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LISA LUCIA LOSETO

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Abstract

Mercury is increasing to toxic levels in Arctic biota living at the top of food webs. The rapid bioaccumulation and biomagnification of methylmercury (MeHg) in food chains, and the subsistence lifestyle of northern populations, has resulted in high levels of Hg in their blood. No prior measurements of MeHg sources to Arctic ecosystems have been made. In southern latitudes wetlands are considered important sources of MeHg with sulfate-reducing bacteria (SRB) thought to be responsible. Thus, the production of MeHg in Arctic wetlands was evaluated as well as SRB presence. Frozen soil collected from 18 High Arctic wetlands prior to ground thaw, had low MeHg levels, averaging 0.065 ng g^{-1}. When soils were incubated for 30 and 60 days at typical summer Arctic soil temperatures (4°C and 8°C) MeHg increased up to 100 fold. These laboratory observations were supported by field measurements of wetland surface water, where MeHg increased from concentrations near detection limits (0.02 ng L^{-1}) at the inflow to an average of 1.21 ng L^{-1} at the outflow. Both lab and field data showed MeHg production in High Arctic wetlands; however SRB prevalence in soil was low throughout.

Arctic wetlands were further evaluated as sources of MeHg in Arctic ecosystems, as well since snowmelt water provides 60 to 80% of water to Arctic terrestrial systems it was also evaluated as a source of MeHg. Yields of MeHg in snowmelt water leaving basins were higher (ca. 1.5 ng m^{-2} day^{-1}) than those measured in temperate catchments characterized by wetlands, and highest MeHg concentrations in lakes and wetlands corresponded with inputs from snowmelt water in the late spring. Results evaluating wetlands as sources varied from wetlands providing relatively high levels of MeHg at the wetland outflow, to wetlands acting as MeHg sinks. In the wetland studies DOC levels often predicted MeHg concentrations in wetlands (r^2 =0.55; $p < 0.01$) and moreover their importance as sources of MeHg to downstream lakes. Catchments with wetlands did not have an observable effect on MeHg levels in lake water. This was the first study to evaluate sources of MeHg entering Arctic ecosystems, and showed that although wetlands produced MeHg, the export to downstream lakes was dependant on site characteristics such as DOC levels, furthermore snowmelt water was the most significant source of MeHg to Arctic ecosystems measured here.

Résumé

Le mercure intesifie aux niveaux toxiques aux biotes de l'Extrême Arctique qui reside à l'haut des chaînes alimentaires. Le bioaccumulation et bioamplification rapide de méthylmercure (MeHg) aux chaînes alimentaires, et la manière de vivre de subsistance de communautés des nord ont eu pour résultat des niveaux supérieurs de Hg dans le sang des peuples. Aucunes mesures précédentes des sources de MeHg aux écosystèmes Arctiques ont été faites. Des zones humides méridional sont considéré comme des sources importantes de MeHg, et des bactérie sulfatoréductrice (BSR) sont considéré à être responsable. Ainsi, la production de MeHg dans les zones humides arctique a été évaluée de même que la présence de BSR. Le sol gelé, recueilli de 18 zones humides de l'Extrême Arctique avant que la terre dégèle, avait les niveaux bas de MeHg, en moyenne 0.065 ng g^{-1}. Quand le sol a été incubé pendant 30 et 60 jours aux temperatures typique de l'été Arctique (4°C et 8°C), MeHg a augmenté 100 fois. Ces observations au laboratoire ont été soutenues par les mesures d'eau de surface des zones humides, dans lesquelles MeHg a augmenté des concentrations près des limites de détection (0.02 ng L^{-1}) à l'afflux à une moyenne de 1.21 ng L^{-1} au écoulement. Les données de laboratoire et de champs ont montrées la production de MeHg aux zones humides de l' Arctique; cependant, la prédominance des BSR dans le sol était basse partout. Les zones humides de l'Arctique était aussi évalué comme les sources de MeHg dans les écosystèmes Arctiques. De plus, puisque l'eau de fonte de neiges fournit 60 à 80 pour cent de l'eau aux systèmes terrestres Arctiques, il a été aussi évalué comme une source de MeHg. Les rendements de MeHg dans l'eau de fonte de neige sortant des bassins étaient plus hauts (ca. 1.5 ng de 2 jours par m^{-2}) qu'eux mesurés dans les captages modérés caractérisés par zones humides. Les plus hautes concentrations de MeHg dans les lacs et zones humides ont correspondu avec les données de l'eau de fonte de neige dans le fin printemps. Les résultats évaluant des zones humides comme les sources ont varié des zones humides fournissant les niveaux relativement supérieurs de MeHg au écoulement des zones humides servant comme des plombs de MeHg. Aux études des zones humides, les niveaux de le carbone organique dissous souvent prédites les concentrations de MeHg dans les zones humides ($r^2 =0.55$; $p <0.01$) et, de plus, montrent leur importance comme sources de MeHg aux lacs an aval. Les captages avec des zones humides n'ont pas eu un effet visible sur les niveaux de MeHg dans l'eau de lac. Ceci était la première étude qui évalue des sources de MeHg entrant les écosystèmes Arctiques, et montre que, bien que des zones humides ont produit de MeHg, l'exportation aux lacs en aval étaient dépendant des caractéristiques de la site telles que des niveaux de le carbone organique dissous. De plus, l'eau de fonte de niege était la source de MeHg la plus significative aux écosystèmes Arctiques mesurés ici.

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TABLE OF CONTENTS

Chapter 1: Literary Review: Mercury in Arctic Environments

1.3 Mercury and Methylmercury in the Arctic

1.5 Identifying Sources of Mercury and MeHg to the Arctic

Chapter 2: Methylmercury Formation in High Arctic Wetlands

2.2 Materials and Methods

2.3 Results

Chapter 3: Sources of Methylmercury in the High Arctic

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVEATIONS

Hg	mercury
THg	total mercury
MeHg	methylmercury
POP	persistent organic pollutants
DMS	dimethyl sulfide
MDE	mercury depletion event
DOC	dissolved organic carbon
DIC	dissolved inorganic carbon
TOC	total organic carbon
SRB	sulfate-reducing bacteria
PCR	polymerase chain reaction
MPN	most probable number
CFU	colony forming units
DSR	dissimilatory sulfate reductase
ANOVA	analysis of variances
EPA	environmental protection agency
HDPE	high density polypethylene
HCl	hydrochloric acid
UTM	universal transverse mercator

1.0 LITERARY REVIEW: MERCURY IN ARCTIC ENVIRONMENTS

1.1 Introduction

Methylmercury (MeHg) is a toxic form of mercury that bioaccumulates in organisms and biomagnifies up food chains to high levels in the biota [1]. Mercury poisoning can be caused by ingesting food containing high levels of Hg, such as fish or other animals at near the top of food chains [2]. Concerns of MeHg contamination has been identified as a health and environmental problem in the remote Canadian Arctic [3].

Canada's Arctic region lies north of the 60° latitude, encompassing an area of 3.38×10^6 km^2 representing almost half of Canada's land area. The Canadian Arctic ranges over the Beaufort Sea in the west to Baffin Bay and Davis Strait in the east, and from the northern tip of Ellesmere Island to Hudson Bay in the South (Figure. 1.1). Although the Arctic is great in size, it has some of the lowest population densities in the world with a total population of 105, 000 [4]. The low population and lack of intense development would suggest that the Arctic is a relatively pristine environment; yet, in recent years, studies have shown that contaminants originating from other parts of the world are accumulating in the Arctic [5,6]. High levels of contaminants have been reported in Arctic fish, large marine mammals as well as in the Aboriginal groups that live in the north [7,8].

Among the trace metal contaminants mercury (Hg) is present at high concentrations in the Arctic[9] and thus is a high priority in the federal department of Indian and Northern Affairs [10,11]. Sources of MeHg to the Arctic are not known or understood, whereas the pathways of many persistant organic pollutants (POP's) to

Arctic ecosystems are better documented. Elevated levels of POP's in Arctic ecosystems, with the few to no local sources [5] is caused by the volatization of certain POP's at warm temperatures in temperate environments that travel, cool and condense, at high latitudes [12], and high altitudes [13]. This process has been referred to as the distillation effect or cold condensation [14].

Similar to POP's, MeHg also biomagnifies at each trophic level in food chains reaching toxic concentrations. The low diversity of organisms and dominance of large, long-lived species in the Arctic environment assists persistent toxins to bio-concentrate in organisms [5]. The high levels of MeHg in Arctic wildlife places Aboriginals at risk because they lead subsistence lifestyles which has resulted in higher Hg levels in Northern Aboriginals than in people living in the southern regions of Canada, where industry and chemical use is more wide spread [7].

Little is known about the sources of MeHg that bioaccumulate in the Arctic to reach the toxic levels observed, yet this information is imperative to the northern community lifestyles and the Arctic environment. The objective of this chapter is to review what is known about MeHg and Hg in the Arctic environment in efforts to outline gaps where further research is required. This chapter will lead into the hypothesis of the next two chapters.

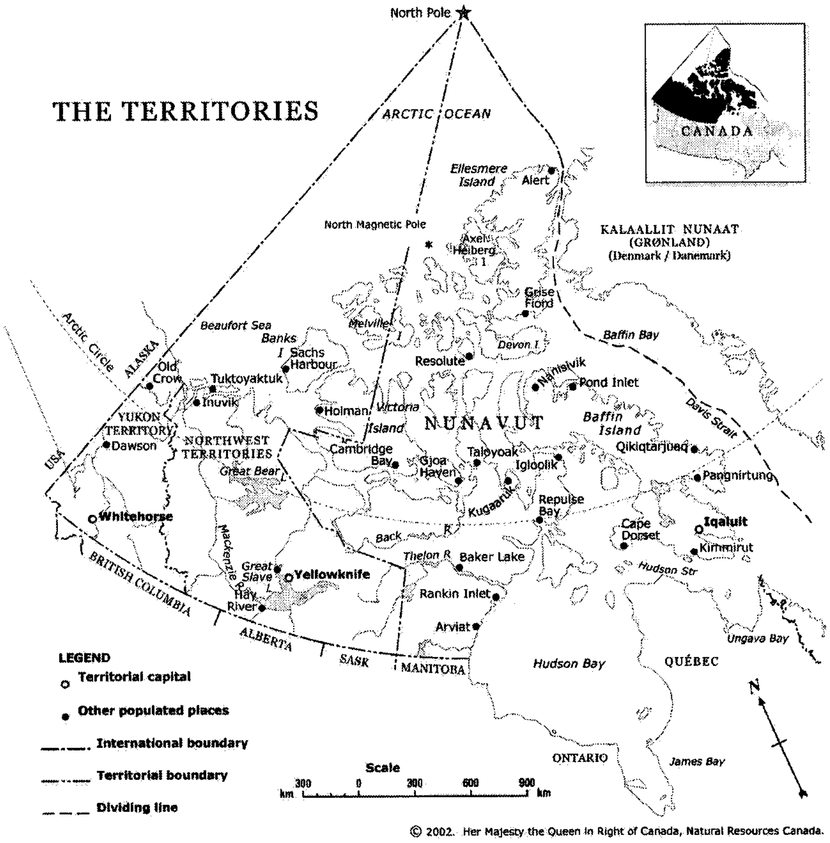

Figure 1.1 Map of the Canadian Arctic.

1.2 Mercury in the Environment

Mercury is a metal that is naturally present in the earth, however; it is estimated that two-thirds of the Hg currently in the atmosphere was derived from anthropogenic activity [15,16]. Natural sources of Hg to the environment include outgassing from the earths mantle (i.e. volcanic eruptions), evasion from water and land, and wind entrainment of dust particles [15]. Hg can also be re-emitted by degassing of Hg that was previously deposited [17]. Anthropogenic sources of Hg include release during metal smelting and refining [18], chlor-alkali plants, pulp industries, waste incineration and treatment, and the combustion of fossil fuels and coal, which have contributed to the global increase in mercury after industrialization [19].

Hg is a unique metal, it can be in a gas or liquid phase at room temperature [20], it has a constant volume of expansion over all temperature ranges and amalgamates with noble metals to form alloys [17], demonstrating unique physico-chemical properties. Elemental Hg has three oxidations levels, it can exist as Hg^{o} (g) which comprises 95% of the Hg in the atmosphere [21], or as Hg^{o} (aq), a form that volitizes from lakes. The Hg oxidation state at +1 is rarely observed in the environment [17], rather Hg^{o} (g) will oxidize to Hg^{2+} also known as the mercuric form. Hg^{o} can remain in the atmosphere for 6 to 24 months [22], enabling it to travel long distances, making Hg a global pollutant. Hg^{o} in the atmosphere oxidizes to Hg^{2+} usually in the solid-liquid phase interface in cloud droplets, O_3 and Cl_2 are thought to be the main oxidants [21]. This form of Hg re-enters the biosphere usually in wet precipitation[20]. SO_2 and CO are thought to the predominant reductants of Hg^{2+} [21].

Hg can exist as various organic metal species. Monomethylmercury is a form that bioaccumulates in organisms, dimethylmercury is an unreactive species, and lesser amounts of ethylmercury can be found in the environment. Monomethylmercury is often the species referred to more generally as methylmercury (MeHg). Unlike inorganic Hg, it is difficult to eliminate MeHg from biological systems, resulting in its bioaccumulation in organisms [20]. This is a serious toxicological concern because MeHg is a neurotoxin, that concentrates in kidneys, liver, the central nervous system and particularly targets the brain, as it can cross the blood brain barrier [2]. It can cause such symptoms as involuntary muscle movements, impaired hearing, speech, vision and gait, at high levels it can cause detrimental neurological damage and in extreme cases, death (e.g. Minimata), making it a health hazard.

The low MeHg levels in the air and water are deceiving because once MeHg enters microscopic organisms concentrations can biomagnify up to a million times up food webs reaching dangerously toxic levels [1]. MeHg is thought to enter the biota at the phytoplankton level via the diffusion of the uncharged CH_3HgCl species [23]. Although this species has a similar lipid solubility as $HgCl_2$ (K_{ow}=1.7) it is efficiently biotransferred to the next level at about four times the magnitude of $HgCl_2$ [23], whereas elemental Hg does not effectively transfer up the food chain. MeHg associates with the soluble fraction of the diatom (or general unicellular organism) that is partly retained in the fatty tissues; however in fish MeHg concentrates in the muscle rather than fatty tissue, therefore biomagnification is not explained by lipid solubility alone [24]. In fish MeHg has a high specificity to the intestine wall, whereas inorganic Hg was found at the microvilli interface, which resulted in a low uptake. MeHg increases in proportion to

THHg up the food chain from 10% in the water to 30% in zooplanton to 95% in fish [1,25]. Since the majority of Hg present in higher trophic organisms is in the form of MeHg, often only THg is measured and is assumed to be MeHg. Biomagnification is well demonstrated in aquatic ecosystems where food chains are often longer and result in the top consumers having extremely high levels of MeHg. Therefore, understanding MeHg sources that enter the ecosystem to biomagnify to toxic levels is critical in the mitigation and minimization of contamination.

1.3 Mercury and Methylmercury in the Arctic

1.3.1 Human Health Perspectives

Just over half the population across the Arctic is comprised of Aboriginals groups (56, 000), which include the Yukon First Nations, Metis, and Inuit; however, in Nunavut Inuit represent 80% of the population [4]. The natural environment is an integral part of Aboriginal lifestyles as they depend on it for food and a way of life. Unlike many Western societies, traditional/country food plays an important role in Aboriginal culture, traditions, economics and their spiritual well being [26]. From the hunting to the eating of traditional food, many values can be observed such as teaching and sharing, as well food is essential to the way Aboriginals conceptualize their health (Egede, 1995 in [27]).

Country food is also the primary means of contaminant transfer to them from the environment. Diets differ immensely across the Arctic (Kuhnlien, 2002 in [27]), but all populations consume large amounts of country foods relative to non aboriginal Canadians. Many of traditional foods include large animals that are long lived and in many cases are at the top of trophic levels, such as fish and marine mammals [28]. The second most common food eaten by the Inuit is char and seal (Kuhnlein, 2002 in [27]) both are high in Hg [10]. To compensate for the high meat intake in Northern communities the guidelines for consumption of Hg in meat has been reduced to 0.2ppm from 0.5ppm [29].

Among the Arctic Aboriginal, the Inuit consume the most traditional food eaten per day. Females in the age group of 20-40 consumed 194g/day and males in the same group ate 245g/day (Kuhnlein and Receveur, 2001 in [3]). Consequently, Hg levels in Inuit are the highest among other northern aboriginal groups, often surpassing the health and safety guidelines [30,31]. Inuit women have high levels of Hg in maternal blood cord averaging 2.1ug L^{-1} in the west near Inuvik to 10.2 in the east in Nunavik, with maximum values of 29ug L^{-1} [30,32]. The US EPA maternal blood guideline is below 5.8ug L^{-1}. Hg blood levels in Inuit also exceeded the acceptable limit of 20ug L^{-1} (devised by Wheatley et al., 1979) [30]. High Hg trends in Inuit are resultant from the high intakes of Hg in their diets, which approach and often exceed the provisional tolerable daily intake (Kuhnlein and Receveur, 2001 in [3]).

Few studies have been completed on the evaluation Hg effects on neurological behaviour of the Inuit; however studies in the New Zealand Faroe Islands have shown associations with maternal Hg and children's performance on neurobehaviour tests [33,34]. Hg in country food is a health concern, specifically for Inuit, but the same traditional foods (i.e. fish and marine mammals) are also high in polysaturated fatty acids (PUFA) and contain excellent sources of vitamin C, A, D and E, omega fatty acids, and iron, zinc, selenium, copper, magnesium and manganese and thus are important to the health of Inuit [27]. A shift away from traditional food may be linked to obesity, diabetes and cardiovascular disease among young Aboriginal peoples [35]. Country foods provide the Aboriginal communities with important health benefits as well as social and traditional structure, they depend on this food for the survival of their people. Almost all wildlife subsistence foods were over the health and safety guidelines provided for Inuit, this conflicts with their traditional lifestyle by jeopardizing their health.

1.3.2 Wildlife

The Northern Contaminants Program has released two reports 1996 and in 2003 (Canadian Arctic Contaminants Assessment Report) that are compilations of research on contaminants in the Arctic biota. These reports have helped close the gap on many questions regarding levels and movement of contaminants within the biota. Large data sets were collected for many freshwater fish and marine mammals such as ringed seals and beluga [8,36,37]. Despite all the data collection there still remains many uncertainties surrounding the temporal and spatial trends of Hg in wildlife across the Arctic.

The cold Arctic climate enhances the persistence of contaminant because the low temperature forces slow growth in many animals, assisting in the accumulation of Hg in long lived organisms over time. High biomagnification factors are observed between fish and marine mammals in the Arctic due to the high caloric intake required by mammals needed to maintain body heat in cold temperatures [38,39], exemplifying how the Arctic biota is particularly vulnerable to contaminant bioaccumulation.

Freshwater fish are often above the subsistence and commercial guidelines for Hg across the Arctic [11], whereas levels in sea run or salt water fish were near or below the consumption guidelines. In particular the freshwater fish, Arctic Char show different trends than most fish when evaluating size and age dynamics with Hg concentrations. That is, in most cases Hg increases with fish size, due to bioaccumulation over time; however, Arctic char do not show this trend, because of their extremely slow growth rates [40]. Therefore small fish can have very high levels of Hg due to the slow growth rates and high Hg sequestion over time.

Of the marine mammals investigated the largest data set exists for ringed seals because they live all across the Arctic, and samples are easily obtained from hunters. Hg levels in seals are considerably variable, as levels differ spatially across the Arctic [41]. As well, the temporal Hg levels in seals is unclear, as some areas appear to have reduced Hg levels over time and other areas show increases [36]. Beluga whale have shown increases in Hg over time, but only in the Beaufort Sea [42]. The rises in Hg in the Beaufort Sea near Mackenzie basin is hypothezied to be related to temperature rises within the Mackenzie region (Stern et al., 2001 in [43]). Beluga whale and narwhal both exhibited MeHg levels above the guideline for MeHg in both the tissue and muktuk (whale blubber) [36].

Large terrestrial mammals such as caribou have low levels of MeHg often lower than the detection limit of 0.1 ppm [44]. The low levels of MeHg result from the short food chain. Caribou are herbivores thus, they lack of trophic levels below them to allow for MeHg to accumulate.

Wheatley and Wheatley (1988) provided one of the few historical wildlife reference data for polar bear hair from a Dorset (400AD) and Thule (1150AD) archaeological site near Pond Inlet NU. Historical levels ranged from 0.3 to 1.3 ppm, whereas present levels have been measured to range from 2.5 to 10.2 ppm [45]. Hg is deposited in hair and thus is often used, as a measure of Hg levels in an organism, however how long Hg remains in hair is unknown.

1.3.3 Temporal Increases of Hg in the Arctic

The overall rise of Hg in the Arctic has been debated, due to the lack of historical data. One tool that has been more recently used to paint a picture of the past environmental condition is paleolimnology (e.g. [46] [47]). Studies have tried to account for global increases in Hg by measuring sediment core profiles from lake and ocean sediments [9]. Dating the cores can give insight as to when and how much Hg was deposited, and what the baseline levels were prior to industrialization. Studies in Greenland lakes showed Hg was more concentrated near the surface of lake sediments suggesting that Hg has increased in the north since industrialization [48].

The method of historical reconstruction using paleoliminological methods can be erroneous as Hg is very dynamic; it can be votilized to a gaseous phase, and bind to particulate and be remobilized in the sediment. Gobiel et al., (1999) tried to take these factors into account by examining the interactions of Hg with iron (Fe) and organic matter. The study revealed that Hg is recycled with Fe during redox changes in Arctic Ocean sediment, concluding that sedimentation rates and mixing rates are critical factors governing Hg surface enrichments [49]. Some of the Hg movement was explained by Fe redox cycling, but the overall Hg redistribution within sediments is poorly understood, therefore sediment cores are not reliable tools for historical reconstruction of Hg deposition trends to the Arctic (or elsewhere).

1.4 Identifying Sources of Mercury and Methylmercury to the Arctic

1.4.1 Atmospheric Inputs to the Arctic Landscape

High MeHg concentrations in organisms suggest that there must be significant inputs of MeHg entering Arctic ecosystems or Hg must be bioavailable to be methylated to MeHg. MeHg entering the Arctic by atmospheric means has not been evaluated, and the formation of MeHg in the atmosphere is not entirely understood [50,51]. It is thought that Hg^{o} may react with methyliodide (CH_3I) or dimethyl sulfide (DMS) in the atmosphere to form MeHg. Studies by Hall et al., (1995) showed that CH_3I may methylate Hg, but the levels produced were 3 orders of magnitude lower (ca. 2×10^{-5} ng L^{-1}) than concentrations observed in precipitation, thus this process could not account for a significant source of MeHg formation, and DMS was not able to methylate Hg. The study took place in a laboratory; therefore true reactions may be different in the atmosphere.

In Southern Sweden MeHg in precipitation was an important source to terrestrial and aquatic ecosystems (Hultberg et al., 1994 in [50]). Hultberg et al., (1994) found MeHg in rain to vary between 1.9 to 4.0 mg ha^{-1} yr^{-1}. The rain was collected near a heavily industrialized area, whereas regions in Northern Sweden far from pollutant point sources showed much lower MeHg inputs from the atmosphere of 0.7mg hg^{-1} yr^{-1} (Munthe and Iverfeldt 1994 in [50]). Similar low levels were measured in Northern Ontario in the ELA region, where MeHg inputs in rain were only 0.39mg $ha^{-1}yr^{-1}$ [52]. From these findings it was concluded that MeHg in precipitation is only an important source when industries are nearby [51], suggesting the atmosphere is not a significant means of MeHg transport to the Arctic. Additionally, MeHg in the atmosphere is thought to be short lived because of the presence of hydroxyl radicals that oxidize MeHg [53]. The life time of monomethylmercury in the presence of OH in the atmosphere was estimated at 0.5h [54]. As well in non polluted areas MeHg was found to only represent 0.8 to 0.9% of the THg in precipitation [51].

Since there are no direct sources of MeHg to the Arctic biota from nearby industrial pollution, the following options need to be investigated a) MeHg is entering ecosystems from unknown external sources, b) significant amounts Hg must be available for methylation, or c) Hg methylation processes are unlike those in temperate environments. Recently, a phenomena referred to as mercury depletion events (MDE's) was observed at the Alert meterological station located at the northern tip of Ellesmere Island, Nunavut [55] and in the sub arctic in Kuujjuarapik, Quebec [56]. MDE's take place at the onset of polar sunrise and result in the removal of Hg from the atmosphere. Gaseous elemental mercury (GEM) in the atmosphere was measured all year round, background levels averaged 1.5 ng m^{-3} that plummet to less than 0.1 ng m^{-3} at polar sunrise, which was followed by an increase in June to 1.7 to 1.9 ng m^{-3}. The background levels of 1.5ng m^{-3} are consistent with the background levels at other monitoring sites in Wisconsin and Ireland [57]. MDE's are unique to Arctic environments, which may be due to the long periods of darkness, and the abundance of halogens from the surrounding ocean [55].

During the MDE's Hg in snow increased from 3.5 fold [58] to 20 fold [59] across the Arctic [60] and subarctic [56]. Fifty percent of the Hg deposited onto the snow is lost within 12hrs of deposition. Hg leaving the snow may be related to environmental factors such as air temperatures and solar radiation. At temperatures below 0^{o}C photoreduction processes are thought to dominate where Hg^{2+} is photoreduced to Hg^{0} to volatize out from the snowpack [61]. At warmer temperatures Hg may leave the snowpack via snowmelt water. MDE's result in increased levels of Hg in Arctic snow, although much of the Hg will not remain in the snowpack, some will, and it is the fate of the remaining Hg that is important when evaluating sources of MeHg to Arctic ecosystems.

