30	30	
Om	Correlation Coefficient	.332	.205	.639(**)	.663(**)	.574(**)	.307	.306	.703(**)	1.000
	N	36	36	36	36	30	30	30	30	36

* Correlation is significant at the 0.005 level (2-tailed).

** Correlation is significant at the 0.001 level (2-tailed).

APPENDIX G Correlations for Burnaby Lake composite core sediments

Table G-1 Spearman's rho Correlations with Bonferroni Correction- Burnaby Lake composite core sediments (Enkon 2002)

		Hg	Mn	Fe	Pb	TOC	S	Cu	Ni	Zn
Hg	Correlation Coefficient	1.000								
	N	15								
Mn	Correlation Coefficient	.533	1.000							
	N	15	15							
Fe	Correlation Coefficient	.454	.832(**)	1.000						
	N	15	15	15						
Pb	Correlation Coefficient	.876(**)	.463	.461	1.000					
	N	15	15	15	15					
TOC	Correlation Coefficient	.634	.197	.020	.448	1.000				
	N	15	15	15	15	15				
S	Correlation Coefficient	.467	.027	.041	.229	.624	1.000			
	N	15	15	15	15	15	15			
Cu	Correlation Coefficient	.788(**)	.668	.664	.835(**)	.159	.080	1.000		
	N	15	15	15	15	15	15	15		
Ni	Correlation Coefficient	.652(**)	.576	.420	.571	.091	.163	.843(**)	1.000	
	N	15	15	15	15	15	15	15	15	
Zn	Correlation Coefficient	.862(**)	.496	.525	.976(**)	.372	.181	.886(**)	.626	1.000
	N	15	15	15	15	15	15	15	15	15

* Correlation is significant at the 0.005 level (2-tailed).
** Correlation is significant at the 0.001 level (2-tailed).

APPENDIX H Correlations for Microcosm #1 data

Table H-1 Spearman's rho Correlations with Bonferroni Correction for Microcosm #1 data

		pH	conductivity	D.O.	DOC	Hg	Fe
pH	Correlation Coefficient	1.000					
	Sig. (2-tailed)	.					
	N	16					
Conductivity	Correlation Coefficient	.346	1.000				
	Sig. (2-tailed)	.189	.				
	N	16	16				
D.O.	Correlation Coefficient	-.649(*)	-.059	1.000			
	Sig. (2-tailed)	.006	.828				
	N	16	16	16			
DOC	Correlation Coefficient	.754(*)	.345	-.638	1.000		
	Sig. (2-tailed)	.031	.403	.089	.		
	N	8	8	8	8		
Hg	Correlation Coefficient	-.500	-.265	.154	.651	1.000	
	Sig. (2-tailed)	.049	.322	.570	.081	.	
	N	16	16	16	8	16	
Fe	Correlation Coefficient	.539	.158	-.221	.533	.000	1.000
	Sig. (2-tailed)	.031	.560	.411	.174	1.000	.
	N	16	16	16	8	16	16

** Correlation is significant at the 0.008 level (2-tailed).
* Correlation is significant at the 0.001 level (2-tailed).

Table I-1 Spearman's rho Correlations with Bonferroni Correction for the February 28, 1997 on Still Creek stormwater event (Sekela *et al.* 1998)

		Cr	Cu	Hg	Fe	Mn	Ni	Pb	Zn
Cr	Correlation Coefficient	1.000							
	Sig. (2-tailed)	.							
Cu	Correlation Coefficient	.257	1.000						
	Sig. (2-tailed)	.623	.						
Hg	Correlation Coefficient	.600	.771	1.000					
	Sig. (2-tailed)	.208	.072	.					
Fe	Correlation Coefficient	.143	.943(*)	.829	1.000				
	Sig. (2-tailed)	.787	.005	.042	.				
Mn	Correlation Coefficient	.086	-.714	-.143	-.543	1.000			
	Sig. (2-tailed)	.872	.111	.787	.266	.			
Ni	Correlation Coefficient	.714	-.086	.371	-.143	.543	1.000		
	Sig. (2-tailed)	.111	.872	.468	.787	.266	.		
Pb	Correlation Coefficient	.086	.886	.543	.829	-.829	-.314	1.000	
	Sig. (2-tailed)	.872	.019	.266	.042	.042	.544	.	
Zn	Correlation Coefficient	.029	.943(*)	.600	.886	-.771	-.200	.943(*)	1.000
	Sig. (2-tailed)	.957	.005	.208	.019	.072	.704	.005	.

** Correlation is significant at the 0.001 level (2-tailed).
* Correlation is significant at the 0.006 level (2-tailed).

Table I-2 Spearman's rho Correlations with Bonferroni Correction for the February 28, 1997 on the Brunette River stormwater event (Sekela *et al.* 1998)

		Cr	Cu	Hg	Fe	Mn	Ni	Pb	Zn
Cr	Correlation Coefficient	1.000							
	Sig. (2-tailed)	.							
Cu	Correlation Coefficient	-.841	1.000						
	Sig. (2-tailed)	.036	.						
Hg	Correlation Coefficient	.464	-.515	1.000					
	Sig. (2-tailed)	.354	.296	.					
Fe	Correlation Coefficient	-.486	.580	-.725	1.000				
	Sig. (2-tailed)	.329	.228	.103	.				
Mn	Correlation Coefficient	-.429	.493	-.870	.943(*)	1.000			
	Sig. (2-tailed)	.397	.321	.024	.005	.			
Ni	Correlation Coefficient	-.667	.647	-.250	-.116	-.029	1.000		
	Sig. (2-tailed)	.148	.165	.633	.827	.957	.		
Pb	Correlation Coefficient	-.429	.638	-.783	.943(*)	.886	-.058	1.000	
	Sig. (2-tailed)	.397	.173	.066	.005	.019	.913	.	
Zn	Correlation Coefficient	-.771	.986(**)	-.551	.600	.543	.638	.657	1.000
	Sig. (2-tailed)	.072	.000	.257	.208	.266	.173	.156	.