Lindberg et al., (2002) examined the fate of deposited Hg in snow during snowmelt. Results showed that prior to polar sunrise bioavailable Hg was undetectable and after MDE's bioavailable Hg increased. The bioavailable Hg concentrations decreased in June during snowmelt, but the overall fractionation of bioavailable Hg of the THg in snow increased during melt from 13% to 55%. Bioavailable Hg in snow may in part be responsible for the biomagnification of MeHg in Arctic ecosystems, but it is not a direct measure of MeHg leaving the snowpacks. The authors used a mer-lux bioreporter that utilizes genetically engineered bacteria (*V. anguillarum*) to emit light when Hg^{2+} is taken up [62], thus MeHg entering the ecosystem from snowmelt water was not measured. Studies are still required to determine if and how MeHg may be produced in the snowpack by biotic or abiotic means.

1.4.2 Terrestrial Sources Common in Temperate Environments

Wetlands have been shown to contribute the most significant amount of MeHg in non polluted environments to freshwater lakes [63-65]. Wetlands were identified as significant sources of MeHg to aquatic systems in a comparison study that investigated MeHg leaving catchments that contained varying amounts of up stream wetlands [63]. Basins with wetlands had 26 to 79 times higher concentrations of MeHg leaving a per unit area than drainage basins without wetlands (1.84 – 5.55mg ha^{-1} yr^{-1} versus 0.07mg ha^{-1} yr^{-1}) [63]. St. Louis et al., (1996) conducted further studies of wetlands in catchments, which revealed that the type of wetland (i.e. riverine, basin) could influence the amount of MeHg entering downstream lakes.

The notion of in lake production of MeHg has been supported for a long time, yet there is no known method to determine the direct amount of MeHg produced from within the lake. This is due the difficulty of measuring the simultaneously occurring processes of Hg methylation and demethylation of MeHg [50]. Studies have shown Hg methylation in lake sediments [66] and in the water column [67, 68], but the significance of these processes has yet to be determined. In a recent study by Sellers et al., (2001) in-lake production of MeHg was found to be the greatest source of MeHg even in the presence of upstream wetlands. This was determined by calculating inputs and outputs to the lake systems and then identifying the residual MeHg as the amount of MeHg produced within the lake. Despite the good attempt to quantify the in lake MeHg production, this study did not directly measure Hg methylation within the lakes.

Compounding the difficulty of identifying sources of MeHg to aquatic systems are the many other variables that influence the presence of MeHg. Such variables include pH of lakes [69] the DOC levels [25] and many other physical variables such as temperature, hydrology and watershed characteristics [70]. Of these variables DOC is the most indicative of MeHg and THg levels in water, that is, high MeHg and THg are often associated with high DOC [25]. On average THg and MeHg increases by 0.2 ng L^{-1} and 0.02ng L^{-1} respectively with every 1 mg increase in DOC in lakes [71]. Although not entirely understood, the high association with DOC to MeHg and THg has been observed in many ecosystems [65,71,72]. DOC is usually high in wetlands environments, which has implications to downstream processes, thus watershed characteristics are important when evaluating MeHg sources. Hence, levels of MeHg will vary in lake systems depending on the surrounding environment [50], but overall, wetlands are important sources of MeHg.

Wetlands represent approximately 18% of Canada's land surface, but characteristics differ greatly in response to climatic and physiographic environmental influences [73]. Wetlands occupy 1-2% of the Arctic Archipelago [74]. High Arctic wetlands differ from temperate and sub arctic wetlands, not only because they endure short and cool summers, but because they persist in desert environments, where only 20-30mm of precipitation is received as rain [75]. As a result High Arctic wetlands exist as basin fens and/or seepage fens [73,76], where an abundant supply of water can be found [76]. Basin fens are dominated by moss and sedge vegetation, usually a low-centre lowland polygon may be present that encloses shallow pools. Seepage fens occur on slopes where a constant source of water is available during the growing season, the source of moisture is often a late-lying snowbank [76]. These soils have relatively consistent vegetation cover due to the melt water supply that is often derived from late-lying snowbanks that provide water for most or all of the growing season, that accumulates over and within the shallow thawed ground, where it favours wetland development.

1.4.4 Biotic Production of Methylmercury by Microbial Activity

Microbial activity is thought to be responsible for Hg methylation [77]. The bacteria that has been identified as the dominant Hg methylators are sulfate reducing bacteria (SRB) [77]. Due to their anaerobic nature they are found in reduced environments devoid of oxygen, as it is a growth inhibitor. Temperate wetlands often have reducing environments because they are inundated with water, such conditions provide suitable environments for SRB to persist and methylate Hg. SRB undergo anaerobic respiration whereby sulfate is required as an electron acceptor to oxidize organic compounds. The organic compounds oxidized are often simple such as formate or acetate [78], which were previously reduced to these forms by other organisms. The oxidation of organic compounds by SRB results in the reduction of sulfate to sulfide. This reaction defines SRB as a unique group of bacteria [78].

$$4\ AH_2 + SO_4^{2-} + H^+ \rightarrow 4\ A + HS^- + 4\ H_2O \qquad (1)$$

where, AH_2 represents the variety of electron donors obtained from oxidation of organic compounds [79]. It is in this metabolic process that a methyl group is donated to Hg. The transfer of methyl to Hg is thought to be enzymatically driven and is described in detail in [80]. Details about the Hg species that enters SRB and further explanation on rates of methylation are described in [81,82].

Bacteria can live in a wide array of environments and can be grouped based on their habitat characteristics. Psychrophiles are cold loving bacteria that can persist in the cold regions of Antarctica [83]. SRB have adapted to the cold environments and are present beneath Arctic glaciers [84] and in Arctic Ocean sediments [85,86]. SRB that survive and persist in cold environments have low metabolic rates [87], which suggests if Hg methylation is occurring in the Arctic, rates may be low. If SRB in High Arctic wetlands have adapted to cold temperatures, they may also be producing MeHg in Arctic ecosystems.

1.4.5 Abiotic Methylmercury Production

The majority of research on Hg methylation has been carried out by microbiologists and therefore have investigated this process purely as a biological one. Biological Hg methylation has generally been accepted, yet direct evidence is still lacking [20,88]. There is a small group of studies that have evaluated possible abiotic Hg methylation, these processes can include the biological production or origin of a methyl donor.

Weber (1993) reviews abiotic methylation of Hg^{2+}, by three mechanisms; methylcobalamin, methyltin compounds and humic matter. Of the three, humic matter is suggested to be the most important abiotic Hg methylator. Humic matter represents the insoluble acidic fraction of DOC. Studies have shown humic matter to methylate Hg in aquatic systems [89] as well, fulvic matter was found to methylate Hg [90]. Humic matter represents 60% of DOC in river water and 70% in wetlands [88]. Given the low DOC in Arctic systems due to low productivity, humic material may not be important when evaluating sources of MeHg. Perhaps processes that are unique to the Arctic are responsible. More research is required in this field, as abiotic processes may be more prevalent in the Arctic environment since the short warming season may limit biological Hg methylation.

1.5 Closing Statements and Thesis Hypothesis

The Arctic environment is a sink for contaminants often originating from industrialized regions of the world. As a result Arctic wildlife and northern Aboriginal communities are carrying the burden of Hg contamination at or near toxic levels. This problem needs to be addressed at the root, which begins with understanding MeHg pathways, trends, transformations and sources to Arctic ecosystems. Understanding these processes is critical to mitigating the biomagnification of MeHg to dangerous levels. Whether the Arctic behaves in a similar manner as temperate systems, whereby wetlands, and SRB are important sources has yet to be examined. Perhaps Arctic ecosystems have unique processes or mechanisms contributing to the high MeHg in the biota. Regardless, understanding MeHg dynamics in Arctic ecosystems is necessary for the health and well being of Arctic environments and people. This thesis will attempt to identify input sources of MeHg to Arctic ecosystems, with the following hypothesis:

1. H: Wetlands in the High Arctic produce MeHg
2. H: Snowmelt water is a source of MeHg to High Arctic ecosystems
3. H: High Arctic wetlands are sources of MeHg to downstream lakes

The majority of research in temperate environments supports the importance of wetlands in catchments as a MeHg sources to lake systems therefore the second chapter tests the first hypothesis. This chapter is presented as a manuscript because it was prepared and accepted for publication. Results from chapter two reveal that wetlands can produce MeHg, thus chapter 3 evaluates the ecological significance of wetlands as sources to downstream lakes. As well since snowmelt provides the largest input source of water to High Arctic ecosystems it too is investigated as a source of MeHg to downstream ecosystems. Chapter three is comprised of four studies that set out to test the second and third hypothesis. The objectives and field methodology of the four studies are described in chapter three. This chapter is not presented in a manuscript fashion, rather is in a typical thesis format.

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Manuscript Claim

This paper was accepted for publication by the journal Environmental Toxicology and Chemistry on April 19 2003. The manuscript is titled: Methylmercury production in High Arctic wetlands. Lisa L. Loseto is the primary author, Steven D. Siciliano is the secondary author and David R.S. Lean is the last author. The sample collection and field work was carried out by Lisa Loseto. All water and soil chemistry laboratory work on MeHg and THg was done by Lisa Loseto. Steven Siciliano ran all DNA analysis on the soils, which included the rDNA extraction and analysis and the extraction for the dissimilatory sulfate-reducing gene. The culturing of sulfate reducing bacteria by the most probable number technique (MPN) was carried out under the guiding partnership with Josee Bourdeau. Lisa Loseto wrote the manuscript under the supervision of Dr. Steven Siciliano and Dr. David Lean.

The hypothesis is not explicitly stated in the text of this manuscript, but corresponds with the first hypothesis stated at the end of chapter 1.

Abstract

Mercury in the top predators living in High Arctic ecosystems is present at elevated levels. Since only methylmercury (MeHg) bioaccumulates in food chains, the sources need to be identified. In temperate environments, wetlands are considered to be principle sources of MeHg with sulfate-reducing bacteria (SRB) thought to be responsible. This study investigated whether High Arctic wetlands produced MeHg, and if SRB were involved in the MeHg formation. Frozen soil was collected from 18 High Arctic wetlands prior to ground thaw and when analyzed for MeHg values were low averaging 0.065 ng g^{-1}. When soils were incubated for 30 and 60 days at typical summer Arctic soil temperatures (4°C and 8°C) MeHg increased up to 100 fold. These laboratory observations were consistent with field measurements of wetland surface water, where MeHg concentrations increased from near detection limits (0.02 ng L^{-1}) at the inflow to an average of 1.21 ng L^{-1} at the outflow. Both lab and field data showed MeHg production in High Arctic wetlands; however SRB, prevalence in soil was low, and DNA analysis of the dissimilatory sulfate reducing gene (DSR) specific to SRB was positive at only one site. This study showed that wetlands in the High Arctic can produce MeHg, but SRB may not the dominant Hg methylators.

2.0 METHYLMERCURY PRODUCTION IN HIGH ARCTIC WETLANDS

2.1 INTRODUCTION

Contaminants from other parts of the world have been accumulating in the Arctic [1,2]. Mercury is increasing to levels, which may be toxic in some of the North American Arctic biota living near the top of the food web [3]. Mercury in the Arctic atmosphere as Hg^{o} is photochemically oxidized to Hg^{2+} by sunlight received at polar sunrise in the presence of BrO, released from the Arctic Ocean [4,5]. Once Hg is oxidized to Hg^{2+}it is deposited onto the Arctic landscape, demonstrating an important input pathway [6]. However, most of the Hg deposited by this process is though to be inorganic (Hg^{2+}), yet it is the toxic organic form, methylmercury (MeHg) that is of concern. The rapid bioaccumulation and biomagnification of MeHg in food chains [7], and the subsistence lifestyle of northern populations, has resulted in high levels of Hg in their blood [8,9]. Little is known about the sources and pathways of MeHg to High Arctic ecosystems. No prior measurements of MeHg sources have been made in the Arctic. However, Lindberg et al., (2002) found the Hg deposited during polar sunrise rapidly became available to microorganisms during snowmelt [6]. Transformations of deposited and ambient Hg to MeHg in the Arctic are critical to the assessment of Hg risk in northern ecosystems.

Mercury typically enters the food chain after the conversion from an inorganic form to MeHg [7]. In temperate environments, this conversion is thought to be carried out by sulfate-reducing bacteria (SRB) [10,11]. The reducing environment of wetland soil favours SRB growth [10,12], and wetlands are important sources of MeHg, as they contribute significant amounts of MeHg to downstream lakes [13,14].

The Canadian High Arctic is comprised of polar and semi-polar deserts, and is underlain by continuous permafrost [15]. The High Arctic receives only 20 to 30mm of precipitation as rain [16]; as a result, wetlands persist in low-lying areas where moisture is maintained in the shallow active layer of thawed permafrost [17]. SRB capable of Hg methylation are normally found in warmer, temperate environments; however, SRB do exist and have adapted to the very cold conditions of the Arctic Ocean sediments [18,19], as well as beneath Arctic glaciers [20]. The presence of SRB in Arctic wetlands has not been previously examined, nor has their ability to methylate Hg in cold environments.

The objective of this study is to determine if MeHg is produced in High Arctic wetlands by measuring MeHg in wetland soils prior to and after laboratory incubations, as well as measuring MeHg in surface waters flowing through a wetland during the growing season. The presence of SRB in soils is assessed.

2.2 MATERIALS AND METHODS

2.2.1 Study Area

Wetlands were sampled in the Canadian High Arctic, the majority of which were on Cornwallis Island, Nunavut (Figure 2.1). On Cornwallis Island, winters are long and cold, and summers are short and cool, with temperatures often rising above freezing in early to mid June [17]. The soils on Cornwallis Island have little soil horizon development due to the harsh climate conditions, extensive cryoturbation and high carbonate content. Soils are composed of mostly gravel and sandy loam derived from dolomite sandstones, limestones, calcareous sandstones and shale [21]. In the low relief areas, soils have relatively consistent vegetation cover due to the melt water supply that is often derived from late-lying snowbanks that provide water for most or all of the growing season [17].

2.2.2 Wetland soil field sampling

Wetlands were sampled in the spring and summer of 2001. One wetland was located on Bylot Island, another on Sommerset Island at Fort Ross (an old Hudson Bay trading post established in the early 1900's), and the remainder (*n* = 16), were near Resolute Bay (Qausuittuq) (74°45' N 94°56' W), on Cornwallis Island, Nunavut (Figure 2.1). Wetland site 4 on Cornwallis Island was located downslope from a sewage sludge dump used for the past 30 years. This site was selected as an example of direct anthropogenic impacts to contrast with the more remote sites. Soil samples from wetlands (*n*=18) were collected prior to snowmelt, between May 26 and June 08, 2001. Five soil samples were collected at each wetland in a pentagonal shape with a distance of 2 metres between apexes from each site using an ice corer. Soil analyzed for MeHg and total mercury (THg) was taken from the centre of the soil core. The vegetative layer, which was often comprised of peat moss was carefully removed, then the first 5-7 cm of dark organic soil was collected and kept frozen until analysis at the University of Ottawa.

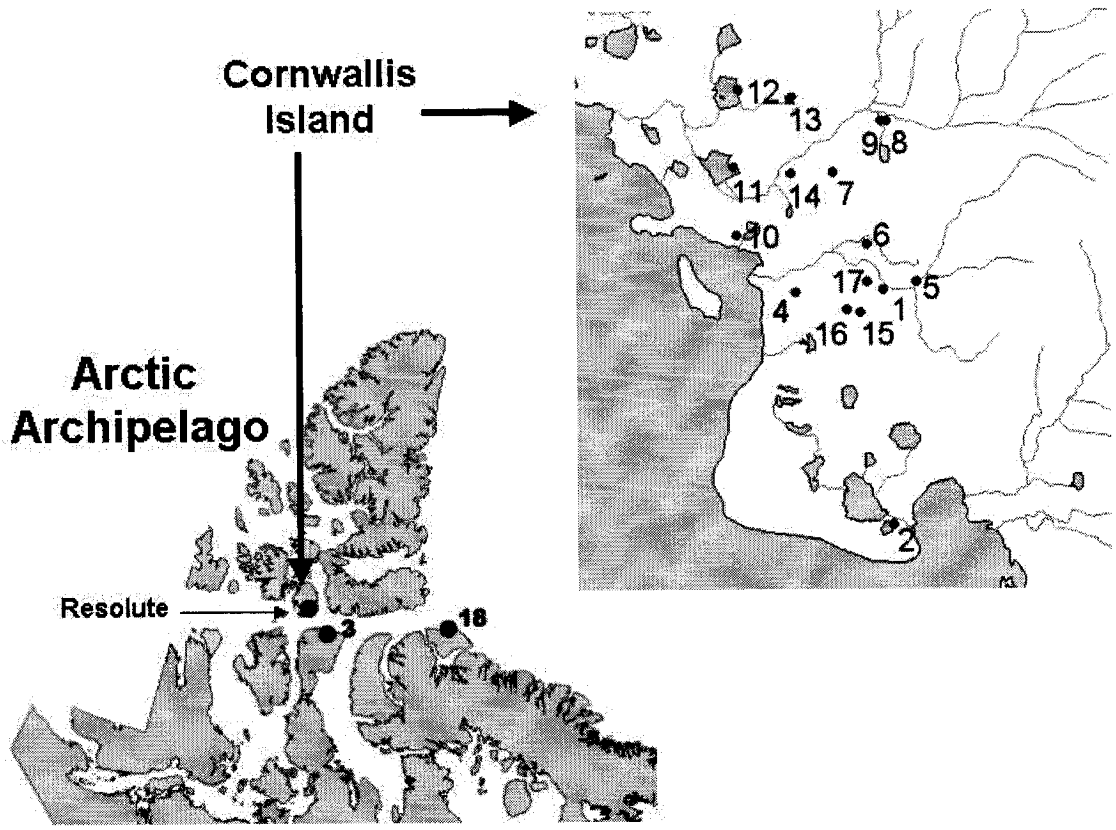

Figure 2.1 Geographical locations of wetlands sampled in this study. Sixteen wetlands were located on the south-western side of Cornwallis Island, near Resolute Bay. Site 3 was located on Sommerset Island and site 18 on Bylot Island, Nunavut.

2.2.3. Incubation of Soils

Two laboratory incubation treatments were performed on the wetland soils to determine if isolated soil samples could produce MeHg at typical Arctic soil summer temperatures. Incubation temperatures were selected based on thermocouple readings at 5cm depths in wetland soils near Resolute Bay [22]. Six sub samples from each site were transferred to petri dishes, and sealed with parafilm™ in order to avoid contamination and to maintain the moisture status of the soils.

The first treatment was a 30-day incubation at 4°C, after which three of the six sub samples for each site were removed for MeHg analysis. The remaining three samples from each wetland were incubated for another 30 days, but the incubation temperature was increased to 8°C. Incubations took place in the dark, as the soils would not normally be exposed to light because they were collected from under a thick peat mat. MeHg concentrations in the incubated soils were determined at the end of the first and second incubation treatments.

2.2.4 Chemical Analysis of Soil

MeHg was determined by capillary gas chromatograph-atomic fluorescence spectrometry following an acidic-potassium bromide/dichloromethane extraction [23]. Blanks and matrix spikes were used to assess daily analytical performance. Recoveries averaged 70% and reagent blanks contained no detectable MeHg. MeHg concentrations are expressed on a dry soil weight basis. THg was determined after freeze drying, and analysis using Environmental Protection Agency (EPA) method 7473. This method employs a Milestone AMA 254 analyzer, which detects mercury by pyrolysis followed by gold amalgamation atomic absorption spectrophotometery. Detection limits of 0.1 ng g^{-1} were achieved by this method using a 100 mg sample. Soil moisture content was determined by loss of moisture after heating at 100°C for 24 hours. Organic matter in soils was measured by weight loss on ignition after soils were heated to 500°C for 48hrs.

2.2.5 Wetland surface water sampling

To support the laboratory incubations a field study was carried out at wetland site 16 (located north of Resolute Bay), where surface water was sampled for MeHg analysis. This site was selected because it was easily accessed from the field location and has been subject to previous hydrological studies [24,25]. Surface water samples from the wetland were collected during the growing season (June 27, July 04, July 12) in duplicate at the inflow, middle and outflow. Water entered the inflow from resurfacing ground water from ground ice melt water and snowmelt water from surrounding snowbanks [25]. All samples were collected in 1L high density polyethylene (HDPE) bottles that were pre-cleaned (by rinsing three times with deionized water, then filling with 125mL of HCl and 2.5ml of 2% mixed brominating reagent, for storage, then prior to use 500ul of hydroxylamine hydrochloride is added to remove bromine, the bottle was then rinsed three times with deionized water). The bottles were rinsed three times with water from the sample site then filled. Five mL of concentrated HCl was added to preserve the MeHg in water until analysis at University of Ottawa. THg in water was collected in a 50ml polypropylene tubes following procedures developed at the Geological Survey of Canada [26] and were preserved with 1 ml of bromine chloride (27g of KBr in 2.5L of HCl followed by 38g of $KBrO_3$) (EPA Method 1631). Dissolved organic matter (DOC) in water was collected in 50ml of water that was stored in the dark at 4°C until analysis. All water samples were kept refrigerated in the dark until shipment to laboratories for analysis.

2.2.6 Chemical Analysis of Water

MeHg in water was determined by capillary gas chromatograph-atomic fluorescence spectrometry following a solid-phase extraction on sulfide columns and an acidic-potassium bromide elusion and dichloromethane extraction [23]. Recoveries averaged 60% and blanks contained no detectable organic mercury. THg in water was analyzed by using stannous chloride reduction followed by cold vapour-atomic fluorescence spectroscopy as outlined in EPA Method 1631. The method detection limit (3σ of all blanks) for THg was 0.68 ng L^{-1} and a percent recovery of 98% ± 4%. Dissolved organic carbon (DOC) in surface wetland water was determined using an IO Analytical Model 1010 TOC analyzer using a sodium persulfate oxidizing agent.

2.2.7. Microbial Community Analysis

SRB were enumerated using the traditional most probable number (MPN) technique [27] and compared with values obtained using DNA gene sequencing. Soil dilutions were prepared in anaerobic dilution water and placed into tubes containing modified iron sulfate agar with lactate as a carbon source, reduced with thioglycolic acid (7.5 mL L^{-1}) and ascorbic acid (7.5 g L^{-1}) [27]. Dilutions were made to 10^{-8} (5 reps per dilution and 3 reps/site) and incubated for two weeks in the dark. Presence of SRB was determined positive in tubes showing blackened colonies (precipitate of ferrous sulfide).

The prevalence of SRB was determined using the MPN tables and expressed as colony forming units per gram of dry weight (CFU gdw^{-1}) [27].

Recently SRB communities have been identified using DNA gene sequences. DNA was extracted from the soil using polymerase chain reaction (PCR) techniques to amplify the genes as previously described [28]. 16S ribosomal DNA (rDNA) for SRB belonging to the *delta-Proteobacteria* was amplified by PCR using general eubacterial and specific delta-proteobacter/SRB primers. Since SRB are wide spread among the delta protobacteria, the dissimilatory sulphite reductase gene (DSR) was specifically amplified using previously published primers and conditions [29]. The DSR gene distinguishes the DNA as belonging to SRB because it is the enzyme responsible for catalysing the last step in reduction of sulfate to sulfide.

2.2.5 Statistical Analysis

Analysis of variances (ANOVA) was used to assess site differences in MeHg and THg concentrations using Systat 10 software. Data was tested for normality using the Anderson-Darling test and homogeneity of variance assessed with Levene's test for normal distribution. MeHg in wetland surface water was normalized prior to running the ANOVA by log transformation. Pearsons correlation analysis was used to evaluate the strength of positive and negative relationships among variables.

2.3 RESULTS

2.3.1 Soil site characteristics

Soil from the sixteen wetland sites on Cornwallis Island had an overall mean pH of 7.6, which is characteristic of the calcareous bedrock (Table 2.1). Soil pH from Sommerset (6.6) and Bylot Island (5.5) were slightly acidic. Soils generally had high moisture content, averaging 62% (Table 2.1). The organic matter ranged from high levels of 75% at site 2, to low levels of 5% at site 5, the mean was 30% (Table 2.1). Soil moisture positively correlated with organic matter ($r = 0.87$; $p < 0.05$).

MeHg concentrations in wetland soils were low, averaging 0.065 ng g^{-1} ($\sigma =$ 0.074; $n = 75$) and concentrations differed among the sites ($p < 0.05$) (Figure 2.2). Site 4, located downslope from a dump, had the highest MeHg concentration of 0.32 ng g^{-1}, and correspondingly had the highest THg levels (250 ng g^{-1}). THg in the wetland soils was low, averaging 46 ng g^{-1} ($\sigma = 75$; $n = 75$) and ranged between 10 and 250 ng g^{-1} (Figure 2.2). A positive but weak relationship was measured between MeHg and THg concentrations in the soils ($r = 0.46$; $p < 0.05$). Little of the THg was present in the form of MeHg, typically near 0.1% (Table 2.1).

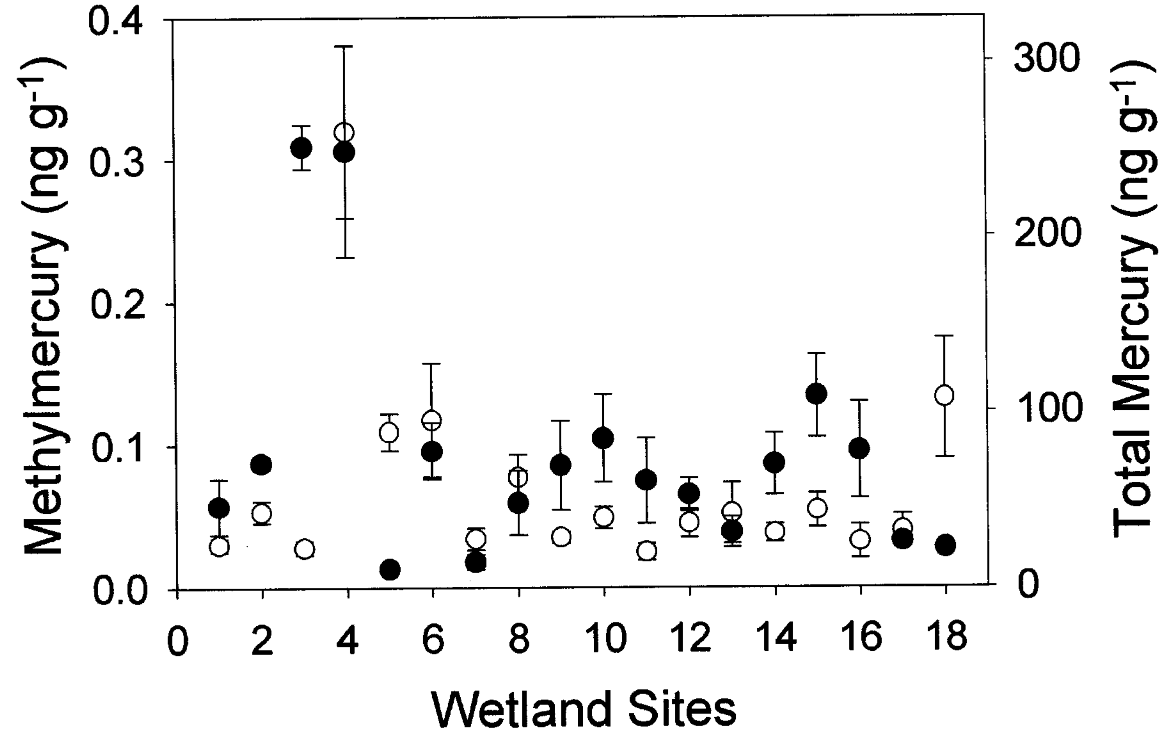

Figure 2.2 Methylmercury (open) and total mercury (closed) in soil from18 different wetlands in the Canadian High Arctic. Error bars are standard error of the mean.

Table 2.1 Soil Site Characteristics

	UTM[1]							
Sites	Easting	Northing	Moisture (%)	OM[2] content (%)	% MeHg of THg[3]	SRB[4] (cfu gdw^{-1})[5]	pH	Site Character.
1	443469	8295937	59.3	20.7	0.07	0.0	7.93	
2	443750	8288890	77.0	74.4	0.07	43.0	6.78	Sommerset Is.
3	456000	7990000	87.9	57.8	0.01	108.0	6.66	Resolute Bay
4	440870	8295850	92.9	71.3	0.13		6.58	Near a dump
5	444478	8296190	26.5	3.0	1.04	1063.0	8.64	
6	443000	8297300	80.7	60.5	0.15	67.8	7.76	
7	442000	8299500	46.3	12.5	0.23	91.1	7.88	
8	443597	8301006	46.5	13.9	0.16	44700.0	8.04	
9	443425	8301015	42.0	17.3	0.05	766.5	7.92	
10	439109	8297610	73.8	39.0	0.06	0.0	7.36	
11	439021	8299673	65.4	16.9	0.04	97.4	7.85	
12	439156	8301961	65.4	23.8	0.09	22.2	7.81	
13	440744	8301698	61.9	23.4	0.17	67.6	7.60	
14	440744	8299471	73.6	48.1	0.05	51.4	7.62	
15	442800	8295250	55.8	10.9	0.05	631.0	7.89	
16	442400	8295350	80.2	50.7	0.04	107.6	7.42	
17	442982	8296190	43.5	10.4	0.15	287.2	6.70	
18	950000	8250000	36.1	7.6	0.59	144.2	5.50	Bylot Is.

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[1] universal transverse mercator

[2] organic matter

[3] total mercury

[4] sulfate-reducing bacteria

[5] colony forming units per gram dry weight

2.3.2 Soil Incubations

Up to a 100 fold increase in MeHg occurred when soils were incubated for 30 days at 4°C (Figure 2.3). Following the initial incubation, temperatures were increased to 8°C for another 30 days, whereby the mean MeHg concentrations dropped at most sites (Figure 2.3). MeHg at the sites differed from one another after both incubations ($p < 0.05$). Sites 4, 6, 16 and 18 had the highest MeHg concentrations after the first 30-day incubation (Figure 2.3). Site 4, the site close to a dump had the highest concentrations at 13.9 ng g^{-1}, and site 9 had the lowest concentrations of 2.84 ng g^{-1} after the first incubation.

After the second incubation MeHg decreased at some sites; others remained similar and a few soils continued to form MeHg (Figure 2.3). Sites 4, 8 and 18 were the only sites in which MeHg levels increased after the second incubation. Site 18 increased slightly, whereas site 8 increased by 25% containing 10.7 ng g^{-1} and site 4 increased by 15 % and contained the highest MeHg levels (16.4 ng g^{-1}). Sites 4 and 18 initially had relatively high MeHg in the frozen soil, but site 4 had very high THg relative to all sites. Site 18 located on Bylot Island, had the lowest soil moisture and organic matter present (Table 2.1). Site 8 also had low moisture and organic matter, but had the highest culturable SRB measured by MPN analysis (see below). The site characteristics listed above may have influenced the continued Hg methylation in soils. Sites that did not have significant changes in MeHg formation, and sites that decreased after the second incubation did not share a common characteristic that could explain the lack of MeHg formation.

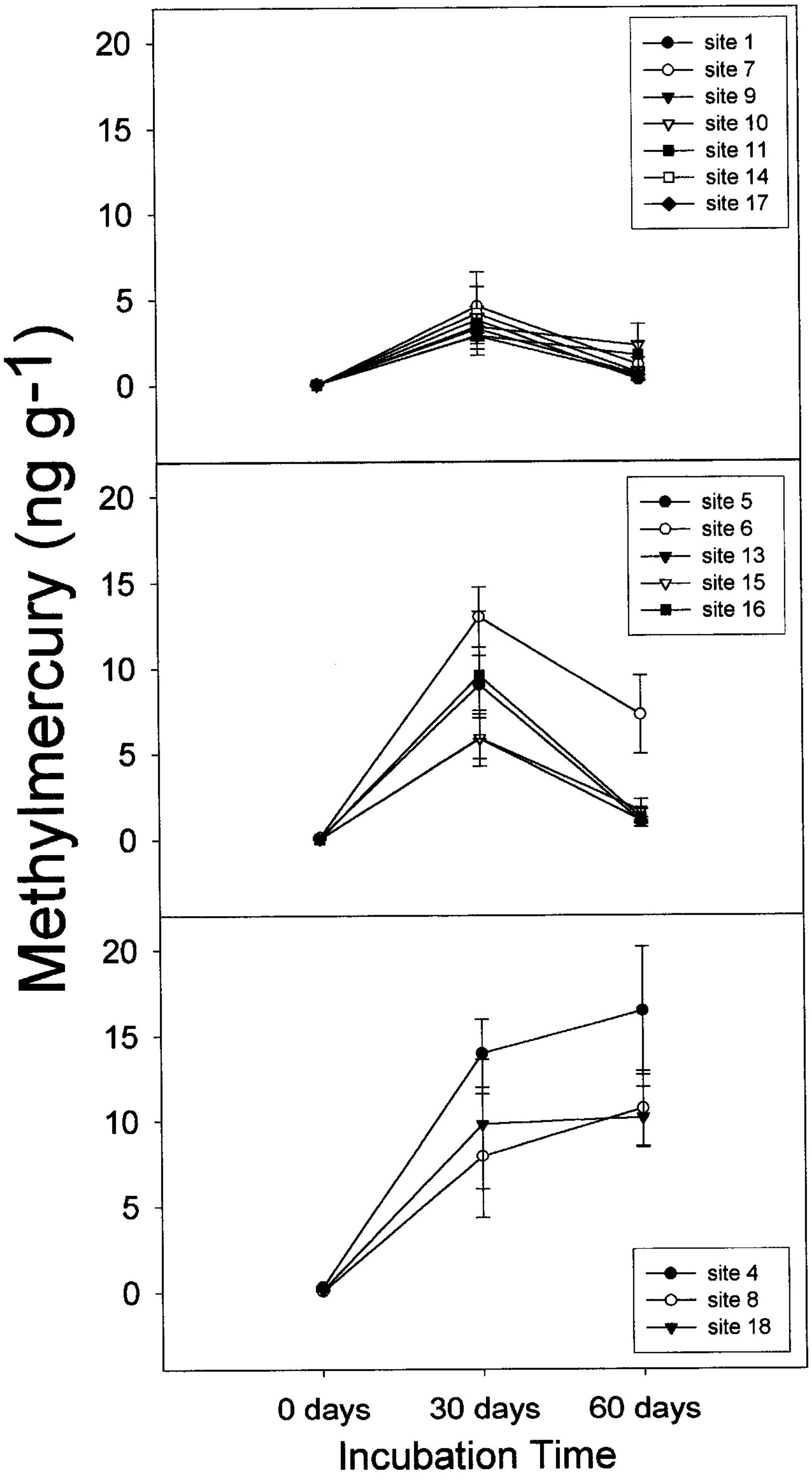

Figure 2.3 Methylmercury concentrations in frozen soil, and after the two incubations, in sites that did not have large changes after the second incubation, sites that had a large decrease after the second incubation and sites that continued to form MeHg. Error bars are the standard error of the mean.

2.3.3 Wetland surface water

MeHg concentrations at wetland site 16 did not differ during the warming season ($p = 0.2$), but concentrations at the sites along the wetland did differ spatially ($p < 0.05$), whereby concentrations increased toward the outflow (Figure 2.4a). MeHg levels at the inflow region were near and at the detection limit (0.02ng L^{-1}) on all three sampling days. At the middle of the wetland MeHg concentrations increased on June 27 and July 04. The wetland outflow had the highest MeHg concentrations on all three sampling occasions averaging to 1.21 ng L^{-1} (Figure 2.4a).

DOC levels slightly decreased along the wetland from late June to mid July, but changes were not significant ($p = 0.09$) (Figure 2.4b). DOC differed spatially ($p = 0.036$), as the middle of the wetland had the lowest mean DOC levels of 2.1 mg L^{-1}, and DOC was the highest at the outflow (above 3 mg L^{-1}). Overall, DOC levels across the wetland are low, but characteristic of Arctic ecosystems. DOC and MeHg were positively related, but were not significant ($r = 0.43$; $p = 0.08$). Highest DOC and MeHg levels always occurred at the outflow (Figure 2.4 a, b). THg ranged from 0.8 ng L^{-1} (in the middle of the wetland) to 2.76 ng L^{-1} (at the inflow area), having an overall mean of 1.5 ng L^{-1} ($\sigma = 0.8$, $n = 4$).

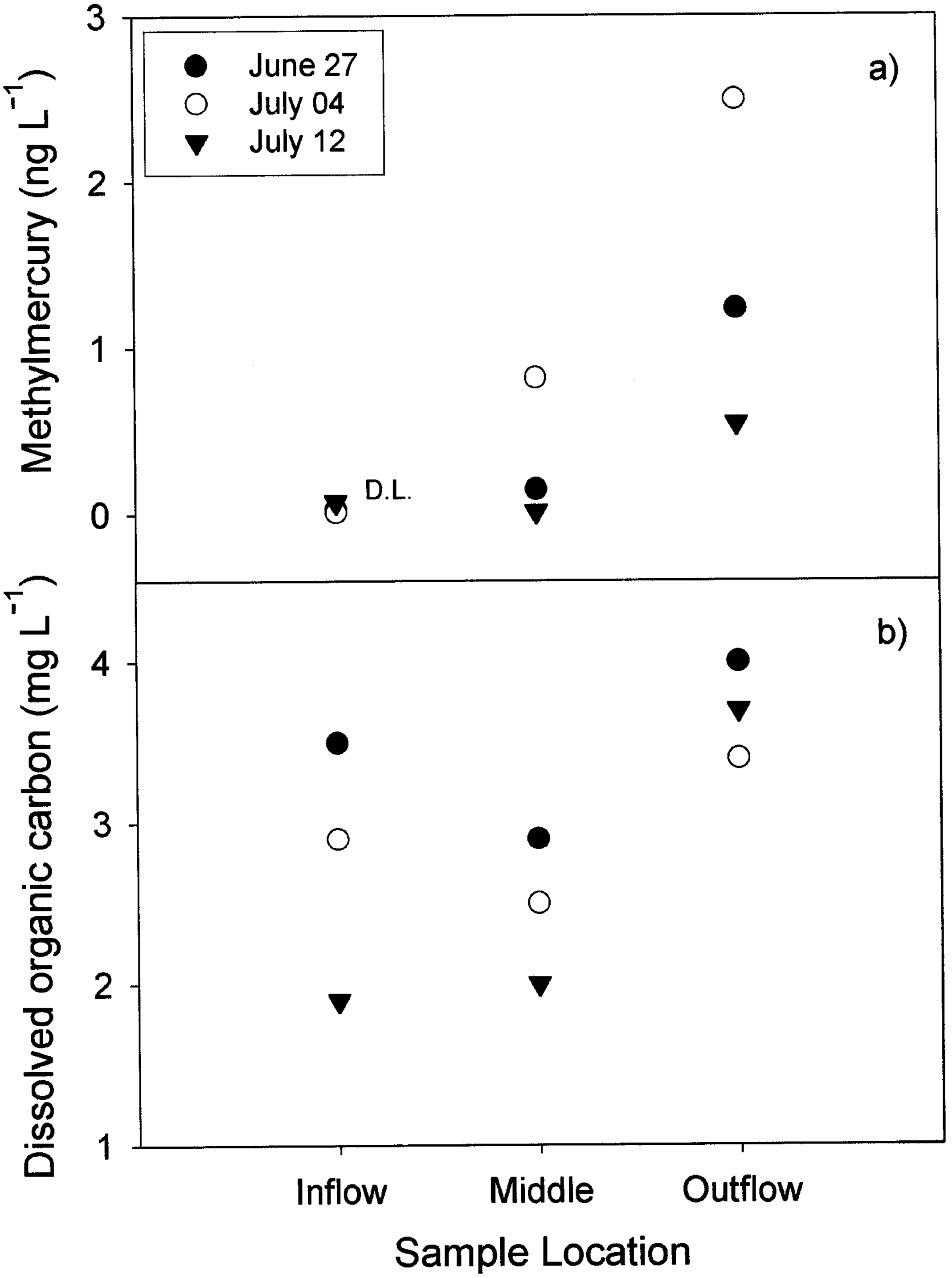

Figure 2.4 a) Methylmercury concentrations b) dissolved inorganic carbon levels, in the surface water of an Arctic wetland in the inflow, middle and outflow, collected during the warm season.

2.3.4 Microbiological Community

Culturable SRB determined from the MPN analysis were low relative to temperate regions, averaging between 10^2 and 10^3 colony forming units g^{-1} dry soil (CFU gdw^{-1}) (Table 1). SRB abundance showed no association with MeHg concentrations in the wetland soils. Wetland site 8 had exceptionally high SRB relative to the other soils, and had relatively high MeHg concentrations prior to and after the first incubation (Figure 2.3). The presence of SRB was not related with any of the physical or chemical variables (Table 2.1).

To further identify the presence of SRB, DNA was extracted and amplified using PCR. DNA yields from the soils were low, averaging 118 ng g^{-1} (n=36). Amplification of the delta-proteobacteria community occurred only after enriching the DNA with the eubacterial primers (63f and 1378r), and then selectively amplifying SRB with a primer pair (385f-907r). The delta-proteobacteria primers used are not specific for SRB, thus the presence of the DSR genes was assessed. The DSR gene only amplified at site 6 with primers (DSR1F and DSR4R), site 6 did not have high SRB counts compared to the other sites when analyzed with MPN.

2.5 DISCUSSION

MeHg in Wetland Soil

Significant amounts of MeHg were produced in High Arctic wetland soils with small increases in temperature, similar to that experienced during the short Arctic summer. Initially, the frozen soil had low levels of MeHg, but after a 30-day incubation period at only 4°C MeHg levels increased up to a 100 fold. Most soils experienced a decrease after the subsequent incubation for another 30-day period at 8°C.

Incubations took place in closed systems, thus resources such as sulfate, Hg, organic substrate and oxygen may have been limiting. Since these resources are commonly thought to be essential in MeHg production, our observations may be a conservative estimate. The continued production of MeHg at sites 4, 8 and 18 after the second incubation suggest resources were not depleted. High THg levels at site 4 may have enabled MeHg production to continue because more Hg substrate was available, yet THg concentrations at site 8 and 18 were much lower, and Hg methylation continued (to a lesser extent relative to site 4). In contrast, the high THg at site 3 did not stimulate further MeHg formation after the final incubation. This suggests that the importance of Hg presence in soil depends on interactions with other soil variables that may determine Hg bioavailability for methylation. Although MeHg degradation was not measured here, it needs to be considered, as concentrations are the difference of MeHg production and degradation. Perhaps the continued production of MeHg at sites 4, 8 and 18 was due to by low degradation rates, rather than high MeHg production.

The production of MeHg after the first incubation showed that MeHg formation is associated with rising temperatures. MeHg pulses in late spring and early summer have been observed in many systems [30-32]. In estuarine sediments, a seasonal cycle of MeHg production was observed, whereby MeHg levels peak in the spring, that then decrease in the late season likely due to degradation processes, after which levels resume again the following spring [31]. The low MeHg measured in the frozen soils may represent depleted levels commonly observed in late summer, that will rise again as the warming season begins. Warming temperatures after a winter season often initiate biological and biogeochemical activity, and the production of MeHg in High Arctic environments may be no exception. Incubation results show that temperature is an important factor governing MeHg production in wetlands, that needs to be considered when evaluating MeHg dynamics in a changing climate.

Although the frozen wetland soils had low MeHg concentrations, the percent of MeHg was (0.02 to 1% of THg). This is similar to soils of wetlands in Kejimukujik, Nova Scotia (0.2% of the THg) [33]. Given that Kejimukujik has the highest levels of Hg in the blood of loons seen in North America, (mean concentrations of 3.35 $\mu g\ g^{-1}$) [34], the impact of MeHg formation on Arctic wildlife deserves attention since many freshwater fish are over the consumption guidelines (0.2 $ug\ g^{-1}$).

MeHg in Wetland Surface Water

MeHg measured in wetland surface water supported the observed MeHg production in the laboratory incubations. Low MeHg at the inflow revealed that there are little to no input sources of MeHg to the wetland; and MeHg rises throughout the wetland showed within wetland MeHg production.

The spatial increase of MeHg toward the wetland outflow may be explained by measured increases in bioavailable Hg in snowmelt water [6]. Melt water arriving at the inflow may be providing bioavailable Hg, that was previously deposited during mercury depletion events at polar sunrise. The bioavailable Hg flowing through the wetland soil could have been converted to MeHg, explaining the high levels at the middle and outflow region of the wetland.

High MeHg levels observed at the outflow were similar to levels observed during elevated MeHg pulses in prairie streams [35]. These and other authors have suggested that MeHg pulses are in part due to MeHg being released from organic matter [32]. DOC levels were low in this study, (2 to 3 mg L^{-1}), well below the 10 to 20 mg L^{-1} observed in the prairie ecosystem, but typical of Arctic systems. Though DOC was low, the highest DOC and MeHg concentrations at the outflow may suggest an important association, whereby DOC mitigates MeHg levels in Arctic wetland systems, perhaps by transport. Both bioavailable Hg and DOC may have contributed to the high levels of MeHg leaving the wetland. That is bioavailable, Hg was taken up in wetland soil and converted to MeHg that was transported with DOC as water travelled to the outflow.

The high MeHg concentrations at the outflow are comparable to temperate environments in catchments containing wetlands [13]. Thus, Arctic wetlands may also be important sources of MeHg to downstream lakes that contribute to the high levels of Hg in freshwater fish. Thus the role of wetlands as MeHg sources to Arctic aquatic ecosystems needs to be critically evaluated.

MeHg and Sulfate Reducing Bacteria

The low culturable SRB, and lack of the DSR gene presence, show that these soils had little to no SRB. SRB recovered using the MPN technique was low relative to other extreme environments such as acid mine drainage tails (10^6) [36]. SRB populations determined with MPN techniques are often three orders of magnitude lower than those estimated with molecular techniques [37]; however, in our study this was not the case. The DSR gene specific for SRB was only amplified at one site, which did not have high culturable SRB or MeHg relative to other sites. In addition, 16S rDNA was only amplified after an enrichment of the eubacterial DNA, indicating either very little SRB presence or unsuitable primers for Arctic microbial communities. This was the first attempt to extract SRB from frozen Arctic soils, thus results from both the MPN method and the DNA extraction may be erroneous and require further investigation.

The high MeHg in wetlands and the low detection of SRB do not correspond with the large body of recent literature supporting the role of SRB as the predominant Hg methylators [10,38]. SRB abundance in Arctic terrestrial soils has not been evaluated, but they are present beneath Arctic glaciers and in ocean sediments [19-21], and exist in cold temperatures at low metabolic rates [39]. If SRB have adapted to High Arctic wetland environments, they have only approximately two months to methylate Hg at levels significantly high enough to contaminate wetlands and downstream lake systems. This seems difficult to achieve given the short growing season.

Perhaps processes outside of SRB Hg methylation in soils are producing MeHg. Few studies have penetrated the possibility of other microorganisms methylating Hg; however, the cold and harsh climates of the Arctic may not warrant biological formation of MeHg, rather abiotic mechanisms may dominate Hg methylation processes. A review of abiotic Hg methylation pathways suggests that humic matter is the most probable and significant abiotic Hg methylator [40]. Given the low DOC levels in Arctic environments, humic matter may not be a suitable candidate. Evidently, unknown MeHg formation processes are taking place in Arctic environments.

2.6 CONCLUDING REMARKS

This is the first evaluation of MeHg production and concentrations in High Arctic wetlands. It is also the first estimate made for SRB presence in Arctic wetland ecosystems. Our study showed that significant amounts of MeHg were produced in High Arctic wetlands, supporting previous observations that wetlands are important areas of MeHg formation, but unlike that in low latitudes SRB may not be the dominant Hg methylators. The unique conditions of the Arctic may consequently employ different mechanisms of Hg methylation that may include abiotic pathways [40] or other unidentified Hg methylating micro organisms. These findings show that temperature and MeHg relationships should be further investigated in light of climate change.

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3.0 SOURCES OF METHYLMERCURY IN THE HIGH ARCTIC

3.1 INTRODUCTION

Mercury is accumulating to toxic levels in Arctic biota living at the top of food webs [1]. MeHg is the form of Hg that biomagnifies in food chains, yet sources to Arctic ecosystems are not known and have not been thoroughly investigated. In temperate environments, wetlands contribute significant amounts of MeHg to downstream lakes, and are therefore considered important sources of MeHg [2-4]. Only one study has evaluated MeHg production in Arctic wetlands and showed that wetlands can produce MeHg [5]. In that study (chapter 2) the importance of High Arctic wetlands as MeHg sources to downstream aquatic systems was not determined.

Wetlands in the High Arctic differ from those in temperate regions, as they persist in polar and semi-polar deserts where the mean precipitation is only 200-300mm a year, of which only 20-30mm is in the form of rain [6,7]. Consequently, snow is a major water resource providing 60-80% of the available water to the terrestrial Arctic, in a short two to three week period [7].

Snowmelt water transports large loads of solutes to Arctic ecosystems [8], as well as organic contaminants [9]. The deposition of elemental Hg onto snow during mercury depletion events (MDE's) represents a Hg pathway to Arctic ecosystems [10,11]. Although much of the deposited Hg is revolatizied back to the atmosphere [12] it is the fate of the remaining Hg in the snowpack that may influence Hg processes in the Arctic. Lindberg et al., (2002) measured increases in bioavailable Hg to microorganisms during snowmelt (determined by mer-lux), but no direct measures of MeHg in snowmelt water have been made. The Hg deposited on snow is inorganic, but it is MeHg that bioaccumulates to high levels in the biota. If the Hg deposited onto snow is available for methylation it may be converted to MeHg and transported in snowmelt water to Arctic ecosystems. Therefore, snowmelt water should be evaluated as an input source of MeHg as snow receives Hg inputs in the spring, and melts to provide the bulk of water to the Arctic. This chapter investigates two possible sources of MeHg to High Arctic ecosystems. The two hypothesises being tested are:

2. H: Snowmelt water is a source of MeHg to High Arctic ecosystems.
3. H: High Arctic wetlands are sources of MeHg to downstream lakes.

Four studies were carried out to test these hypothesises, they are briefly outlined below, and the objectives for each study are summarized in Table 3.1. Although this study evaluates MeHg sources to High Arctic ecosystems, measurements of THg were taken at all sites, and are thus discussed throughout.

Amituk Study

Amituk Lake and the surrounding basins were intensely studied from 1992 to 1995 by Environment Canada to determine the annual budgets of persistent organic pollutants (POP's) and Hg. Mass balance budgets of several organic contaminants for the entire basin have been calculated [13], as well elemental Hg levels have been investigated [14], but to date no studies have evaluated the MeHg sources to Amituk Lake. Fish from this lake have the highest Hg levels among fish from other lakes on Cornwallis Island

[15]. The objective of this study is to evaluate snowmelt water as a source of MeHg leaving three tributaries that enter Amituk Lake. Here snowmelt water was sampled in the tributaries at the onset of snowmelt, toward the end of snowmelt and again at low flow.

Lake Study

High Arctic wetlands can produce MeHg [5], but whether wetlands are important sources of MeHg to downstream aquatic systems is not known. Therefore, the objective of this study is to evaluate the significance of wetlands as MeHg sources to High Arctic lakes. This will be evaluated by measuring MeHg in lakes with wetlands present in the basin and in lakes without wetlands present in the basin. Wetland surface water and groundwater in the surrounding lake catchments are measured for MeHg and THg.

Wetland Transect Study

Since High Arctic wetlands were shown to produce MeHg [5], a wetland was evaluated for the potential to be a source of MeHg. The objective of this study is to examine whether High Arctic wetlands are producing significant amounts of MeHg that would be observed leaving the outflow as a source to the downstream lake. Measurements are taken during the growing season at the inflow, middle and outflow of the wetland.

Eastwind Lake Study

Wetlands on Cornwallis Island were reported to produce large amounts of MeHg [5]; however, some of the most lush wetlands in the High Arctic are located on Ellesmere Island. Therefore, the objective of this study is to examine wetlands outside of Cornwallis

Island as sources of MeHg to downstream lakes. More specifically this site was selected on Ellesmere Island as a comparative checkpoint because all other studies took place on Cornwallis Island. This site was purposely sampled at the peak of the warming season to eliminate any snowmelt water influences on MeHg levels, as well we suspected Hg methylation within wetlands to be highest as this time.