** Correlation is significant at the 0.001 level (2-tailed).
* Correlation is significant at the 0.006 level (2-tailed).

APPENDIX J Quality control data for mercury in sediment

Table J-1Quality control data for mercury in sediment, analyzed on a Lumex AA. Results in ug/kg, dry wieght. Environmental Resource Associates: Reference Sample Catalog #540 Lot # D035-540.

QC Data (ppm)	Weight (mg)	Conc. (ppm)	% Recovery
era-24.6	18.6	26.0	105.8%
era 24.6	35.2	21.9	89.0%
era 24.6	31.6	20.5	83.5%
era 24.6	20.9	25.2	102.3%
era 24.6	33.3	23.9	97.2%
era 24.6	4.7	29.6	120.3%
era 24.6	31.0	23.0	93.5%
Ave		23.5	95.6%
std dev		3.0	
conf@95%		1.86	
check-30	100	26.3	87.7%
check-30	100	28.3	94.3%
check-30	100	24.6	82.0%
check-50	100	57.4	114.8%
check-50	100	45.7	91.4%
check-50	100	52.6	105.2%
Ave			95.9%
Blank	1	-2.0	
Blank	1	-1.3	
Blank	1	-3.0	
Blank	1	2.9	
Blank	1	0.8	
Blank	1	-0.2	
Blank	1	-0.7	
Ave		-0.5	
std dev		1.9	

APPENDIX K Wilcoxon Paired Sample Signed Rank Test for mercury stream sediment data in the Brunette Watershed.

Table K-1 Wilcoxon Paired Sample Signed Rank Test for 1973, 1989, 1996 and 2003 mercury stream sediment data in the Brunette Watershed

		N	Mean Rank	Sum of Ranks
1989 - 1973	Negative Ranks	0(a)	.00	.00
	Positive Ranks	27(b)	14.00	378.00
	Ties	0(c)		
	Total	27		
1993 - 1973	Negative Ranks	0(d)	.00	.00
	Positive Ranks	28(e)	14.50	406.00
	Ties	0(f)		
	Total	28		
2003 - 1973	Negative Ranks	5(g)	10.80	54.00
	Positive Ranks	23(h)	15.30	352.00
	Ties	0(i)		
	Total	28		
1993 - 1989	Negative Ranks	12(j)	15.08	181.00
	Positive Ranks	17(k)	14.94	254.00
	Ties	0(l)		
	Total	29		
2003 - 1989	Negative Ranks	22(m)	16.27	358.00
	Positive Ranks	7(n)	11.00	77.00
	Ties	0(o)		
	Total	29		
2003 - 1993	Negative Ranks	24(p)	16.71	401.00
	Positive Ranks	6(q)	10.67	64.00
	Ties	0(r)		
	Total	30		

a 1989 < 1973, b 1989 > 1973, c 1989 = 1973, d 1993 < 1973, e 1993 > 1973, f 1993 = 1973, g 2003 < 1973, h 2003 > 1973, i 2003 = 1973, j 1993 < 1989, k 1993 > 1989, l 1993 = 1989, m 2003 < 1989, n 2003 > 1989, o 2003 = 1989, p 2003 < 1993, q 2003 > 1993, r 2003 = 1993

Table K-2 Test Statistics for data from 1973-2003

	1989 - 1973	1993 - 1973	2003 - 1973	1993 - 1989	2003 - 1989	2003 - 1993
Z	-4.541(a)	-4.623(a)	-3.393(a)	-.789(a)	-3.038(b)	-3.466(b)
Asymp. Sig. (2-tailed)	.000	.000	.001	.430	.002	.001

a Based on negative ranks.
b Based on positive ranks.
c Wilcoxon Signed Ranks Test

APPENDIX L Mercury concentrations in stream sediment adjusted for a 66.8% loss caused by drying the sediment

Table L-1 Mercury concentrations in stream sediment adjusted for a 66.8% loss caused by drying the sediment (*u*g/kg, dry weight).

Stations	1973 Hg (*ug*/kg)	1989 Hg (ug/kg)	1993 Hg (*ug*/kg)	2003 Hg (*ug*/kg)
1	73	200*	220*	121
2	67	183*	220*	44
3	87	133	229*	109
4	18	75	85	34
6	18	133	95	172
7	32	133	142	131
8	23	58	85	99
9	33	75	192*	74
10	20	150	132	94
11	17	NA	172	97
13	45	67	75	18
14	50	58	83	55
15	15	67	25	95
16	22	83	25	132
17	23	42	100	143
19	30	158	102	169
20	37	175*	115	47
21	30	192*	158	55
24	88	584**	170	166
25	48	92	587*	41
26	25	108	107	104
27	37	117	113	81
29	122	150	257*	185*
30	168	267*	202*	86
31	100	150	249*	115
32	62	609**	152	77
33	57	692**	1451**	119
34	NA	334*	357*	30
35	NA	200*	229*	54
37	NA	292*	NA	170
Mean	50	192*	211*	97

* indicates concentrations higher than Environment Canada Interm Sediment Quality Guideline of 174 *u*g/kg
** indicates concentrations higher than Environment Canada Probable Effect Level of 486 *u*g/kg