Table 3.1. Study sites and the corresponding objectives of the four studies that examine sources of MeHg to Arctic aquatic systems

Study Site	**Objectives**
Amituk Watershed	Evaluate snowmelt water as a source of MeHg to a downstream lake
Lake Study	Examine the significance of wetlands as sources of MeHg to downstream lake systems
Wetland Transect	Determine whether this wetland produced large amounts of MeHg that could be observed exiting the outflow
Eastwind Lake	Use site as a control because all other studies took place on Cornwallis Island

3.2 STUDY AREA AND METHODOLOGY

3.2.1 STUDY AREA

3.2.1a Canadian High Arctic

The Arctic is described as the region north of the treeline. It is often divided into the High and Low Arctic, based on relationships between Arctic vegetation and mean July temperatures [16]. The Arctic receives approximately the same amount of solar energy input as in mid latitudes, but the mean summer time temperatures are lower than 5°C. This is due to the influencing climatological factors such as the Arctic Circumpolar Vortex, and oceanic circulation. The circumpolar vortex is a cold low-pressure system that recedes in the summer, reducing its influence on Arctic climate and air masses. The oceans and channels that separate the central northern islands, influence climate during the melting season because energy is used to melt or sublimate sea ice and ice bergs. The Arctic has a highly reflective surface because of the presence of ice caps, snow and glaciers, which all have characteristically high albedos (approx. 0.7-0.9), and thus permits little surface radiative heating [6].

February and January are the coldest months of the year. Temperatures above freezing usually occur in the summer months, June, July, and, August. When snowmelt begins the air becomes moist, and fog becomes a common occurrence in the summer season. Rainfall or snowfall usually occurs during this time of year, averaging 20-30 mm over the central islands. Most precipitation events occur in September when approximately 50-75 cm falls on the central islands [6].

During snowmelt the underlying ground remains frozen until it is exposed, at which point the surface albedo decreases and the absorbed net radiation increases, causing the top layers of permafrost to thaw to form the active layer [17]. Physical properties of the active layer such as thickness, soil type and ice content influence water movement, water storage, water supply and biogeophysical processes [18]. Surface flow is common in the High Arctic as a result of shallow active layers being underlain with continuous permafrost [18].

Water sources and the overall water balance characterize vegetation communities and wetland types [19]. Wetlands in the High Arctic persist because the continuous permafrost allows melt water to accumulate in low relief areas [20]. In the low relief areas, the soils have relatively consistent vegetation cover as a result of melt water often derived from late-lying snowbanks which provide water for most or all of the growing season in Arctic polar deserts [20]. This water accumulates over and within the shallow thawed ground where it favours wetland development.

Two field studies were conducted near Resolute Bay, Cornwallis Island and one took place the east coast of Cornwallis Island, Nunavut. The last study was on the western-central side of Ellesmere Island near Eureka (Figure 3.1).

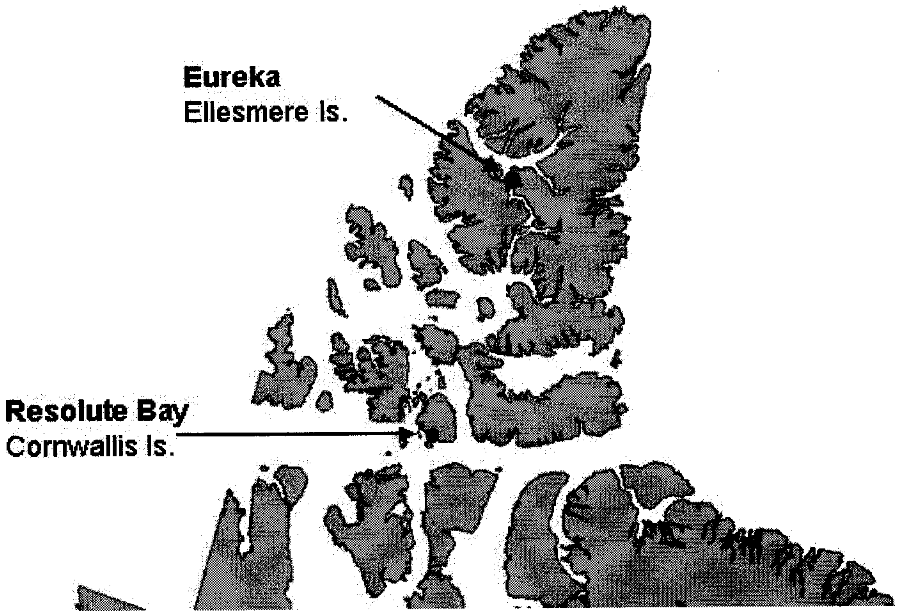

Figure 3.1 Map of the Canadian High Arctic showing the two islands where studies took place, Cornwallis Island and on Ellesmere Island.

3.2.1b Cornwallis Island

Vegetation comprises only 20% of the total ground cover on Cornwallis Island, and is very discontinuous in nature. Wetlands are limited to lowland areas, and seepage slopes beneath snowbanks, generally where there is abundant supply of moisture most of the growing season. Lowlands comprise 15% of Cornwallis Island with the remainder of the island being plateaus and rolling hills with a maximum altitude of 359 m [21]. Winters are long and cold, temperatures average -30° to -40°C and summers short and cool, with temperatures usually rising above freezing in early to mid June, with mean summer temperatures of 3 to 4°C [20]. Soils on Cornwallis Island have little soil horizon development due to the harsh climate conditions, extensive cryoturbation and high carbonate content [21]. Soils are composed of mostly gravel and sandy loam derived from dolomite sandstones, limestones as well as calcareous sandstones and shale [22].

3.2.1c The Fosheim Peninsula, Ellesmere Island

The Fosheim Peninsula on west-central Ellesmere Island, just north of 80° has some of the most dense and diverse tundra sedge meadows relative to the other Queen Elizabeth Islands [23]. According to regional zonation of vegetation, the Fosheim Peninsula falls within the Enriched Prostrate Shrub zone [19]. This zone is dominated by a large diversity of vascular plants. The area of the Foshiem has also been referred to as a polar oasis because of the warm climate. The mountains of northern Ellesmere and Axel Heiberg islands surrounding the intermontane area create a regional scale warm anomaly [24] that enables the enriched prostrate shrub vegetation zone to exist.

3.2.2 STUDY SITES AND FIELD DESIGN

A table and schematics for each study are provided at the end of this section to help the reader follow along (Table 3.2) (Figure 3.2). MeHg, THg, DOC, and DIC were sampled for in all studies, and pH, conductivity and temperature reading were taken at all sampling events.

3.2.2.1 Amituk Study

Amituk Lake is located on the south east side of Cornwallis Island NU (75° 02' 57" 93° 45' 51"). The surrounding basin is underlain by Ordovician and Silurian carbonate rocks. The basin is approximately 26km^2 and contains six small watersheds. Of the six basins that drain into Amituk Lake, three were evaluated for MeHg and THg inputs, Rock, Gorge and Mud Creek (Figure 3.3 a,b,c). The creeks were selected based on hydrology and locational differences. Mud Creek is a south facing Creek and begins melt sooner than the other tributaries, Gorge Creek is an East-facing creek and Rock Creek is a North facing creek. Gorge Creek represents the largest water source to Amituk, it drains a 10.29 km^2 basin, Mud Creek also drains a significant area of 5.22 km^2, and Rock Creek drains a much smaller basin area of only 1.08 km^2 [14].

Snowmelt begins in mid to late June and peaks in the first weeks of July and stream flow ceases in mid to late August with freeze up [25]. Stream water chemistry measured at the streams in previous studies found that the ion chemistry was representative of the limestone geology showing high Ca^{2+} and alkalinity, Gorge Creek often showed lower concentrations of the major ions due to lower weathering rates of the basin [25].

Snowmelt water was collected from the three tributaries on JD 174, 184, 211 (June 23, July 03 and Aug 09) 2002. On the first and second sampling days seven samples were collected along the tributaries (approximately 500m apart). The first sample was taken at the headwaters and the last was taken at the outflow, just before entering Amituk Lake. On the last sampling day (JD 211) water was collected at only the headwaters and outflows of the three tributaries, which was during low flow season. Water chemistry and discharge data of for Gorge Creek from 1994 was provided by Semkin [14]. Calcium, chloride and stream discharge were presented with the MeHg data to give a perspective on sources, as calcium is part of the basin geology and chloride better represents an atmospheric input from the nearby ocean.

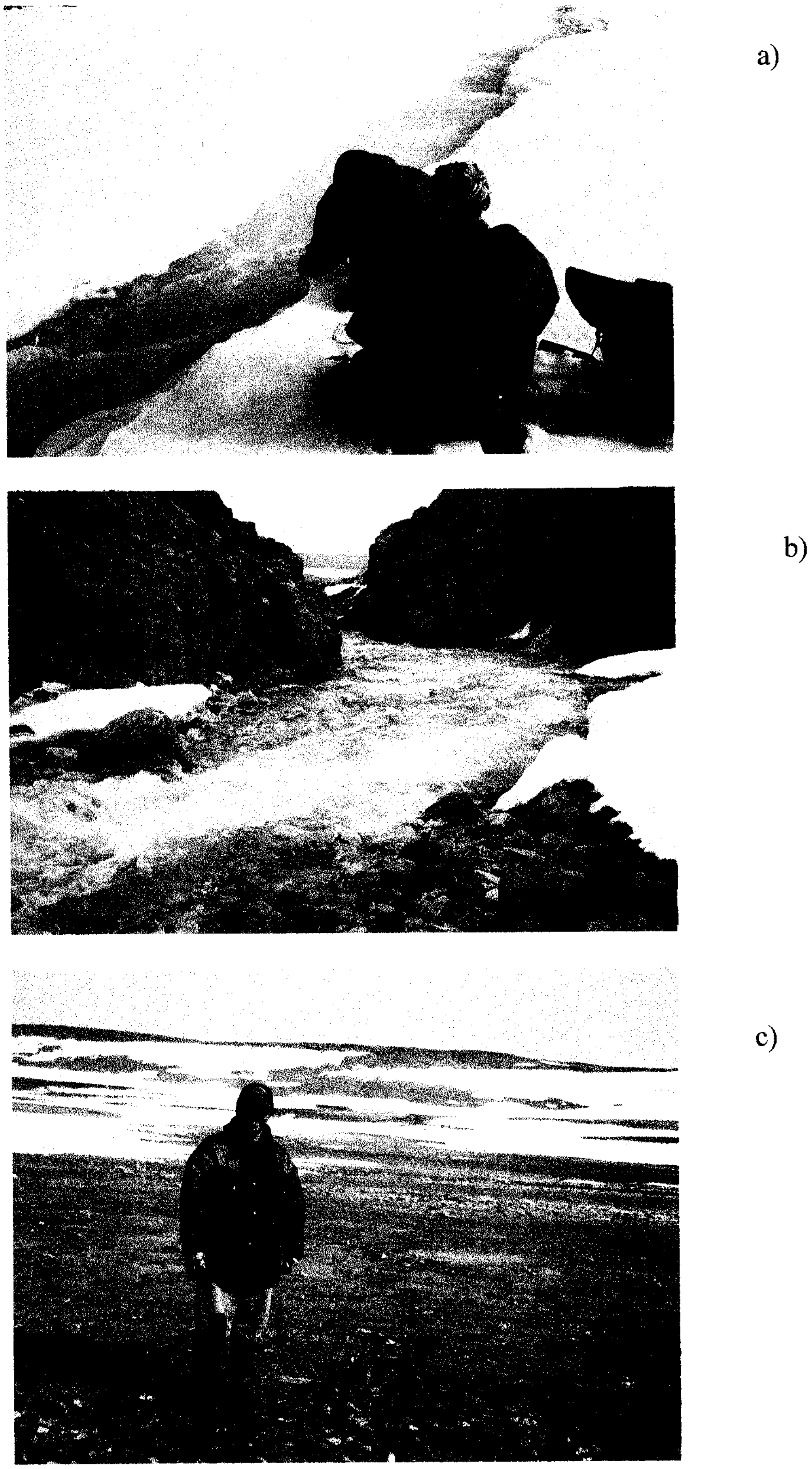

Figure 3.3 a) Rock Creek on JD 174, b) Gorge Creek on JD 184, c) Mud Creek on JD 174, tributaries entering Amituk Lake on Cornwallis Island NU.

3.2.2.2 Lake Study

Eight lakes were selected for study north of Resolute Bay (Qausuittuq), on Cornwallis Island NU. Four lakes were chosen to have wetlands in the catchment basin draining into the lakes (Figure 3.4) and four lakes were selected to have little to no wetland influence. Lake characteristics are listed on Table 3.3. Wetland area ranged from only $6000m^2$ to over $60000m^2$. Wetland area and lake area were determined with a GPS (global positioning system) using the track function. All lakes chosen were headwater lakes to reduce interferences from other lake system inputs. Water samples were collected on a weekly basis at each lake from June 25 nearing the end of snowmelt to August 09, at the end of the summer season. Water samples were collected from the lake surface, off the shore of the lakes.

Wetland surface water entering three of the four lakes (Small, Hok, and Coastal Lake) that had wetlands in the watershed was collected, and groundwater was sampled. The samples were obtained between July 14 to July 16, to represent the peak summer season and to be representative of non snowmelt water entering the lakes. Six samples of wetland surface water were collected all around the basin. Groundwater was collected where there was absolutely no wetland influence above. Groundwater collection was carried out by digging out a hole then placing a garbage bag over the hole for a few hours to let the particles settle and block any ultraviolet rays that could alter water chemistry. Four samples of ground water were taken from the three lake studies.

Table 3.3. Location of lakes, lake area and wetland presence.

Lakes	UTM (Easting)	UTM (Northing)	Lake Area (m^2)	Wetland Area (m^2)
WPL	434894	8303592	78938	--------------
South Tern	438670	8301112	12000	--------------
Sucker	435043	8304465	77500	--------------
Baby	437714	8298356	19436	--------------
EPL	436425	8303618	104742	19485
Small	439391	8297343	155627	62775
Hok	444316	8295091	11107	6694
Coastal	436721	8300745	161674	33055

Figure 3.4 Coastal Lake, a lake representing a catchment with wetland presence.

3.2.2.3 Wetland Transect Study

A wetland site was selected north of Resolute Bay Cornwallis Island NU (437700 8298700) (Figure 3.5). The area of the wetland is 18500m^2, it was fed by a small lake and a by melt water inputs from a snowbank that persisted until the first week in July. The vegetation was largely comprised of moss covered with sedge and grass species that fall into Edlund's classification of a wetland [20].

The wetland was sampled just after snowmelt throughout the growing season on a weekly basis for seven weeks from June 26 to Aug 6 2002. Water was collected at the inflow area, in the centre of the wetland (middle) and just before the outflow of the wetland (Figure 3.2).

Figure 3.5 The inflow area of the wetland site selected for the wetland transect study, on Cornwallis Island NU.
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3.2.2.4 Eastwind Lake Study

The study area was located in the Fosheim Peninsula on west-central Ellesmere approximately 10km east of Eureka (80° 05'N 85° 40' W). Samples were collected on July 20-23, which corresponds with the warmest time of the year. Eastwind Lake falls within the polar oasis area of the Fosheim Peninsula. It is in a low-lying area that receives melt water from several tributaries, of which three were selected for sampling. The three tributaries were selected for sampling based on the surrounding wetland presence (Figure 3.2). One tributary had no wetland contact at all, the second tributary travelled through a wetland before entering a lake and the last tributary was not a riverine type tributary, rather it was a wetland drainage basin that emptied into Eastwind Lake (will be referred to as wetland stream) (Figure 3.6). The two riverine tributaries appeared to be at low flow because the water level was low relative to the deep large creek size that drains large portions of the watershed during snowmelt. The source of water that fed the wetland stream was not a visible snow source, but perhaps was previously, at the time of sampling ground ice water may have dominated the water inputs. The wetland stream was in a low-lying area whereas the other two tributaries originated from steeper slopes. Six samples were collected from each tributary approximately 200m apart.

The wetland stream site was different that the wetland sampled at Cornwallis Island, as there was much more flora and a thicker peat mat, that was densely overlaid with grass and sedge communities. Around 30 to 40cm of peat accumulation was measured above the soil, whereas the moss accumulation on the Cornwallis Island site was closer to 10 to 15cm.

Figure 3.6 Wetland stream entering Eastwind Lake, near Eureka on Northern Ellesmere Island.

Table 3.2 Study sites and the type of samples acquired and the specific location, and the sampling dates

Study Site	Aquatic Sample	Sample Area	Acquisition Time
Amituk Watershed	Tributary water	Gorge, Mud, Rock Creek	Beginning, Middle, End of Snowmelt
Lake Study	Lake water	8 Lakes	Weekly basis Jun 26-Aug09
	Wetland surface water	3 Lake basins	June 15-18
	Ground water	3 Lake basins	June 15-19
Wetland Transect	Wetland surface water	One wetland Inflow, Middle, Outflow	Weekly basis Jun 26-Aug09
Eastwind Lake	Tributary water	One Wetland transect	July 21
		two tributary transects	July 22 and July 23

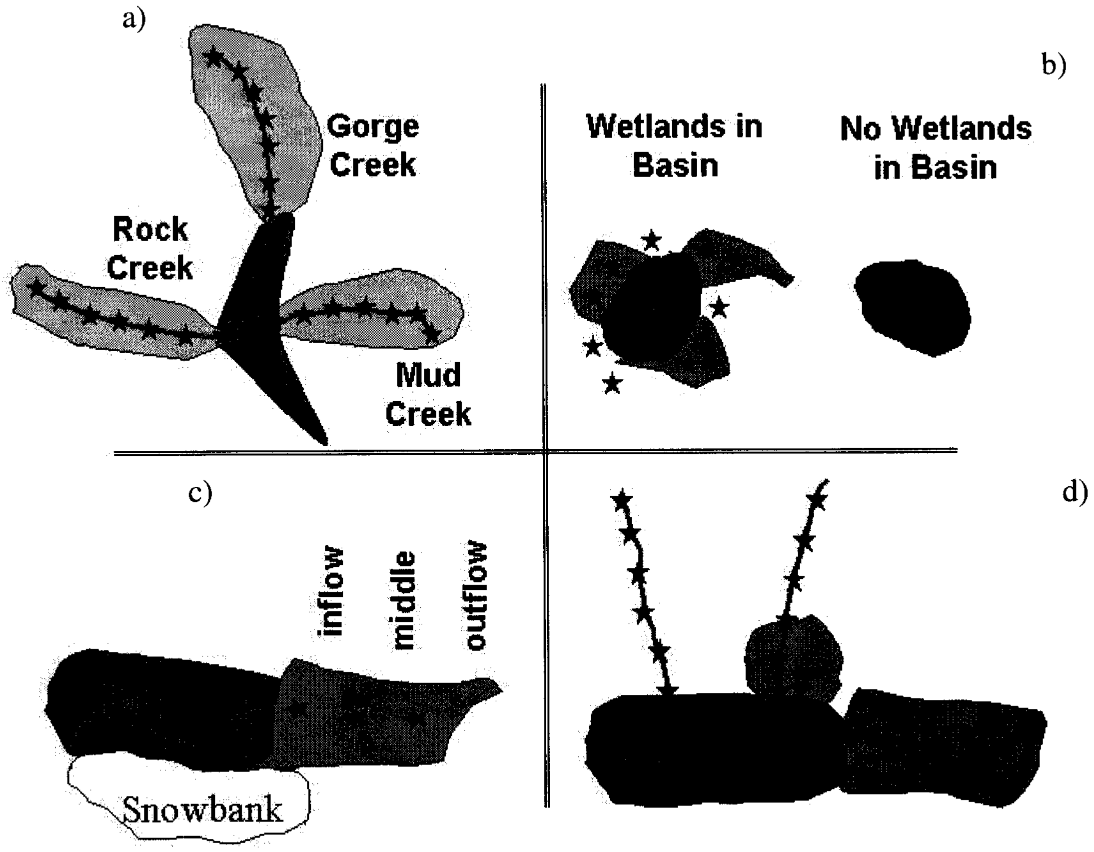

Figure 3.2 Schematic of the sampling scheme for the studies, a) Amituk basin study, three tributaries were sampled b) Lake study, both lakes with and without wetlands were sampled as well as the groundwater and wetland surface water c) Wetland transect study, a wetland sampled at the inflow, middle and outflow d) Eastwind Lake study, three tributaries sampled entering a lake. Brown areas represent wetlands.

3.2.3 Field Sample Collection

Water sampled for MeHg analysis was collected in a one litre high-density polyethylene (HDPE) bottles that were rinsed three times with sample water and then filled with one litre of water. MeHg was sampled in duplicate at the Lake study and at the wetland transect study. Samples were stabilized with HCl in the field to pH 3 and brought back to be extracted and then shipped to the University of Ottawa for analysis. THg in water was collected in a 50ml polypropylene tube following procedures developed at the Geological Survey of Canada [26] and were preserved with 1 ml of bromine chloride (27g of KBr in 2.5L of HCl followed by 38g of $KbrO_3$) (EPA Method 1631). Another 50ml of water was collected for dissolved organic and inorganic carbon measurement and stored at 4°C in the dark until analysis.

3.2.4 Water Chemical Analysis

MeHg in water was determined by capillary gas chromatograph-atomic fluorescence spectrometry following a solid-phase extraction on sulfide columns and an acidic-potassium bromide elusion (in Resolute), followed by a dichloromethane extraction (in Ottawa) [27]. Recoveries averaged 80% and blanks contained no detectable MeHg. THg in water was analyzed by using stannous chloride reduction in cold vapour-atomic fluorescence spectroscopy as outlined in EPA Method 1631. The method detection limit (3σ of all blanks) for THg was 0.3 ng L^{-1} and a percent recovery of 98% ± 4%. Field travel blanks had no detectable THg or MeHg. Dissolved organic carbon (DOC) in surface wetland water was determined using an IO Analytical Model 1010 TOC analyzer using a sodium persulfate oxidizing agent.

3.2.5 Statistical Analysis

Analysis of variances (ANOVA) was commonly used throughout. All residuals from ANOVA's were evaluated for normality (Anderson Darling test for normality) and heterogeneity (Levenes test). In the temporal evaluation of water chemistry at the Amituk basins a repeated measures ANOVA using only input and output values were used because they were the only measurements taken on the last sampling day. Prior to running the repeated ANOVA, a univarite ANOVA was used to show that concentrations along the tributaries did not vary spatially along the transects.

For the lake study, lake treatment effect of wetland presence was evaluated using an ANOVA. ANOVA's were used to determine differences among lakes in water chemistry. In the lake basins, wetland surface water was evaluated for differences among lake sites using ANOVA's. Lastly a factor analysis was used to reduce MeHg data among lakes over the seven sampling times to produce a super lake variable (from PC1 scores that explained 80% of the variance) that was then correlated with air temperature lag times to determine best fit.

In the wetland transect study a repeated measures ANOVA was used to assess site differences in MeHg over time and space. A univariate ANOVA was used to evaluate spatial or temporal difference in THg and water chemistry variables. Due to the non-detectable MeHg and THg readings in many samples from the Eastwind tributaries data was unavailable to evaluate differences amount the streams.

Pearson correlation analysis was used in all studies to assess relations among variables. When running correlations with MeHg measured in duplicate to other variables that were not duplicates a mean *r* value is represented. Statistical analysis was carried out on SYSTAT 10 software and Minitab 11.

3.2.6. Comparative Data Presentation

Concentrations of MeHg and THg were determined in all water samples and presented as ng L^{-1} (equivalent to ppt). In some studies MeHg and THg are also presented as yields per unit area to give an estimate for the bulk transport that will help distinguish sources. This was determined for the catchments at Amituk Lake and as well as for the wetland drainage for the lake studies. This enables the comparison of yields between the studies, as well as with previous literature. MeHg and THg concentrations were calculated as yields using the following formula:

$$Y = [Hg_S] * V / A \tag{1}$$

where, Y is the yield of the amount of THg or MeHg per unit area per day (ng m^{-2} day^{-1}). $[Hg_S]$ is the concentration of the Hg species either THg or MeHg (ng m^{-3}). V is the volume of water moving through the area, and equivalent to the discharge (m^{-3} day^{-1}). A is the area (m^{-2}) of the wetland or a basin etc. This provides a means of comparison among the studies when evaluating fluxes.

The volume of water leaving an area over time (equivalent to discharge) was only obtained for the Amituk basins where discharge was monitored for four years (1992-1995) by Environment Canada. Although these values are from previous years we used them here to give a general estimate.

Discharge was not measured at any other study sites. In the lake study project MeHg and THg was measured at point spots around the lakes in wetland surface water during the peak growing season (July 16-18). Concentrations should be representative of what enters lakes from wetlands after the snowmelt period. Since discharge was not obtained for the wetlands draining into the lakes, it was calculated using Darcy's Equation,

$$Qs = k\mathrm{d_s}(dh/dx) \qquad (2)$$

where, Qs is the volumetric flow rate across a saturated boundary ($\mathrm{m^3\ day^{-1}}$), and k is the hydraulic conductivity, of the medium, in this case moss ($\mathrm{m\ day^{-1}}$), $\mathrm{d_s}$ is the crossectional area ($\mathrm{m^2}$) and dh/dx is the slope gradient determined by the change in height (*dh*) over the change in elevation (*dx*). The hydraulic conductivity used was 400m $\mathrm{day^{-1}}$, which was determined to be average flow rate through moss and peat in Arctic wetlands (Hodgson, unpublished data). Slope was determined at the wetland sites. The crossectional area was the product of vegetative depth (0.15m) by a metre to normalize outflow per metre unit. Then to determine a flux for the entire wetland area entering the lake from the basin, the wetland area was imagined to be a square of which one length was multiplied to obtain an area flux from the wetland. One side of the square wetland was used to represent a boundary region that is needed to calculate flow from 'A' to 'B'.

3.3 RESULTS AND DISCUSSION

3.3.1.a Amituk Study Results

MeHg concentrations in snowmelt water collected along the tributary transects did not differ spatially at all three tributaries ($p = 0.6$) (Figure 3.7). Homogeneity along the tributaries was also observed for the THg concentrations ($p = 0.6$). Since concentrations were similar along tributary transects they were averaged to represent the tributaries on each sampling day (Figure 3.8). MeHg concentrations among the three tributaries did not differ from one another on the sampling days ($p = 0.98$). On the contrary, spatial variability in THg concentrations was observed on the first sampling day ($p < 0.01$) here; concentrations were highest at Gorge Creek, averaging 4.4 ng L^{-1} (σ =1.2), whereas Rock and Mud Creek had a mean of 2.3 ng L^{-1} (Figure 3.8).

MeHg and THg exhibited the same temporal trend at all three tributaries, whereby concentrations were highest the first sampling day, which corresponded with early snowmelt (JD 174). Concentrations of MeHg ranged from 0.2 ng L^{-1} to 0.065 ng L^{-1} with a mean of 0.14 ng L^{-1} (n = 21) and THg had a mean of 3.0 ng L^{-1} (n = 21). As stream discharge rates increased toward the end of snowmelt, concentrations decreased to less than half, MeHg ranged from 0.09 to 0.03 ng L^{-1} ($\chi = 0.06$, $\sigma = 0.02$), and THg averaged 0.95 ng L^{-1} ($\sigma = 0.35$). At the end of the warming season (JD 211) during low flow, concentrations were at detection limit for MeHg and THg.

MeHg and THg decrease temporally in concentration, but the basin yields show a different temporal pattern because yields take stream discharge into consideration. Due to the increased discharge rates at Gorge Creek and Rock Creek, yields are higher on JD 184, even though concentrations are lower (Table 3.4), whereas Mud Creek maintained the same temporal pattern because discharge decreased on JD 184. Gorge Creek had the highest yields averaging 1.65 ng m^{-2} day^{-1} on JD 184. Lowest mean yields for MeHg was observed at all tributaries on JD 211, at low flow, ranging from detection limits at Rock Creek to 0.032 ng m^{-2} day^{-1}at Gorge Creek. Similar yields occur for THg, as Gorge Creek has the highest mean yields on JD 184 of 30 ng m^{-2} day^{-1}, lowest yields were measured on the last sampling day (0.3 ng m^{-2} day^{-1}) (Table 3.4).

MeHg represented between 3.6 to 6.8% of the THg sampled on JD 174, which increased on JD 184 to range from 6 to 7.7 %, the percent of THg as MeHg was not determined for last sampling day because levels were near or at the detection limits (Table 3.4). MeHg and THg were positively correlated ($r = 0.8$; $p < 0.01$).

Stream discharge, Ca^{2+} and Cl^- water data from 1994 at Gorge Creek [14] were plotted with MeHg concentrations to illustrate seasonal trends. At the onset of snowmelt, when flow rates are relatively low Ca^{2+}, Cl^- and MeHg were high, at peak discharge Ca^{2+}, Cl^- and MeHg concentrations drop. At low flow calcium resumes the high concentrations that dominated the beginning of melt, whereas chloride and MeHg remained low (Figure 3.9).

DIC levels increased throughout the warming season, ranging from 8 mg L^{-1} to 20 mg L^{-1} ($p < 0.01$) (Table 3.5), with highest levels at low flow, similar to calcium. Gorge Creek had the lowest DIC levels, due to low weathering in this basin [25]. DOC levels are low throughout the season remaining below 1 mg L^{-1}, but did show temporal variation ($p = 0.013$) (Table 3.5).

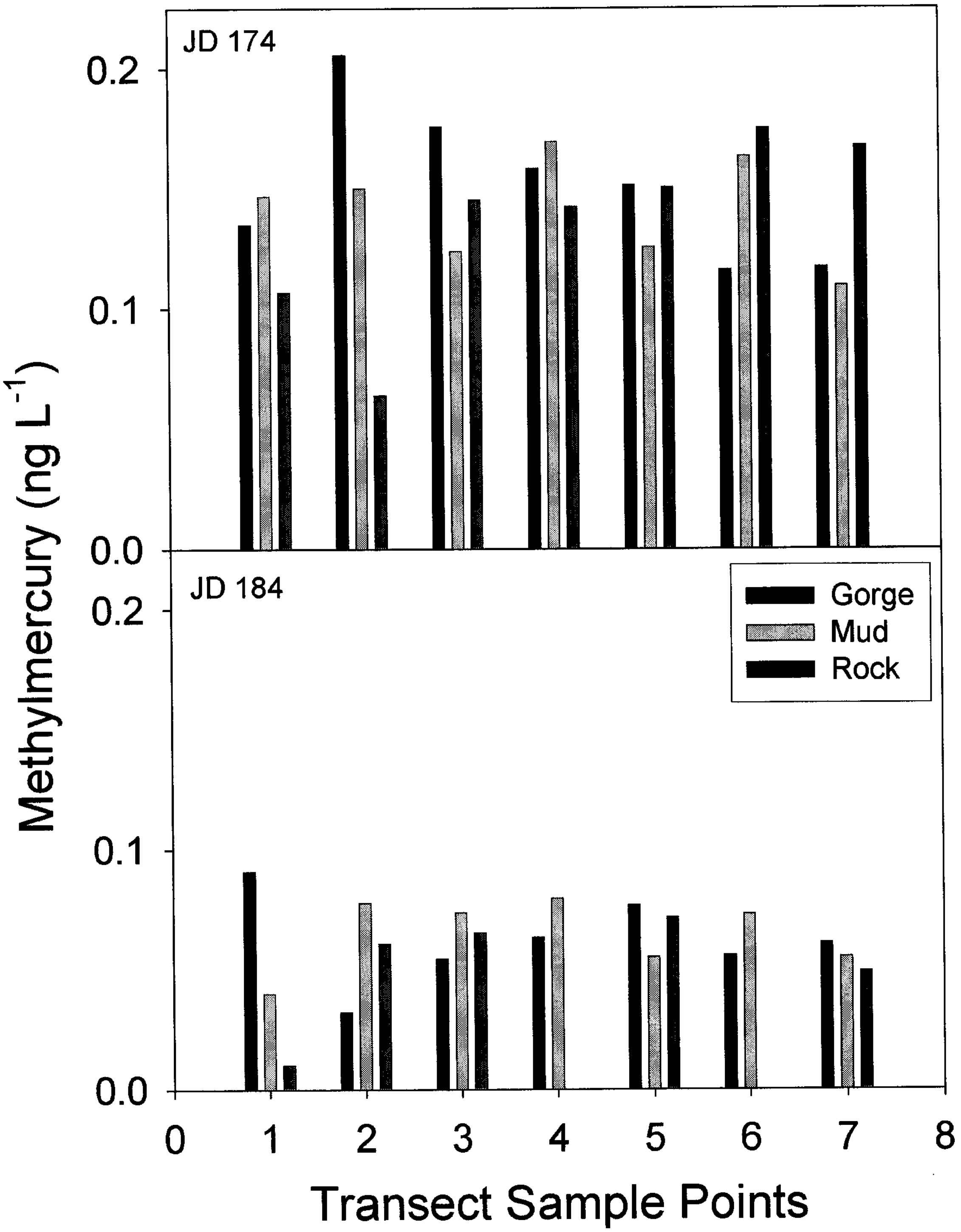

Figure 3.7. MeHg concentrations along the three tributaries, from the inflow (1) to the outflow (7) on the first two sampling days (JD 174, 184).

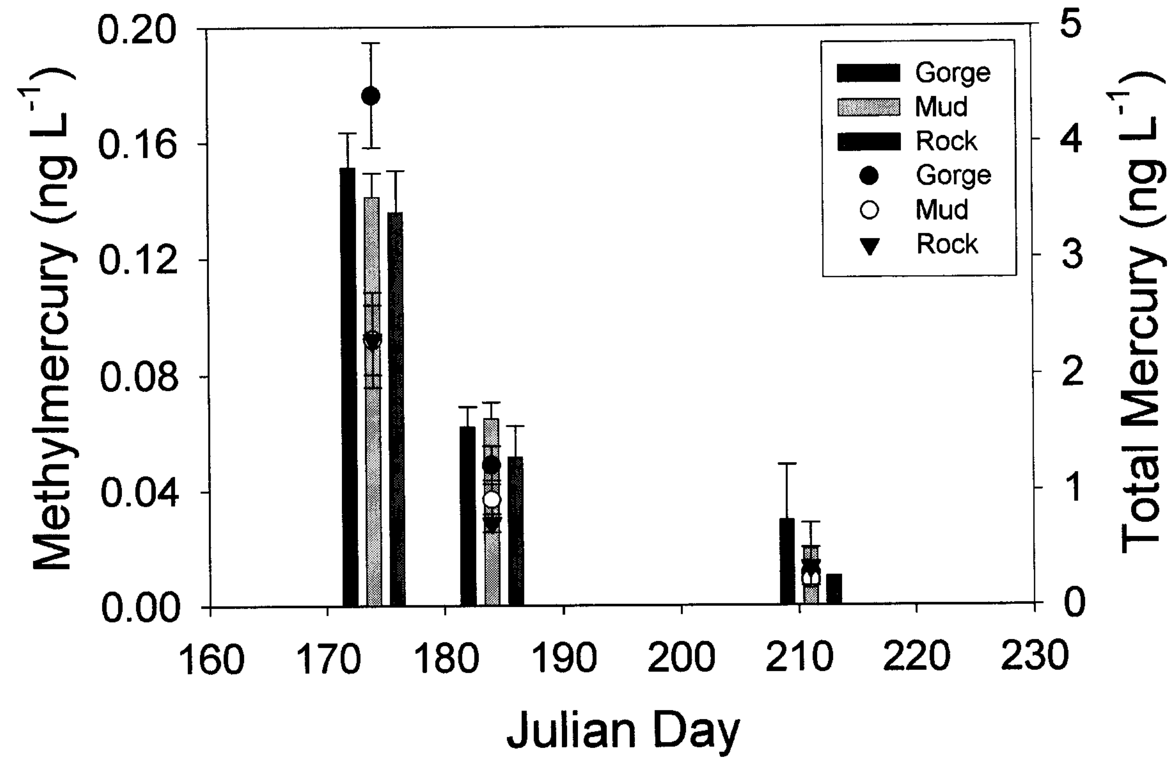

Figure 3.8 Mean MeHg (bars) and THg (symbols) at the three tributaries entering Amituk Lake on the three sampling days. Error bars represent the standard error of the mean.

Table 3.4. Concentrations and yields of methylmercury, total mercury and %methylmercury from the three Amituk Creeks on three days during the warming season. Values for concentrations, yields and %methylmercury are means (+/-SE) from all sampling events.

Julian Day	**174**			**184**			**211**		
	Gorge Creek	**Mud Creek**	**Rock Creek**	**Gorge Creek**	**Mud Creek**	**Rock Creek**	**Gorge Creek**	**Mud Creek**	**Rock Creek**
Concentration MeHg (ng L^{-1})	0.15 ± 0.01	0.14 ± 0.008	0.14 ± 0.04	0.062 ± 0.007	0.065 ± 0.006	0.051 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	dl
Yield MeHg (ng m^{-2} d^{-1})	0.23 ± 0.02	1.25 ± 0.07	0.96 ± 0.1	1.64 ± 0.14	0.23 ± 0.03	1.3 ± 0.28	0.032 ± 0.48	0.005 ± 0.002	dl
Concentration THg (ng L^{-1})	4.41 ± 0.46	2.3 ± 0.4	2.3 ± 0.3	1.22 ± 0.17	0.92 ± 0.17	0.71 ± 0.07	0.28 ± 0.06	dl	0.33 ± 0.12
Yield THg (ng m^{-2} d^{-1})	6.6 ± 0.68	20.39 ± 3.59	16.28 ± 2.1	30.99 ± 4.32	3.37 ± 0.62	18.24 ± 2.3	0.3 ± 0.065	dl	0.26 ± 0.09
% of THg as MeHg	3.60	6.79	6.26	5.94	7.42	7.68			

Table 3.5 Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) means in the three tributaries during the warm season

	DOC (mg L^{-1})			**DIC (mg L^{-1})**		
Julian Day	174	184	211	174	184	211
Gorge Creek	0.19	0.38	0.49	8.70	7.78	17.22
Mud Creek	0.27	0.46	0.67	11.36	15.01	20.54
Rock Creek	0.14	0.41	0.54	13.07	13.88	18.86

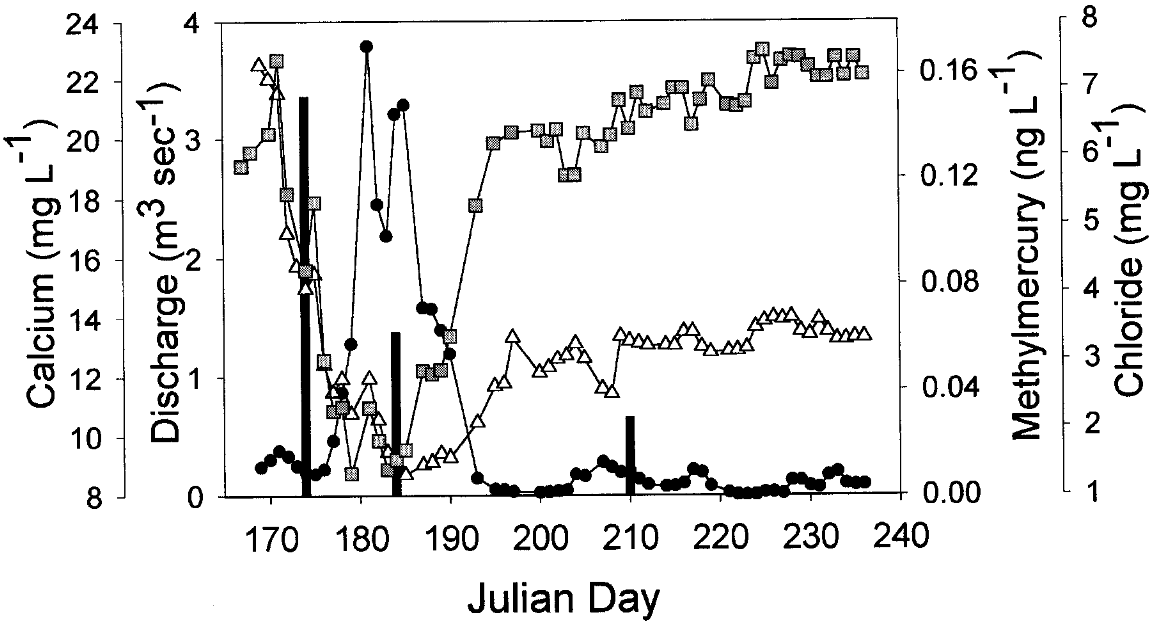

Figure 3.9 Mean MeHg (bars), discharge (black symbols), calcium (grey squares) and chloride (open triangles) at Gorge Creek during and after the main snowmelt event. Discharge, calcium and chloride data were provided by Semkin 1994, Environment Canada.

3.3.1b Amituk Study Discussion

The analogous MeHg and THg concentrations along the tributary transects, showed that there are no point sources within the streams providing or producing MeHg and THg. Rather, the temporal trends support that basin snowmelt water provides an influx of MeHg and THg to Amituk Lake. Previous studies at the Amituk watershed showed that THg concentrations were high at the beginning of snowmelt that decreased with increasing discharge during snowmelt, and was negligible at low flow [14]. This temporal trend was not anticipated for MeHg, as peaks in watersheds are often observed later in the spring resulting from wetland and biological production [28]. Here the basins were devoid of plant life thus little to no MeHg release from the basins was expected.

Approximately 80% of solutes are eluded from snowpacks during the first 20% of melt, which is then followed by more dilute water [8]. Solutes leaving the snowpack in melt water usually follows a preferential elusion sequence [29,30]; however elusion sequences have not been determined for elemental Hg or MeHg.

Elusion sequences may explain the high THg concentrations at Gorge on the first sampling day (onset of snowmelt), relative to Mud and Rock Creek. Mud Creek is a south-facing basin and therefore begins snowmelt earlier than Gorge Creek [14], which may have resulted in a missed detection of the THg peak in snowmelt water because discharge of the basin was approaching its highest levels. Calculated yields for Mud Creek support that THg was eluded earlier in the season relative to Gorge Creek. Although Rock Creek is north-facing it was observed to begin melt just before Gorge Creek [25], thus the peak may have been missed at this site as well or the small drainage basin size may account for the lower levels at Rock Creek.

At the onset of snowmelt, calcium levels were high in snowmelt water because the snow was 'dirty' with limestone/dolomite dust derived from the basins and deposited via wind blow [25]. The high DIC and Ca^{2+} at low flow reflect the basin geology (i.e. limestone/dolomite), whereas Cl^- that is prevalent in the snowpack due to the close oceanic vicinity, remained at lower concentrations at low flow, because it was not characteristic of the basin geology. Thus, the high MeHg and THg peaks during snowmelt demonstrate that MeHg and THg are supplied from snowmelt water, and that watershed basin geology does not influence MeHg and THg.

In temperate systems, snowmelt is a significant source of Hg, supplying one third of the annual THg in one forth of the annual water flux in a small watershed in Sweden [31]. Additionally, spring flow has been shown to carry 50 to 90% of the annual Hg to the watershed [32]. The high flux of THg during spring is thought to be caused by high concentrations of particulate transport loading [33], from soil and land runoff surfaces. This would not be common to Arctic environments because during snowmelt the ground is frozen (begins to thaw when exposed), thus, limiting the amount of particulates available for suspension. Suspended particulate was not measured in this study but given the low DOC and previous measurements by Semkin et al., (1994), particulates were not responsible for the observed high levels of MeHg and THg leaving the basins during snowmelt.

THg in snowmelt water may have been supplied earlier from the mercury depletion events (MDE's). MDE result in the deposition of Hg onto the Arctic landscape resulting in the increase of snow mercury levels [34]. For example prior to a MDE snow Hg levels were measured at 7.8ng L^{-1} that increased to 34ng L^{-1} after the MDE [10], these levels are much higher the THg observed at Amituk basins in the snowmelt water. However, approximately 50% of the deposited Hg is lost from the snowpack within 12 hours [35]. Hg can be removed by photoreduction of Hg^{2+} to Hg^{o} that volatizes back into the atmosphere [12,35] or leaching of Hg^{2+} by meltwater percolation through the snowpack at the onset of the warming season. Therefore, sampling melt water at the end of June was late in the season and much of the Hg that was initially deposited probably left by volatization or early melt water.

Comparing concentrations in snow after a MDE of 34ng L^{-1} found by Lu et al., (2001) with the highest snowmelt water THg concentration of 6.0 ng L^{-1} (Gorge Creek, JD 174), Amituk concentrations represent approximately 20% of the THg deposited onto the snow. This seems reasonable given that 50% is lost within 12hours, and snowmelt was already underway. Recall that between 3 and 7% of the THg was MeHg, which is quite high when evaluating MeHg levels from atmospheric sources. Previous studies found MeHg to comprise less that 1% of the THg in precipitation [36]. Two samples of snow measured by St. Loius et al., (1995) found levels to be higher than that observed in rain water ranging from 0.028ng L^{-1} to 0.179ng L^{-1} [37]. Although MeHg concentrations were highest the first sampling day, the percent of MeHg was higher ten days later, possibly due to less remaining THg that was previously eluded, or in situ production of MeHg.

The relatively high concentration of MeHg in Arctic snowmelt water suggests that it was formed within in the snow before or after deposition, or produced during melt. One possibility is that the ocean may have provided high yields of methyl iodine, a compound that can methylate Hg in the atmosphere [38], and has been shown to methylate Hg in water and basic pH levels in the presence of Cl^- (Celo pers. com). Thus, further investigation of methyl iodine may serve useful in determining MeHg formation mechanisms.

Fluxes from the basins were very high and comparable to yields in temperate environments where wetlands provide high levels of MeHg to downstream lake systems. In temperate ecosystems drainage basins with wetlands have some of the highest yields of MeHg ranging from 0.5ng m^{-2} day^{-1} [3] to 0.36 ng m^{-2} day^{-1} [2]. Yields at Amituk were much higher in comparison, averaging 1.6 ng m^{-2} day^{-1}at Gorge Creek. Demonstrating that snowmelt water from Amituk basins are an important source of both MeHg and THg. The high yields were partly driven by the large flux of water leaving the basins, that may not be representative of all Arctic basins. However, snowmelt does represent a large flush of water supplied to all Arctic ecosystems and therefore must be considered as an important source of MeHg.

Mass budget calculations for the entire Amituk basin revealed that major ions [14] and certain PCB's [39] eluded from the drainage basins often did not mix in Amituk Lake water due to lake isothermic conditions, thus most contaminants and solutes left via the lake outflow to the ocean [14]. Water column mixing was only observed late in the season toward the end of July. Thus, the majority of THg and MeHg leaving the tributaries early in the season did not reside in Amituk Lake, rather left via the outflow to the ocean. Therefore, the high levels of mercury observed in fish at Amituk Lake may be due other mechanisms, perhaps in-lake processes.

3.3.2.a Lake Study Results

General Lake characteristics

Lakes with wetlands did not have higher levels of MeHg than lakes without wetlands in the catchment basin ($p = 0.5$). MeHg concentrations among the lakes were very similar, except for the levels measured at Coastal Lake ($p = 0.01$) (Table 3.6), which maintained the highest concentrations throughout the summer. THg differed among lakes ($p = 0.06$), levels were generally low with mean concentrations often below 1ng L^{-1} (Table 3.6). The amount of THg as MeHg was usually below 10%. DOC in all lakes were low, the highest mean concentrations were at Baby Lake at 2.65 mg L^{-1}, whereas the other lakes maintained DOC levels below 2 mg L^{-1} ($p < 0.01$) (Table 3.6). Due to the calcareous bedrock, the pH of lakes ranged from neutral to basic ($p = 0.2$) (Table 3.6). DIC concentrations differed among the lakes, and the mean levels ranged from 15 to 20 mg L^{-1} (Table 3.6). Lake water conductivity differed among lakes but was often above 100μS. Lastly, lake water temperatures were rarely above 10°C (Table 3.6).

Catchment Observations

Results from the study area analysis revealed that wetland surface water draining into Coastal Lake had the highest MeHg concentrations relative to wetland surface water entering Small and Hok Lake ($p = 0.048$) (Figure 3.10). High MeHg levels were associated with the highest levels of DOC in wetland surface water. A positive relationship was observed for DOC and MeHg in the wetland surface water ($r = 0.83$; $p < 0.01$). The relationship revealed that with every increase in 1mg L^{-1} in DOC, concentrations of MeHg increased by 0.025ng L^{-1}. THg and DOC had a smaller correlation coefficient ($r = 0.4$; $p = 0.1$).

Discharge rates determined for the wetlands entering Hok Lake, Small Lake and Coastal Lake were all very low (Table 3.7). This was largely due to the low discharge rates over the wetland because little water inputs are available after snowmelt. As a result the fluxes of MeHg from the wetlands were low ranging from 0.0008 ng m^{-2} day^{-1} at Small Lake to 0.002 ng m^{-2} day^{-1} at Hok Lake (Table 3.7).

MeHg was present in the groundwater leaving the catchment at low concentrations near detection limit that did not significantly differ among lakes (χ = 0.026 ng L^{-1}). Groundwater MeHg was positively correlated with DOC levels ($r = 0.69$; $p = 0.01$). THg in groundwater was present at relatively high levels, higher than observed in wetland surface water ($\chi = 2.8$ ng L^{-1}, $\sigma = 2.3$). THg was positively correlated with DOC levels ($r = 0.91$; $p < 0.01$) as well as DIC levels ($r = 0.83$; $p < 0.01$).

Temporal Lake Chemistry

Lake MeHg concentrations differed throughout the growing season ($p < 0.01$) (Figure 3.11), but all followed a similar temporal trend (except for Baby Lake), whereby high values were observed in the early season, followed by a drop then a peak then a second drop and a final peak in early August. Averaged lake MeHg peaks and drops appear to follow the summer mean daily air temperature for the Resolute area (Figure 3.12). Calculated correlations of lake MeHg with air temperatures of lag days ranging from the sampling day air temperature to 10 lag days prior to, showed a high correlation with lag day 6 air temperatures (Figure 3.13). Baby Lake, was the only lake that did not correlate well with the sixth air temperature lag day, rather it was best correlated with the mean daily air temperatures three days prior. MeHg levels at the 7 lakes were reduced by factor analysis, to produce a super variable to represent all lakes, using the first principle component scores (explained 80% of the variance in the lakes). When the super lake variable was correlated with the mean daily air temperatures, highest correlations were obtained for the sixth lag day again (Table 3.8). Temporal lake MeHg concentration were also plotted against precipitation events for Resolute Bay and showed two high MeHg peaks occurred shortly after two large rain events (Figure 3.14).

THg concentrations differed among the lakes ($p = 0.05$), with West Plateau Lake and Small Lake having the highest mean concentrations (Table 3.6). The mean THg levels at these lakes were swayed by very high THg concentrations measured on the first sampling day, after which levels dropped for the remainder of the growing season, similar to the other lakes. THg at all lakes appear to be a function of time because concentrations are highest at the beginning of the season and then drop shortly thereafter to remain near the detection limit (Figure 3.11). The two lakes with the highest THg (West Plateau Lake and Small Lake) were sampled two days earlier than the other lakes, possibly owing to the high levels.

Table 3.6 Lake water chemistry at eight lakes on Cornwallis Island NU.

Lakes	MeHg (ng L^{-1})	Total Hg (ng L^{-1})	% MeHg of THg	DOC (mg L^{-1})	DIC (mg L^{-1})	pH	Conductivity (uS)	Water Temp (^{o}C)
WPL	0.057 ± 0.006	1.4 ± 0.4	6.08	1.44 ± 0.2	16.1 ± 2.6	8.1	132.64	6.91
South Tern	0.048 ± 0.007	0.81 ± 0.3	9.19	1.35 ± 0.1	19.2 ± 1.2	8.0	101.09	3.36
Sucker	0.044 ± 0.005	1.2 ± 0.5	6.73	0.89 ± 0.1	15.9 ± 1.1	8.1	124.44	6.00
Baby	0.046 ± 0.006	0.56 ± 0.9	8.82	2.65 ± 0.2	18.9 ± 0.9	7.9	98.77	5.17
EPL	0.055 ± 0.007	0.6 ± 0.1	6.43	1.04 ± 0.1	16.3 ± 1.1	8.0	104.23	5.99
Small	0.05 ± 0.006	0.86 ± 0.9	9.40	1.66 ± 0.2	19.8 ± 1.6	8.0	147.43	3.60
Hok	0.05 ± 0.005	0.7 ± 0.2	8.81	1.46 ± 0.2	19.2 ± 2.0	8.2	140.67	5.84
Coastal	0.077 ± 0.007	0.85 ± 0.1	9.78	1.94 ± 0.1	18.7 ± 1.3	7.9	124	4.27

Table 3.7 Wetland surface water MeHg and THg concentrations and yields (n=6), % MeHg of THg, DOC and the discharges for the wetland area draining into the lakes.

Lake Site	**MeHg (ng L^{-1})**	**MeHg yield (ng m^{-2} d^{-1})**	**Total Hg (ng L^{-1})**	**THg yield (ng m^{-2} d^{-1})**	**% MeHg of THg**	**DOC (mg L^{-1})**	**Discharge (m^3/day)**
Hok	0.0554 ± 0.006	0.00203	1.04 ± 0.2	0.03803	6.1 ± 1	1.96 ± 0.3	245
Small	0.035 ± 0.008	0.00084	1.24 ± 0.09	0.02965	3 ± 0.8	1.6 ± 0.3	1503
Coastal	0.0857 ± 0.02	0.00198	1.2 ± 0.02	0.02715	7.1 ± 0.9	4.46 ± 1.2	763

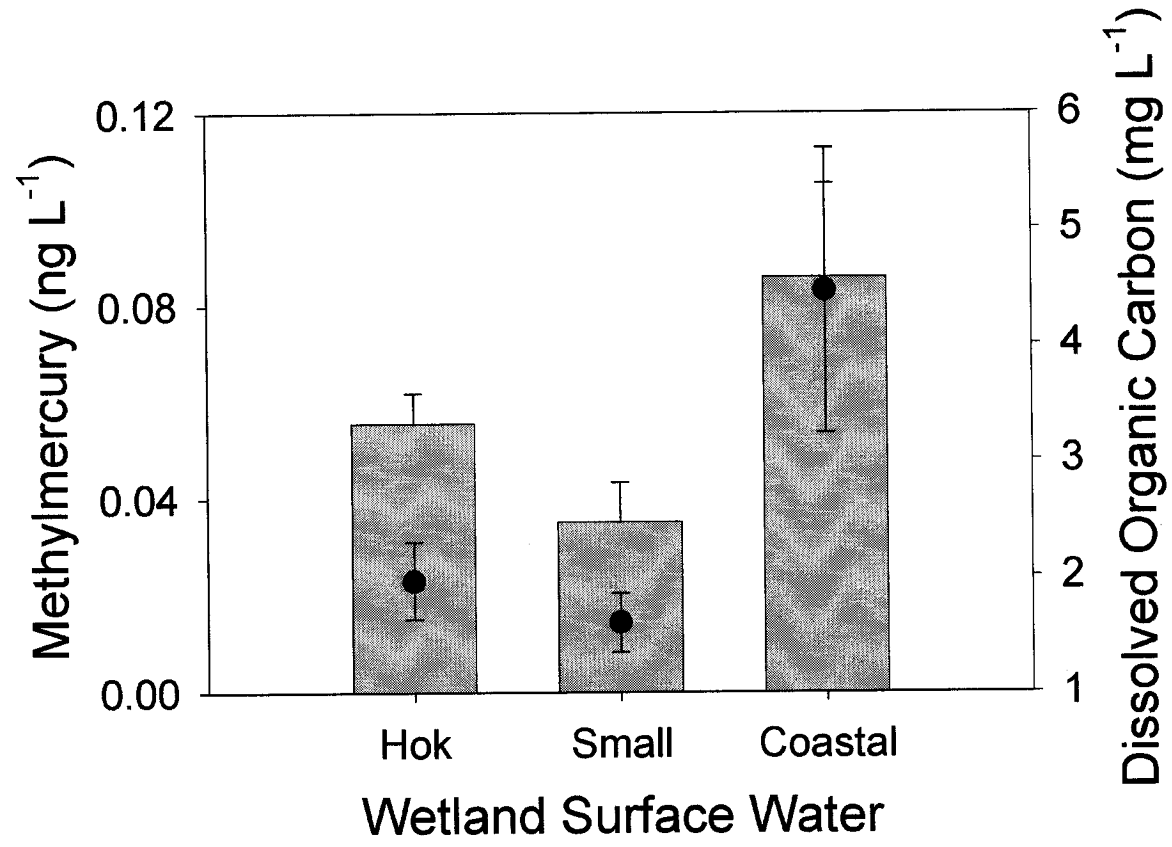

Figure 3.10. Mean MeHg (bars) and DOC (closed symbols) in the wetland surface water of three lake catchments. Error bars are the standard errors (n=6)

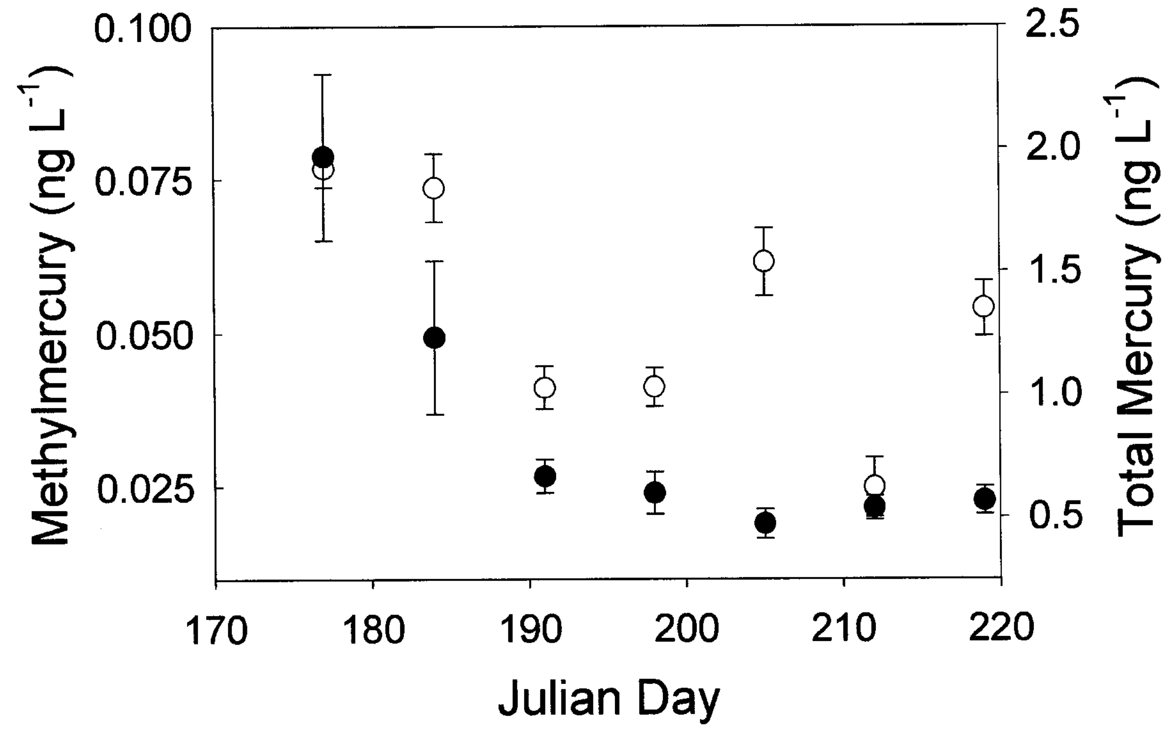

Figure 3.11 Mean MeHg (open symbols) and THg (closed symbols) in eight lakes on Cornwallis Island during the growing season. Error bars represent the standard error of the mean.

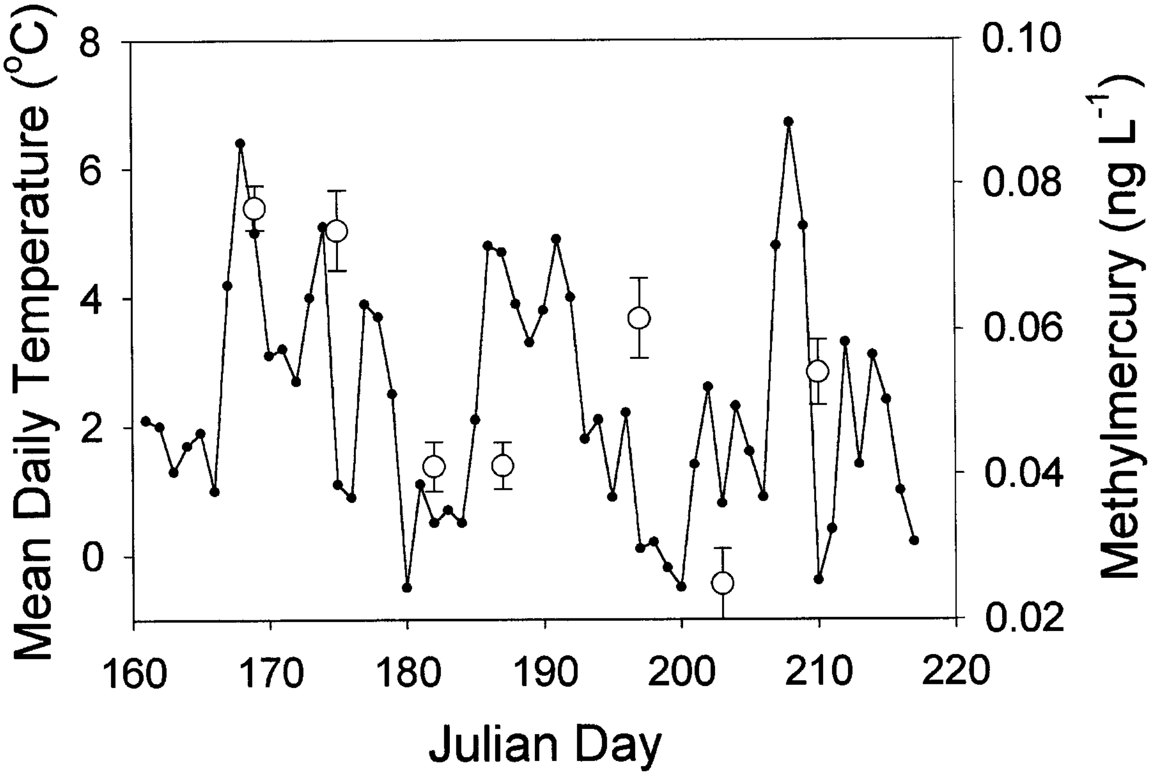

Figure 3.12. Mean MeHg in eight lakes (open symbols) and mean daily air temperature (closed symbols) near Resolute Bay, Cornwallis Island. Error bars represent the error of the mean (n=14).

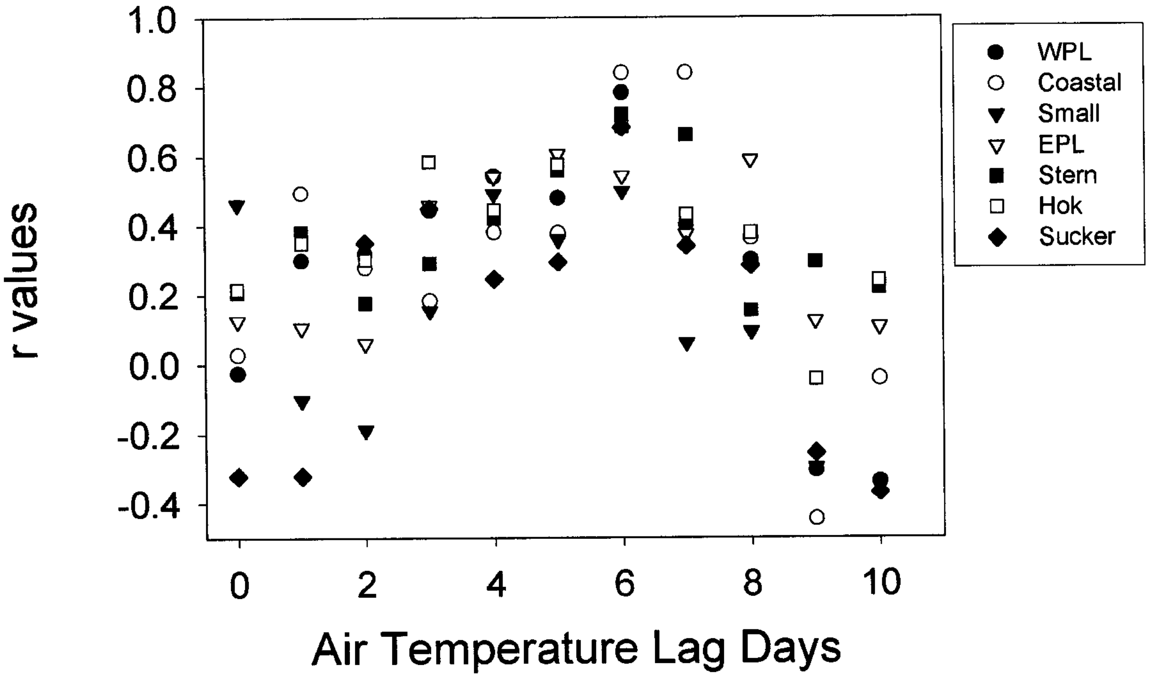

Figure 3.13 Correlation coefficients of the lake MeHg concentration at all lakes (except Baby) at mean daily air temperature from 0 to 10 lag days.

Table 3.8 Correlation of PC1 Scores of Super Lake Variable and Lag day Temperatures

Lag days	***r* values**
0	0.195
1	0.389
2	0.305
3	0.352
4	0.383
5	0.383
6	**0.684**
7	0.517
8	0.42
9	-0.266
10	-0.148

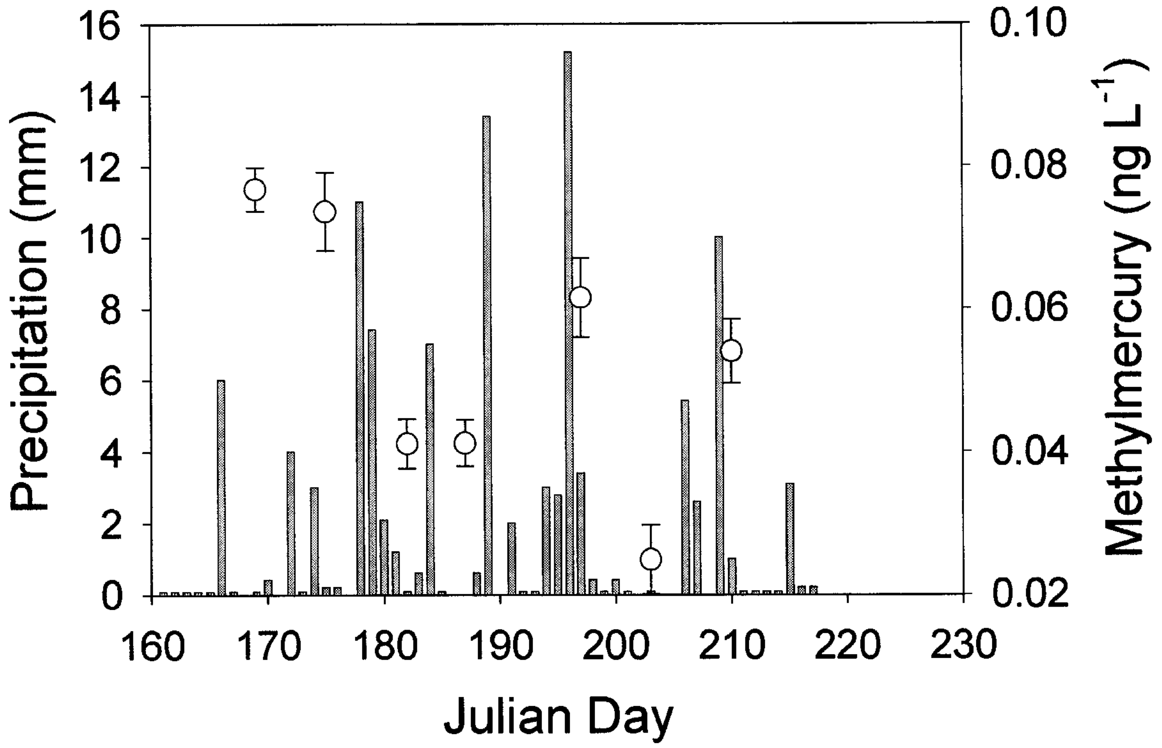

Figure 3.14 Mean MeHg in eight lakes (open symbols) and precipitation events (bars) during the warming season near Resolute Bay, Cornwallis Island. Error bars represent the standard error of the mean (n=14)

3.3.2b Lake Study Discussion

Catchment Influences on lake MeHg levels

Wetland presence did not result in observable differences in lake MeHg concentrations. The lack of wetland treatment effect does not entirely discount wetlands as important sources of MeHg to Arctic lakes, as the highest lake MeHg concentrations at Coastal Lake were associated with high MeHg concentrations in basin wetland surface water. Additionally, the low MeHg at Small Lake and Hok Lake corresponded with the low wetland surface water concentrations in the basins.

In wetland surface water DOC and MeHg were positively related suggesting that DOC is a critical player in determining MeHg levels. This is exemplified in the Coastal Lake basin where wetland surface water had significantly more DOC and MeHg than the other two sites (Hok and Small Lake). This relation is not unusual as MeHg has a high affinity for DOC and humic substances [40]. The relationship is similar to the one generalized by Driscoll et al., (1994; 1995), that showed every 1mg L^{-1} increase in DOC resulted in a 0.03 ng L^{-1} increase in MeHg. In the wetland surface here MeHg increased by 0.025 ng L^{-1} with every 1mg L^{-1} increase in DOC, just 0.005 ng L^{-1} lower than the observed by Driscoll et al., (1994). The DOC and MeHg relations described by Driscoll et al., (1994; 1995) are for lake systems rather than wetlands, but perhaps the same mechanisms hold, suggesting that DOC and MeHg relations in Arctic wetland systems may function under similar mechanisms as temperate environments.

Estimated daily yields of MeHg leaving the wetlands were much lower than yields observed at the Amituk watersheds. The levels here largely reflect the low water flow, which is a function of the gradual slopes of the wetland basin areas, and the little water leaving the wetland after snowmelt due to the few summer precipitation events [7]. Relative to temperate environments yields were approximately 100 folds lower than in catchments that were heavily dominated by wetlands. For example watersheds with forest and wetland cover near Wisconsin averaged 0.5ng m^{-2} day^{-1} in the spring and 0.15 ng m^{-2} day^{-1} in the fall [3], and in a wetland basin in the ELA region 0.36 ng m^{-2} day^{-1} was measured [2] (Table 3.9).

The yields calculated for these sites suggest that Arctic wetlands are minor sources of MeHg relative to temperate wetlands and Arctic snowmelt water (Amituk basins). However, given the lack of hydrological data available for the sites, it is difficult to quantitatively assess the importance of wetlands as sources of MeHg to lakes; a more in depth mass balance study is required.

Yields were not calculated for groundwater inputs because the hydraulic conductivity of the active layer was not determined. Water flow through the active layer would be lower than surface runoff from the wetlands because surface runoff encounters less resistance. This does not imply that groundwater should be overlooked, because after the snowmelt flush is over, the ground thaws, resulting in a groundwater dominated hydrologic regime [18]. The MeHg concentrations at the detection limit in groundwater suggest it is not an important source of MeHg to lakes. These observations are similar to temperate environments where groundwater concentrations were also below detection limits [41]. The opposite is true for THg, as concentrations were relatively high, higher than observed in wetland water, and thus should further evaluated as an input vector to lake systems.

Table 3.9 List of MeHg and THg concentrations, yields and % of MeHg in THg from previous studies

Study	**MeHg** **(ng L^{-1})**	**Yield MeHg** **(ng m^{-2} d^{-1})**	**THg** **(ng L^{-1})**	**Yield THg** **(ng m^{-2} d^{-1})**	**% of THg as MeHg**
Louis et al., 1994					
ELA, wetland	0.626	0.36	5.02	4.8	13
ELA, up/wetland	0.176 - 0.228	0.18 - 0.24	11.8 - 11.4	13.9 - 15.2	1.6 - 2
ELA, upland	0.03	0.09	13.11	26.5	0.23
Hurley et al., 1995					
Wetland/forest Fall	0.291	0.148	3.88	2.01	6.4
Wetland/forest Spring	0.194	0.507	7.6	15.4	3.2

Temporal Shifts in MeHg and THg in Lakes

The temporal trends of THg and MeHg were consistent in all lakes, implicating that factors besides wetlands are influencing all lakes on a seasonal scale (Figure 3.15). The hypothesis that snowmelt water provides a large source of MeHg and THg to Arctic lakes is supported by the high lake concentrations in the early season.

The high mean THg levels at West and Small Lake suggest snowmelt water is a major source of THg, because the highest concentrations were obtained on the first sampling day, which was two days earlier than the other 6 lakes sampled. The drop in THg levels in all lakes throughout the warming season suggests that inputs were reduced, possibly reflecting the reduction in snowmelt water inputs. However, one must keep in mind that the THg measured in lakes is equal to the sum of inputs and outputs from the lake system. Thus, the lake outputs need to be evaluated, since they may be higher than inputs from the surrounding catchment and external environment.

Outputs of THg include biological and chemical reduction of Hg^{2+}. Due to the low solubility of Hg^{2+}, exposure to ultraviolet (UV) radiation results in photoreduction to Hg^{o} [42,43]. At about the same time snowmelt seized, lake ice cover was retreating, exposing the lakes to UV radiation in the 24 hour daylight of the Arctic summer. DOC is an inhibitor of solar radiation, thus in low DOC lakes, particularly below 2 mg L^{-1} UV attenuation is high, which most likely resulted in high photoreduction rates of Hg^{2+} [44]. Therefore, the photoreduction of Hg^{2+} was probably quite high at theses lakes relative to temperate lakes owing to the low DOC levels [42]. High Arctic lakes were shown to have the highest dissolved gaseous mercury (Hg^{o}) (product of photoreduction of Hg^{2+}) relative to lakes in temperate and tropical environment, largely due to low DOC in lake water and UV penetration [42].

Microbiological processes can also represent an output of lake THg. Microbial activity can reduce Hg^{2+} by the toxicological breakdown with the mer-reductase enzyme [45]; however, the low THg levels at these sites would not stimulate reduction of Hg by bacteria [46]. This does not negate the general biological uptake of element Hg that may have occurred in the lakes during the growing season. Given the low DOC, and declines in THg as ice retreated, photoreduction appears most plausible reduction pathway for THg lake outputs.

Snowmelt water appeared to be the most important input sources of THg, but once snowmelt water inputs diminished, groundwater flow begins to characterize the basin hydrology [18]. Despite the relatively high levels of THg in groundwater the overall lake water THg did not reflect high inputs. Therefore, it appears that THg in lake water decreased likely to due a reduction in inputs from snowmelt water, along with increases in outputs that were probably driven by photoreduction induced by UV radiation exposure and low DOC levels.

Lake MeHg showed a temporal pattern unlike THg, as MeHg concentrations fluctuated during the growing season. MeHg was also high at the beginning of the season and then concentrations dropped and levels peaked twice again before the end of the season. Air temperature and precipitation data acquired for the Resolute area were the only data that could best explain the peaks and drops in MeHg levels in the lakes.

High MeHg in lakes in the early season can again be attributed to inputs from the melt flush similar to THg. The first drop nearing the end of the melt season may be responding to reduced melt water supply (providing MeHg and THg). The MeHg peaks and drops that follow relate to mean air temperatures six days prior. This observation was consistent in seven of the eight lakes studied. The lake that did not fit this trend (Baby Lake) was best associated with the daily air temperature on the third lag day. This may have been influenced by the small lake size and shallowness that enabled a quick response to external air temperatures.

Positive relationships with MeHg and lake temperatures has been shown in lakes in northern Ontario Canada [47,48]. These studies found the ratio of Hg methylation to MeHg demethylation increased with warming temperatures. It was hypothesized that the warmer lake temperatures inhibited further MeHg demethylation but not Hg methylation. The epilimnion lake temperatures surpassed 20°C in the temperate lakes [47], whereas temperatures in the Arctic study lakes were rarely over 10°C, suggesting different processes are occurring in Arctic lakes. However, if the processes are microbial driven then perhaps similar processes are taking place, but with organisms that have lower temperature thresholds.

On the other hand, the peaks and drops in lake MeHg may reflect inputs from precipitation events. The last two peaks in MeHg correspond to precipitation events that occurred a day prior, as well the drops occur during periods of low precipitation. It seems unlikely that atmospheric inputs of MeHg would create an increase in lake water without a corresponding peak in THg, because less than 1% of THg in rain is MeHg [36]. Increased lake MeHg levels by precipitation may be caused by inputs from surface runoff water that is supplying MeHg bound to particulates [49]. Precipitation may induce hortonian overland flow, forcing groundwater to resurface and possibly mobilize more particulate bound to MeHg from available sources. Surface runoff water inputs seems more probable than atmospheric precipitation inputs, but this would suggest that all ground surfaces wetland or not, could supply MeHg. Moreover, suggesting wetlands were not important sources of MeHg.

Although conclusions cannot not exclusively deduce whether air temperature or precipitation caused the MeHg temporal peaks, both variables need to be considered when evaluating climatic change the Arctic, as both temperature and precipitation are predicted to increase [50].

Overall, the temporal MeHg fluctuations observed at all lakes show that if wetlands are sources of MeHg the inputs are obstructed by other variables. Interestingly these variables or factors are common to all lakes, suggesting physical characters including catchment characteristics are minor influences. Rather variables such as climate, the atmosphere and other external environmental variables may be more significant to Arctic lake systems (Figure 3.16).

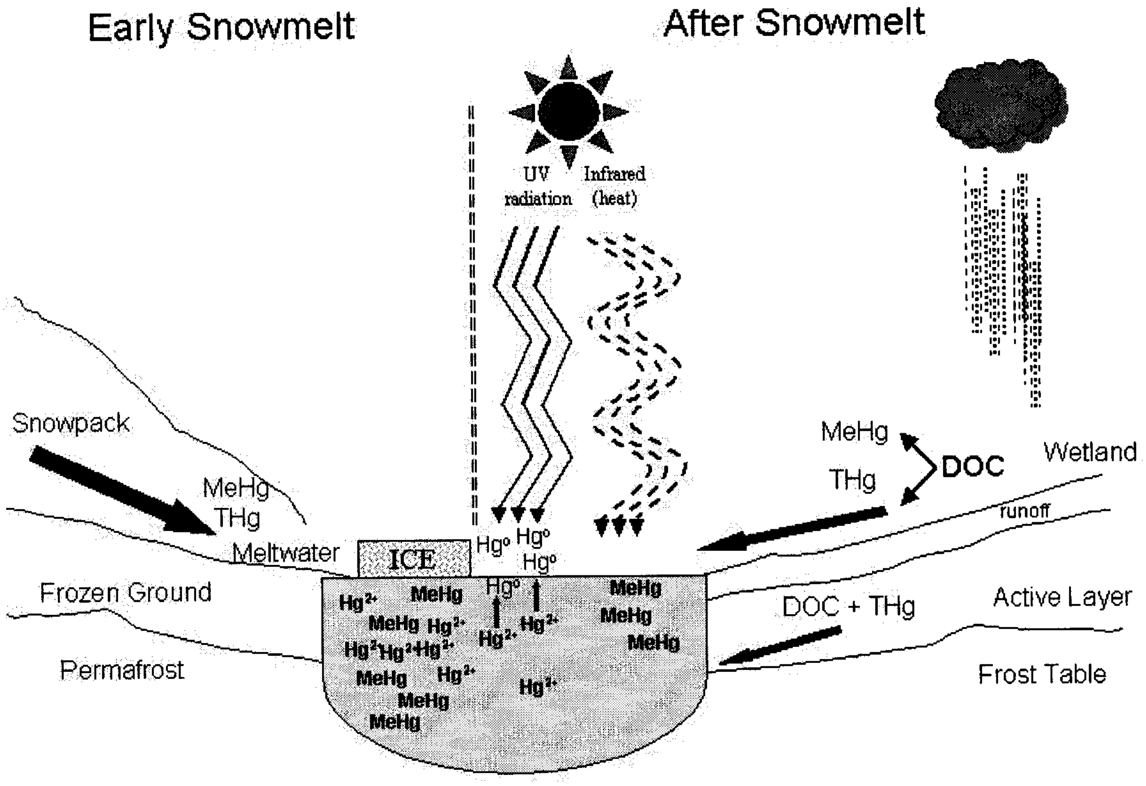

Figure 3.15 Schematic of processes effecting the lake THg and MeHg concentrations in the High Arctic.

3.3.3a Wetland Transect Study

Spatial and temporal trends in Wetland MeHg

MeHg concentrations were generally low ranging from the detection limit of our instruments (0.02 ng L^{-1}) to 0.11 ng L^{-1}, the mean was 0.055 ng L^{-1} ($\sigma = 0.017$). An interaction was observed between the sampling date and the sample location along the wetland transect ($p < 0.01$). The interaction appeared to be driven by the high MeHg levels at inflow at the beginning of the season. The inflow showed a temporal gradient that was not as prevalent at the middle and outflow of the wetland (Figure 3.16), where MeHg is high early in the season (0.1 ng L^{-1}) that drops and remains low (around 0.04ng L^{-1}) until the end of the warming season. The middle and outflow show lower MeHg concentrations at the beginning of the season that slightly increase throughout the growing season. There is little spatial variability among the wetland sampling sites, but the mean MeHg at the outflow is slightly higher than the middle and inflow (Table 3.16).

MeHg and THg were positively correlated ($r = 0.51$; $p < 0.05$), but this relation is most prevalent at the inflow ($r = 0.78$; $p < 0.05$), whereas the middle and the outflow had little association. Highest correlations at the inflow were caused by the high concentrations of both MeHg and THg at the beginning of the season that then drop. Other physical and chemical parameters measured did not show significant associations with MeHg concentrations in the wetland, including DOC.

Spatial and temporal trends in Wetland THg

THg concentrations throughout the wetland were low relative to the prior measurements in this chapter, ranging from 0.3 ng L^{-1} to 1.65 ng L^{-1} having a mean of

0.89 ng L^{-1} ($\sigma = 0.34$ ng L^{-1}). THg differs spatially and temporally across this wetland (Figure 3.17). THg fluctuated over time throughout the season ($p < 0.01$), the highest levels occur at the beginning of the season then drop, and increase again in the middle of the warming season and drop once more, after which concentrations slowly begin to increase again (Figure 3.17). The THg peak in the middle of the season took place after a large rain event in which 15mm was measured by the Resolute Meterological station. Mean THg is lowest at the inflow and increases in the middle and is highest at the outflow ($p = 0.045$) (Table 3.10).

Throughout the wetland THg was positively correlated with DOC ($r = 0.56$; $p < 0.01$), as well as water temperature ($r = 0.38$; $p = 0.08$), correspondingly, DOC and water temperature were positively correlated ($r = 0.7$; $p < 0.01$) (Figure 3.18). The THg positive relation with DOC and water temperature were most pronounced in the middle and outflow, as seen with the closely followed peaks and drops (Figure 3.19). The DOC and THg relation showed that with every 1mg L^{-1} increase in DOC, THg increased by 0.28ng L^{-1}. Concentrations of DOC were generally low ranging from 1 to 3 mg L^{-1}, which is common in Arctic systems. DOC in the wetland water changed throughout the growing season ($p < 0.01$) but remained relatively uniform in space across the wetland.

Wetland surface water temperature differed over time as it fluctuated between 4 and 12°C ($p < 0.01$), and temperatures did not significantly differ spatially across the wetland. The water temperatures were regressed with the mean air temperatures for Resolute Bay and relations were strongly positive. Correlation coefficients were weakest at the inflow and highest at the outflow and ($r^2 = 0.65, 0.68, 0.76$ respectively; $p < 0.05$).

Dissolved inorganic carbon (DIC) was much higher than DOC ranging from 14 to 30 mg L^{-1}, concentrations were the same over space and all sites showed an increase over the course of the season ($p = 0.01$) (Table 3.10). The pH was basic and did not show any temporal variation, but was less basic at the inflow relative to the middle and outflow ($p < 0.01$). The conductivity of the wetland surface water was often near 150 µS and showed no spatially variability, but did increase with time ($p < 0.05$).

Table 3.10. Water chemistry means at the inflow middle and Outflow during the warming season (n=7, MeHg n=14).

	MeHg (ng L-1)	**THg (ng L-1)**	**DOC (mg L-1)**	**DIC (mg L-1)**	**pH**	**Conductivity (µS)**
Inflow	0.053 ± 0.009	0.73 ± 0.16	2.29 ± 0.1	20.2 ± 1.2	7.6	132.6
Middle	0.049 ± 0.004	0.89 ± 0.09	2.11 ± 0.2	20.9 ± 1.7	8.0	155.5
Outflow	0.06 ± 0.003	1.04 ± 0.11	2.29 ± 0.1	22.2 ± 2.0	8.0	147.3

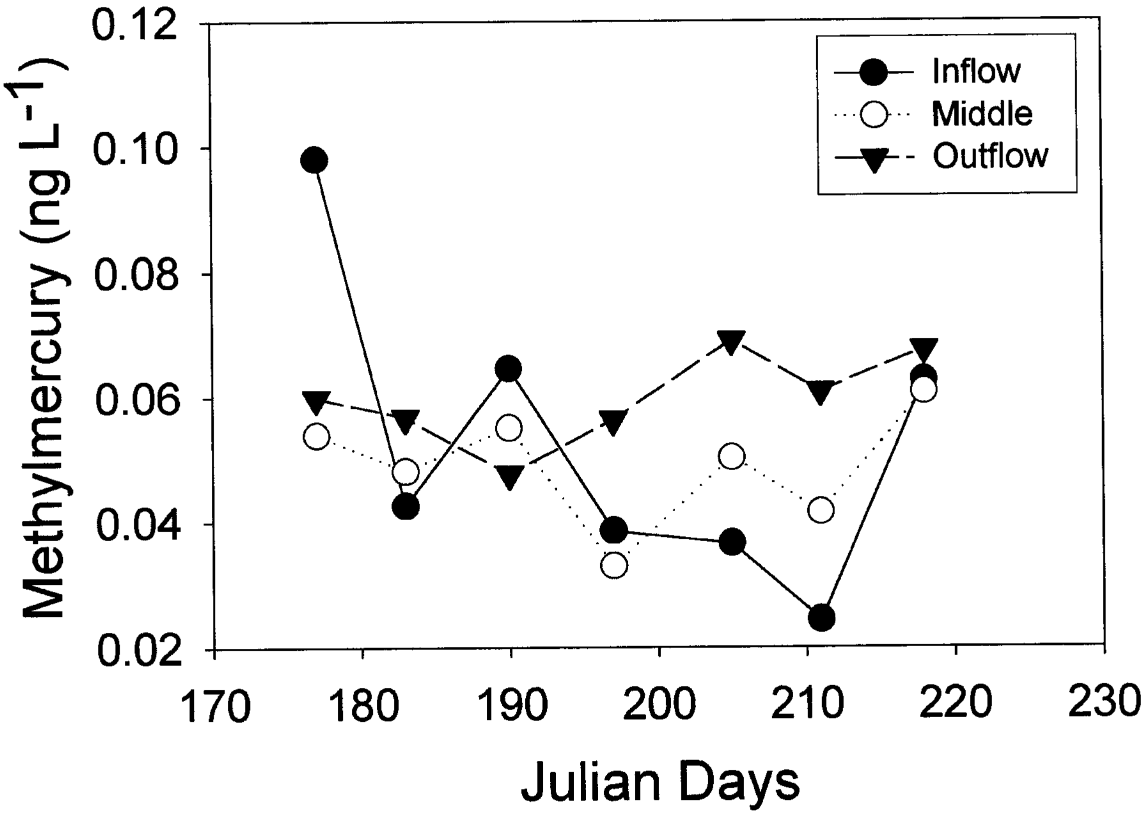

Figure 3.16 MeHg concentrations throughout the season at the inflow, middle and outflow of the wetland transect.

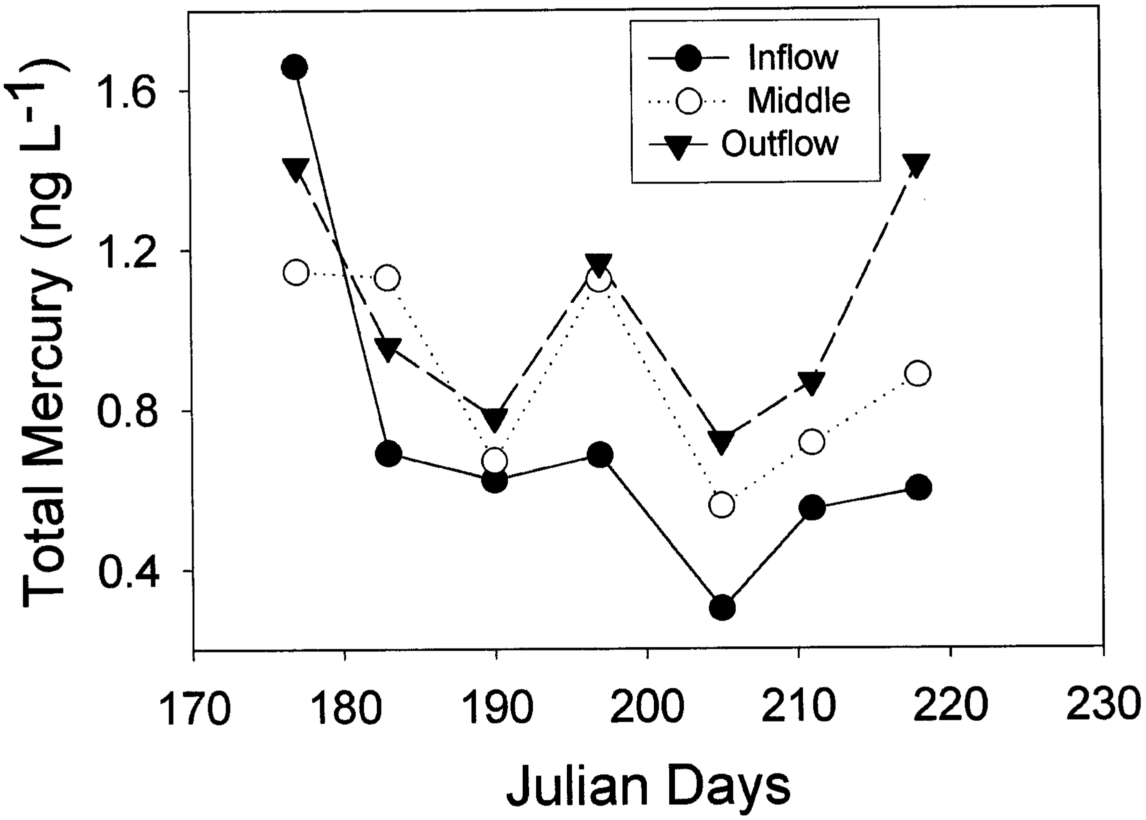

Figure 3.17 THg concentrations throughout the season at the inflow, middle and outflow of the wetland transect.

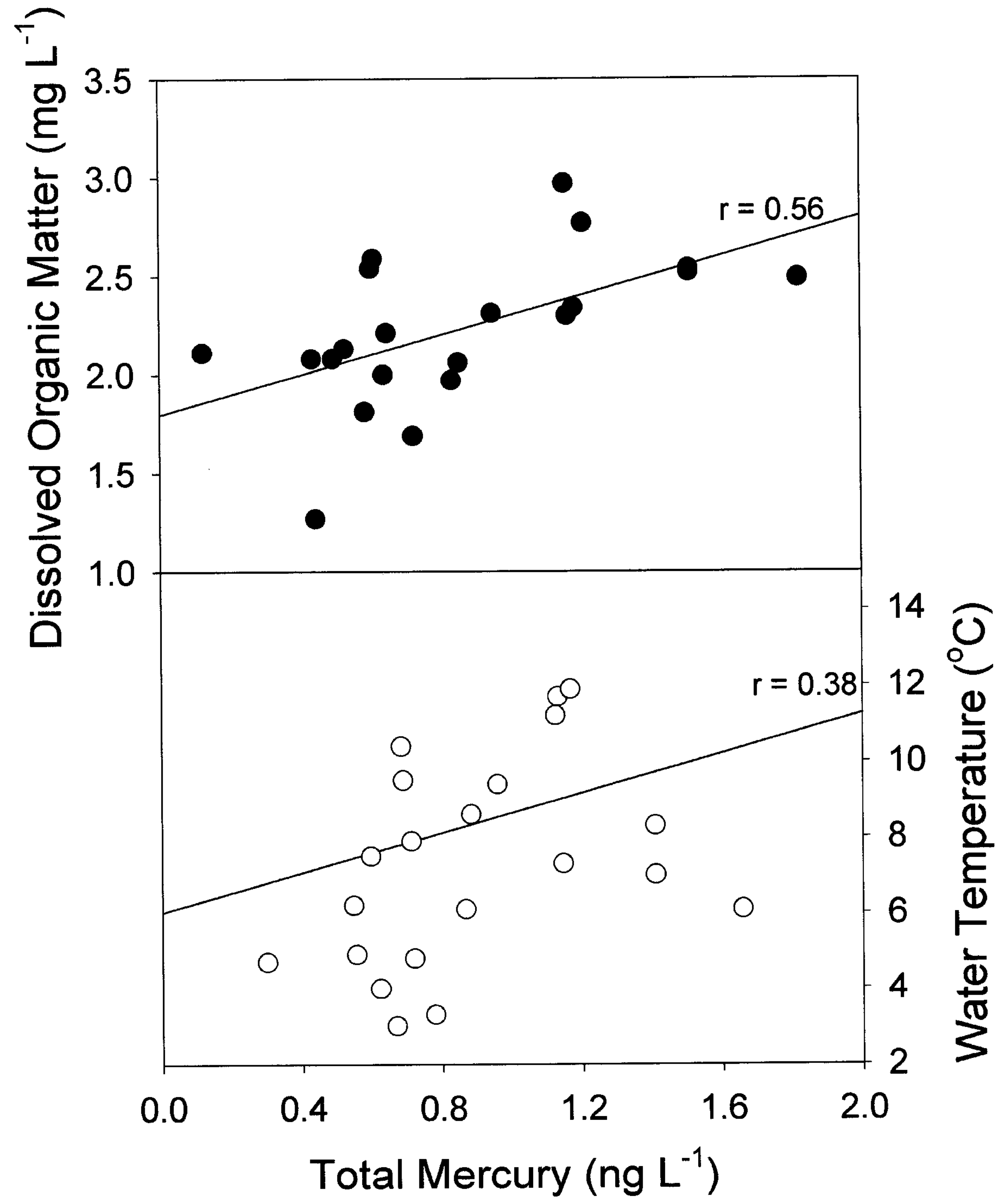

Figure 3.18 THg concentration plotted against DOC and water temperature in wetland surface water leaving three basins entering Hok, Small and Coastal Lake.

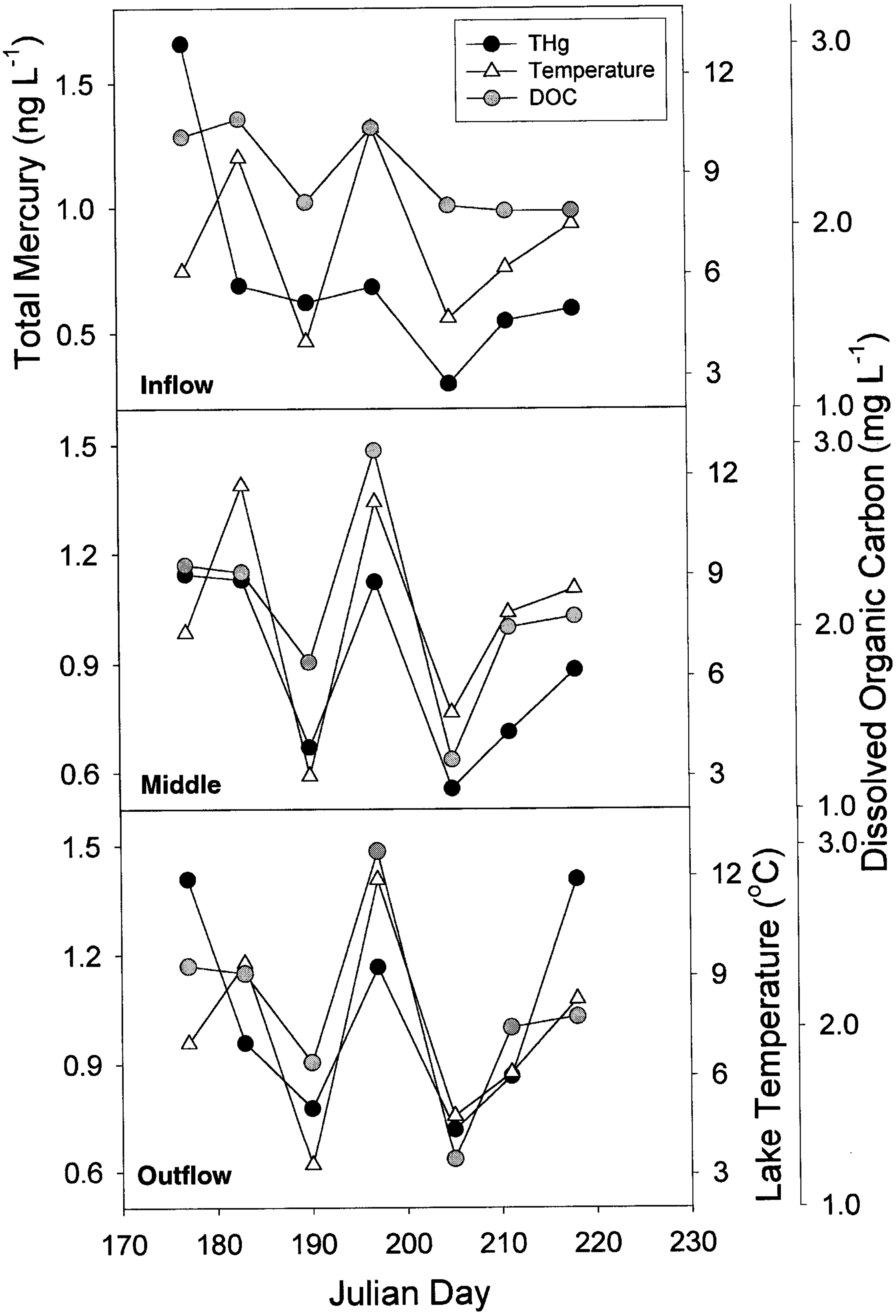

Figure 3.19 THg, DOC and water temperature at the inflow, middle and outflow of the wetland transect.

3.3.3 b Wetland Transect Study Discussion

Wetland MeHg dynamics

This wetland was not providing a major source of MeHg to the downstream lake, as seen by the low MeHg concentrations leaving the wetland at the outflow. Throughout the warming season there was no significant additional MeHg observed within the wetland that would distinguish it as important source to the downstream lake. Highest MeHg concentrations were measured at the beginning of the season at the inflow that was never reflected at the outflow, suggesting this site was a sink for MeHg, rather than a source. This is in contrast to what was observed in Loseto et al., (in press) where wetland outflow concentrations were high, suggesting wetlands are sources. The initial high levels of MeHg at the inflow suggest that snowmelt inputs are important, similar to findings in at the Amituk basins and at the Lake Study.

The low MeHg levels at this wetland are similar to levels in the basin surface wetland waters that entered Small Lake and Hok Lake (Lake Study). The DOC levels at those wetlands were also similarly low to the DOC levels reported at this wetland. Although MeHg and DOC did not show a strong relation the overall low MeHg and DOC levels support the notion that low levels of MeHg are associated with lower DOC levels (< 3 mg L^{-1}). The wetland surface water entering Coastal Lake had higher MeHg concentrations that were positively associated with DOC levels generally above 3 mg L^{-1}. This phenomenon is observed again in next section of this chapter (Eastwind Lake Study). Therefore, it appears that when DOC is below 3 mg L^{-1}, MeHg is generally lower (< 0.06 ng L^{-1}). This generalization does not hold true for the early season observation at the wetland, where MeHg is high and DOC is low. This anomaly was likely caused by snowmelt water inputs of MeHg from the remnant snowbank that had no association with DOC. DOC is often positively associated with MeHg in temperate systems [40,51]. As described earlier in the Lake study discussion DOC acts as a UV inhibitor for Hg^{2+} photodegredation, and has been suggested to protect or shield MeHg from photodegredated by UV radiation as well [52].

Critical DOC levels influencing MeHg dynamics have been document in previous studies [51] [53] showing that levels below 6mg L^{-1} in lake water had lower MeHg and THg than in lakes with DOC concentrations higher than 6mg L^{-1}. Although those relations describe lake systems perhaps water from wetlands operate in a similar manner, but under different ordinations whereby 3 mg L^{-1} of DOC represents an important threshold. Associations with DOC at certain concentrations may represent a shift in DOC structure, as MeHg is found to be strongly associated with particular types of DOC, such as humic substances [40].

This wetland is not a significant source of MeHg to the downstream lake, which is hypothesized to be due to the low levels of DOC that may control MeHg transport or influence photodegredation processes within the wetland.

THg Temporal Fluctuations

In this system THg was shown to be strongly associated with DOC. The temporal fluctuations of THg were unique to this study. In the previous Lake and Amituk basin studies, THg was high at the beginning of the season that then diminished for the remainder of the summer. The amplitude of THg fluctuations of 0.4 to 0.6ng L^{-1} of which only 0.1ng L^{-1} could be associated with analytical error is quite high. Perhaps the fluctuations may effectively portray wetland processes at the atmospheric and soil interface. The shallowness of the surface water may enable high resolution of processes and may not mask the interactions of variables that may become diluted in large lakes.

The THg and DOC levels are relatively low compared with temperate systems, but the relation among them was similar to temperate systems [51,54,55]. In temperate lakes an increase in 1mg L^{-1} of DOC equated to an increase in THg of 0.20ng L^{-1}, whereas THg in the wetland transect water showed an increase of 0.28ng L^{-1}, suggesting that similar DOC and THg regulating mechanisms are present in the Arctic. As described earlier (Lake Study) DOC is thought to shield THg from photodegredation, which may explain relations here.

The following will attempt to explain the temporal patterns of THg and DOC observed at this wetland site. Water temperatures also fluctuate with THg and DOC, and therefore may be an important driving force in the DOC and THg temporal fluctuations (Figure 3.20). Increases in water temperature would further ground ice thaw that may resurface and change hydrological conditions of the wetland. More importantly, water resurfacing from ground ice thaw may release and/or redistribute more DOC to the wetland surface, that may alter the THg concentrations. Groundwater THg levels were measured to be relatively high and associated with DOC in the lake study, thus any groundwater resurfacing may increase THg. Small increases in the water temperature may also induce microbial activity (i.e. decomposition) that could in turn alter the DOC levels to be higher, but this activity may be insignificant as it takes hundreds of years to produce DOC. Therefore, if temperature is controlling the THg and DOC fluxes it is more likely that ground thaw and subsequent groundwater movement are determining factors of DOC and THg levels.

Processes described above may work together with the hydrological conditions to explain the temporal observations as well (Figure 3.20). From the previous sections large amounts of THg was supplied by snowmelt, which explains the early season levels across the wetland. The drop in THg would reflect reduced snowmelt water THg inputs, and the peak that follows may have been caused by the large precipitation event a day prior that may have enhanced groundwater resurfacing. Clearly, many processes and variables can influence the THg and DOC fluctuations, therefore a flowchart is provided to demonstrate how variables may work together to influence the peaks observed in THg at the wetland transect (Figure 3.20). This is by no means a complete description of processes involved, but it gives an idea of the complexity involved in interpreting fluxes in THg.

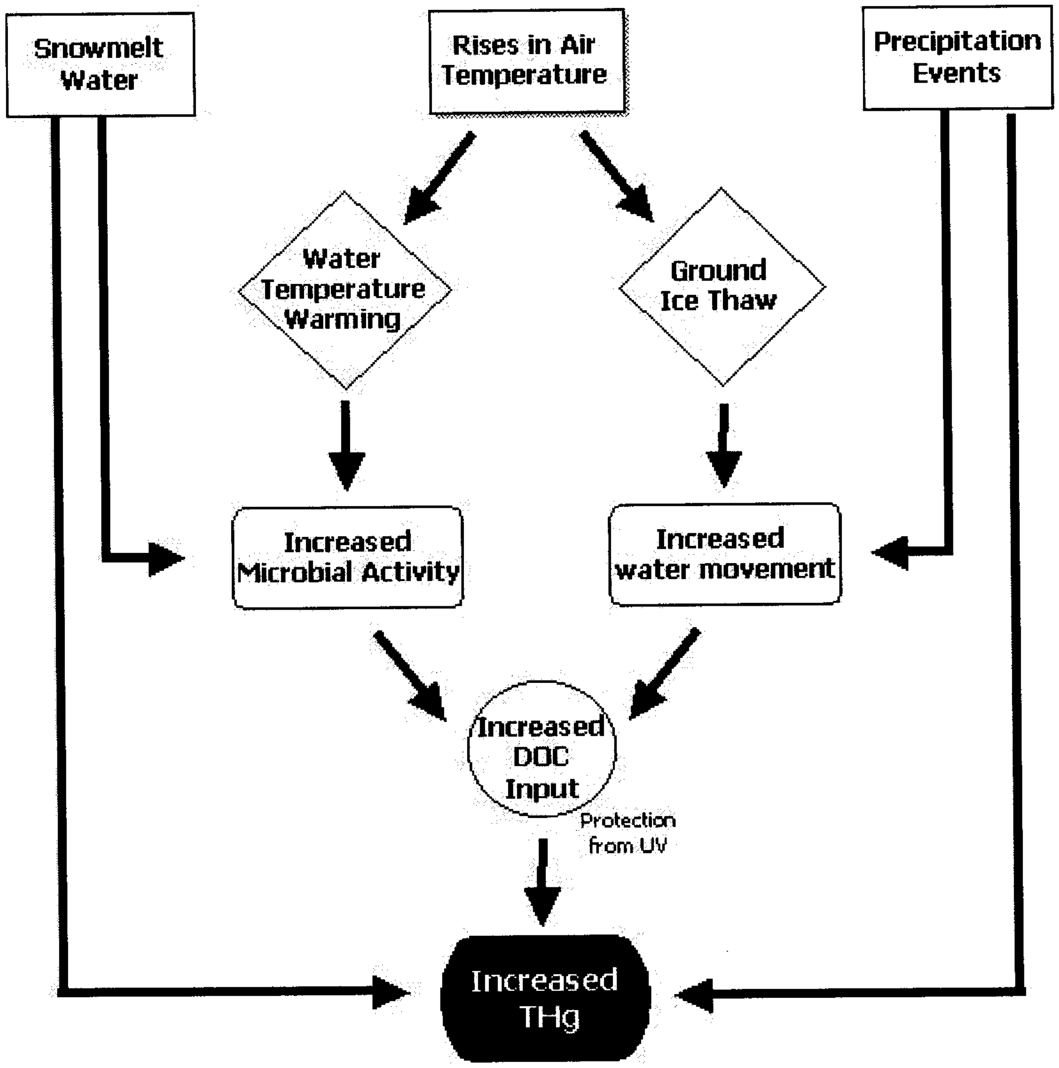

Figure 3.20 Flow chart showing how a variety of variables can influence the THg concentrations in wetland surface water.

3.3.4a Eastwind Lake Study Results

At the three tributaries evaluated, MeHg was not detectable in the tributary with no wetland presence and in the tributary that entered a wetland prior to reaching Eastwind Lake. The wetland stream had a mean MeHg concentration of 0.085ng L^{-1} and ranged from 0.050ng L^{-1} to 0.13ng L^{-1} (Figure 3.21). THg concentrations varied among the basins, the tributary with no wetland presence had THg concentrations near the detection limit, and the tributary that entered the wetland had mean concentrations of 0.59ng L^{-1} ($\sigma = 0.12$ng L^{-1}) and highest concentrations were present at the wetland basin (Figure 3.21).

MeHg and THg at the wetland basin showed spatial variability. The lowest MeHg concentration was near the top of the inflow, and the concentrations increased along the stream with distance toward the outflow, reaching the highest concentrations ($r = 0.93$) (Figure 3.22). On the contrary, THg was high at the inflow (1.0 ng L^{-1}) and decreased toward the outflow to concentrations near the detection limit (Figure 3.22). However, the highest THg concentrations (1.3 ng L^{-1}) were measured at the outflow of the wetland transect (Figure 3.22). THg concentrations averaged 0.7ng L^{-1} ($\sigma = 0.4$ ng L^{-1}).

The tributary that entered a wetland prior to the lake displayed spatial variation along the tributary with lowest THg concentration near the headwaters (i.e. 0.4 ng L^{-1}) and highest concentrations at the outflow (0.70 ng L^{-1}). The tributary with no wetland influence had levels near detection limit throughout the transect.

DOC levels were highest at the wetland tributary, and the lowest levels were at the tributary with no wetland presence (Figure 3.23). One DOC value of 16.5 mg L^{-1} was removed from the calculated DOC mean presented for the wetland tributary, because it appeared to be an outlier, although we believe it was a high value. DIC levels were also higher in the wetland tributary than the other two (Figure 3.23). Conductivity differed among the streams ($p < 0.01$), the wetland tributary averaged 340 µS ($\sigma = 50$), whereas the other two tributaries had levels between 30 and 40 µS (Table 3.11). Conductivity was also positively related to MeHg concentrations ($r = 0.77$; $p = 0.07$, n = 6). Temperatures were highest at the wetland stream (10°C), probably due to the slower hydrological flow relative to the other streams that had lower temperatures near 5°C ($p < 0.01$). The pH in streams were close to neutral, and did not differ from stream to stream (Table 3.11).

Table 3.11 Mean Conductivity, water temperature and pH at the three tributaries entering Eastwind Lake (n = 6)

Tributaries	**Conductivity (µS)**	**pH**	**Water Temp (°C)**
Wetland Stream	336.8	7.5	10.3
Half Wetland Stream	41.4	7.3	6.6
Non wetland Stream	35.7	7.2	4.9

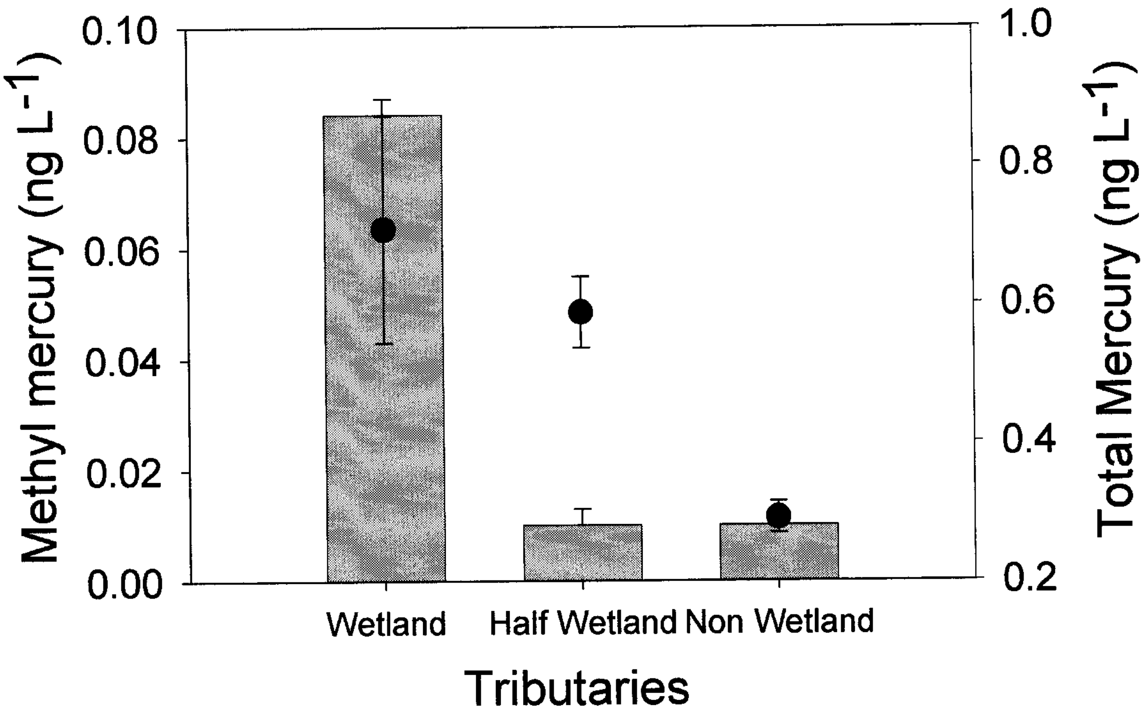

Figure 3.21. Mean MeHg (bars) and THg (closed symbols) at the three tributaries entering Eastwind Lake in late July. Error bars represent the standard error (n=6).

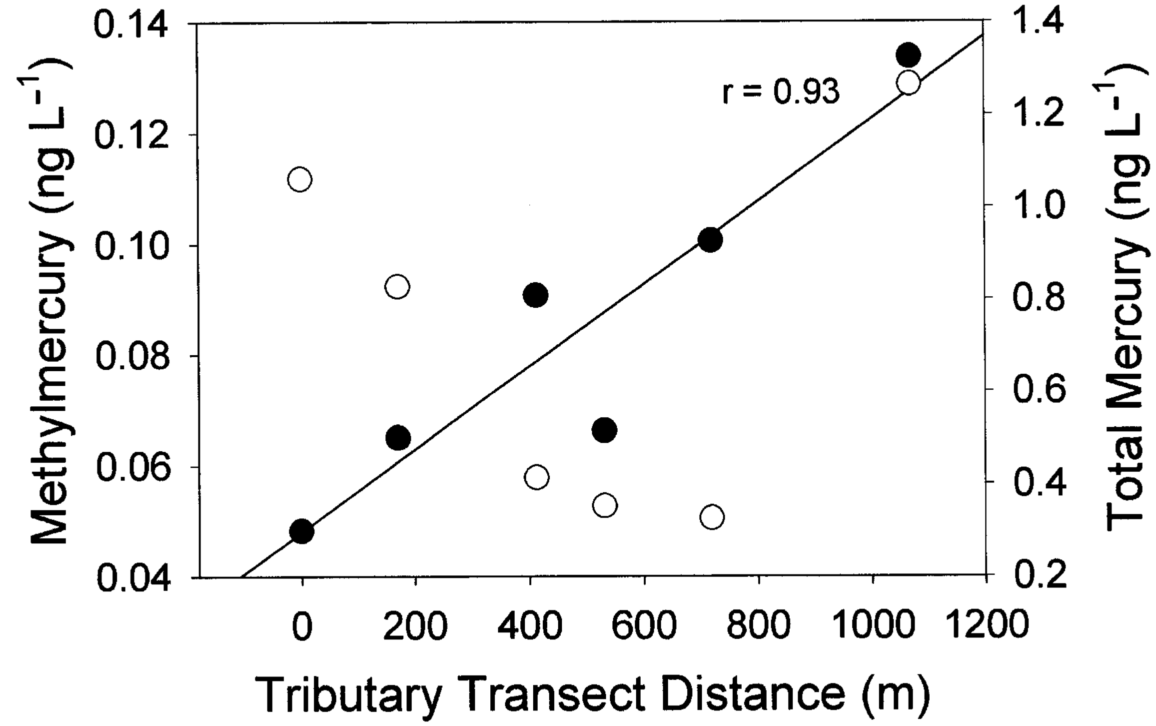

Figure 3.22 MeHg (closed symbols) and THg (open symbols) concentrations along the wetland stream, beginning at the headwater moving toward the outflow to Eastwind Lake.

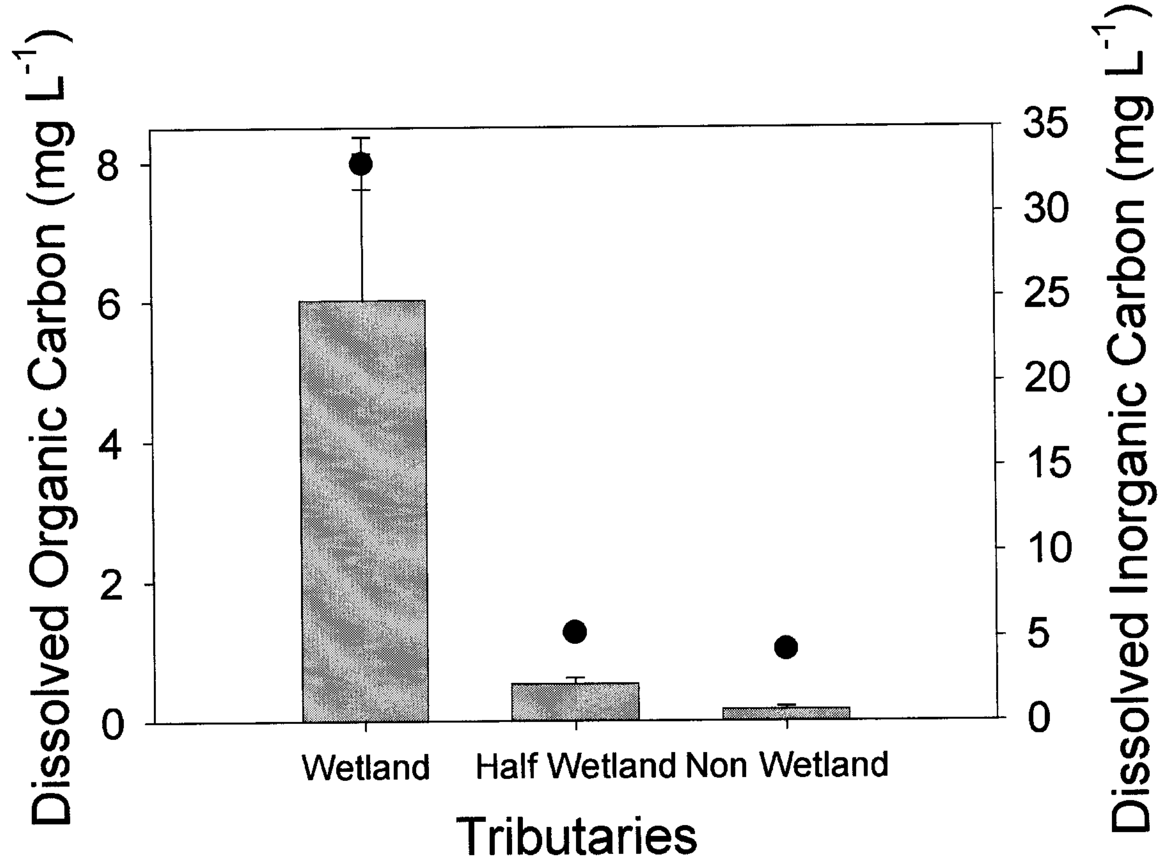

Figure 3.23 Mean DOC (bars) and DIC (closed symbols) at the three tributaries entering Eastwind Lake sampled in late July. Error bars represent the standard error of the mean (n=6).

3.4.4b Eastwind Lake Study Discussion

This study was used as a checkpoint to evaluate MeHg and THg levels outside of Cornwallis Island. Results proved valuable in supporting previous observations and hypothesise. The wetland stream did represent a source of MeHg to the downstream lake (Eastwind Lake), whereas the other two tributaries were not sources of MeHg. The observation of MeHg increases along the wetland toward the lake suggested within-wetland production and a further release of MeHg to Eastwind Lake. This wetland stream was unlike the wetland chosen for the transect study on Cornwallis Island which did not operate as a source of MeHg. DOC concentrations at the Eastwind wetland stream site were higher (> 3 mg L^{-1}) than those observed in the Wetland Transect Study, again supporting the important role of DOC as a determining variable of MeHg in Arctic wetland systems.

The decreasing THg concentrations along the wetland stream corresponded with increases in MeHg concentrations suggest biological uptake of Hg by Hg methylators that produced MeHg along the wetland. Not all Hg was methylated as the MeHg levels are too low to account for the entire reduction of THg. The high concentrations at the output better resemble findings from Loseto et al., (in press) as highest levels were also at the wetland outflow.

The peak of THg at the end of the tributary did not fit the decreasing trend along the wetland stream. This particular sample was taken very close to the lake where the water was stagnant and inundated at the lake mouth; therefore the concentration may better represent lake THg concentrations, rather than the stream.

The other two tributaries with little to no wetland presence served as good comparisons to the Amituk basin tributaries during low flow, as they were at low flow when sampled. MeHg and THg at Amituk dropped to detection limit during low flow, which also occurred here. This supports that after snowmelt there are no more significant MeHg and THg inputs from the streams. THg, in the tributary that entered a wetland increased at the bottom of the tributary as it passed through a wetland. This may have been caused by a shift in landscape physiography. The top of the tributary was rocky and water flow was relatively fast, whereas at the bottom the stream flow decreased as it passed through the wetland consequently changing chemistry dynamics that altered THg levels.

The overall high THg and MeHg levels in the wetland stream may have also been influenced by high resident times due to the slower flow rates relative to the fast flowing streams. Resident times were not determined but are suggested to be longer in the wetland stream by the higher water conductivity, DIC levels and warmer water temperatures. The higher DIC and conductivity were probably caused by the enhancement of solutes by groundwater inputs that may be resurfacing. Stagnant water over the wetland may have increased the probability to methylate any available Hg. Residence time has shown to be an important factor influencing MeHg levels in temperate lake systems [52].

MeHg and THg concentrations at the tributaries in the Fosheim Peninsula were similar to those measured at Cornwallis Island supporting that Cornwallis Island is a good representative of High Arctic islands when evaluating MeHg and THg levels. Wetlands on the Fosheim Peninsula are much more lush than those across the Queen

Elizabeth Islands [23], yet the concentrations and observations did not differ significantly. DOC levels were slightly higher probably due to higher decomposition rates in the more productive ecosystem. The higher DOC and MeHg levels at the wetland stream again support the importance of DOC as a factor influencing sources of MeHg to downstream lakes. Therefore, Eastwind watershed results showed that when the major snowmelt event is over, wetlands can proceed to dominate as MeHg sources to downstream lakes.

3.4. SUMMARY DISCUSSION AND CONCLUSION

The findings from each study are summarized in table format below (Table 3.12).

Table 3.12 Summary of major findings at each field study

Study Site	Summary of Findings
Amituk Watershed	Snowmelt water supplies a large source of MeHg and THg to Arctic Lakes
Lake Study	Lakes with wetlands in their watershed did not show responses of higher MeHg in lake water MeHg in wetland surface water increased with rises in DOC levels Wetlands yields of MeHg were low relative to Amituk basins and yields in temperate environments External environmental factors may influence Lake MeHg and THg
Wetland Transect	This wetland was not a source of MeHg, rather it was a sink THg fluctuated with DOC and temperature throughout the season
Eastwind Lake	MeHg and THg levels were similar to those observed on the Cornwallis Island study sites Wetland stream was a source of MeHg, and had high DOC levels MeHg and THg were low at low flow in tributaries

3.4.1 Snowmelt water inputs of MeHg to the High Arctic (2H)

Yields of MeHg leaving the Amituk basins were higher than those measured in temperate catchments characterized by wetlands. The high yields were largely a result of the high discharge at the Amituk basins, that may not be representative of most Arctic basins, however snowmelt water inputs do dominate the Arctic hydrological regime (60 to 80% of annual precipitation storage) and is therefore an important transport vector that cannot be discounted.

Snowmelt water was not specifically evaluated at the lake study sites, nor at the wetland transect study, but results from both supported the importance of snowmelt water inputs of MeHg and THg. That is, in all lakes, MeHg and THg concentrations were highest in the earlier season, which was nearing the end of the major snowmelt pulse. MeHg and THg were also highest in concentration on the first sampling day at the wetland transect. Hence, high MeHg and THg measured in the early season at these studies suggest that snowmelt water inputs to Arctic ecosystems are important sources. The Eastwind Lake study indirectly supported snow as a source with the non detectable MeHg and THg levels in streams during low flow after the major snowmelt event.

Snow, prior to melt, was not evaluated as a source of MeHg, however; one snow sample was obtained on July 29, after a snow event in Resolute. The MeHg concentration measured in this sample was the highest observed of all the samples collected in the studies. Just over 0.25 ng L^{-1} was measured, whereas most snowmelt water samples were around 0.1ng L^{-1}, THg in the sample was 6ng L^{-1}, which was also high relative to the other snowmelt water samples measured. Although a sample size of only one, it suggests that snow may contain an important source of both MeHg and THg that is then supplied in snowmelt water to Arctic ecosystems. As mentioned earlier, few studies have measured MeHg in snow largely because it does not represent a significant amount of input relative to rain events in temperate environments, but reported concentrations for two snow samples obtained by Loius et al., (1995) were also high. Unlike temperate systems where rain dominates the precipitation events, it is the snow accumulated throughout the year, which melts in a very short time frame that represents an important input source to the Arctic. Therefore, snowmelt water is an important source of MeHg to Arctic ecosystems.

3.4.2 Wetland MeHg inputs to Arctic systems (3H)

Results from studies evaluating wetlands as sources varied from wetlands providing significant amounts of MeHg, to wetlands acting as MeHg sinks. Although lake MeHg concentrations did not reflect basin wetland presence, this did not disclaim wetlands as sources. Many in-lake processes such as demethylation, photodegredation and biological uptake could have masked any effects of wetland inputs of MeHg. Yields calculated for the wetland basins were lower than yields representative of temperate wetland systems, and those calculated for the Amituk basins, suggesting that wetlands were not significant sources of MeHg.

On the other hand determining wetlands as sources of MeHg may be site dependent, as seen with the Eastwind Lake wetland stream and the wetland on Cornwallis Island. The wetland on Cornwallis Island appeared to function as a sink as highest MeHg concentration were observed entering the wetland as opposed to exiting the wetland. In contrast, the wetland stream entering Eastwind Lake had highest concentrations leaving the wetland, and the lowest entering it.

Throughout the studies, DOC levels appeared to generally predict MeHg concentrations in wetlands and moreover their importance as sources of MeHg to downstream lakes. Highest MeHg concentrations were measured in wetland surface water with DOC levels above 3 mg L^{-1}, (Coastal Lake basin, Eastwind wetland stream). The reverse occurred at Small Lake and Hok Lake wetland surface water had low MeHg that corresponded with DOC levels below 3 mg L^{-1}. Low MeHg along the wetland transect also supported the DOC hypothesis, as DOC levels were never above 3mg L^{-1}. Due to the consistent MeHg and DOC relations, concentrations obtained at all studies were combined and regressed. The results show a significant positive relationship (r^2 = 0.55; $p < 0.01$, n = 44) that suggests DOC levels may predict MeHg concentrations across all Arctic wetlands. The means by which DOC can predict MeHg levels is not well understood [56], DOC may facilitate MeHg transport and or reduce photodegredation by UV radiation.

Based on the findings above, whether wetlands are sources of MeHg is dependant on site characteristics such as DOC levels, but in most situations wetlands were not important sources of MeHg to Arctic lake systems.

3.4.3 Other external variables influencing MeHg and THg

Synchronous temporal fluxes in MeHg and THg in lakes suggested external environmental variables influenced the levels. The drop in lake THg after lake ice retreat along with DOC levels often below 2 mg L^{-1} supported that photodegradation by UV radiation is important in reducing THg in lake water.

MeHg in lakes appeared fluctuate in relation to external climatic variables, specifically precipitation events and rising air temperature. It is unclear which variable is predominates and by what means, and thus need to be further evaluated especially in light of climate change, as both are predicted to increase in the Eastern Arctic.

3.4.4 Concluding Statements and Future Research

This was the first study to evaluate sources of MeHg to Arctic ecosystems, it was also the first to examine snowmelt water as a source of MeHg. Results revealed that snowmelt water was the most important measured source of MeHg to Arctic ecosystems. Although, wetlands can produce MeHg, the role of wetlands as sources of MeHg is site dependant on factors such as DOC levels and the amount of water leaving the wetland. Once the major snowmelt event is over, wetlands may begin to function as sources of MeHg, but have to compete or be reduced by many variables such as biological uptake and photodegredation.

This study is the first step in understanding how MeHg is entering Arctic ecosystems to be further biomagnified to toxic levels in the biota. Processes producing the sources of MeHg in snowmelt water was not examined here, however it is hypothesized that the Hg deposited during MDE's is utilized for methylation to MeHg. Hg methylation processes may be unlike those in temperate systems since the source pathway of elemental Hg (MDE's) is endemic to the Arctic. Hence, future work should focus on the processes supplying or producing MeHg in snow and in snowmelt water.

Further, the fate and transport of MeHg in snowmelt water also needs to be evaluated as it may represent the primary supply to Arctic aquatic ecosystems that is then biomagnified up food webs.

Elemental Hg entering the Arctic during MDE's is thought to be a recent phenomenon and is predicted to increase with climate warming as rising temperatures will diminish sea ice cover and facilitate BrO to the atmosphere from the Arctic Ocean [11], which partly drives the photooxidation of Hg out of the atmosphere onto snow. Thus, MeHg formation in snow and the fate of MeHg in snowmelt water requires further study in light of climate change perturbations, as more Hg may be deposited onto Arctic snow that may be methylated and then transported in snowmelt water, providing more MeHg available for biomagnification in the Arctic biota to toxic levels above the dietary guidelines.

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