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The Contribution of Snow Meltwater to the Annual Export of Methyl Mercury from Temperate Shield Ecosystems

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THE CONTRIBUTION OF SNOW MELTWATER TO THE ANNUAL EXPORT OF METHYL MERCURY FROM TEMPERATE SHIELD ECOSYSTEMS

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Abstract

Methylmercury (MeHg), the known toxic form of mercury is generally only 1-3% of total mercury (THg) in precipitation. As such it was thought to be an insignificant source to aquatic ecosystems; however, since other forms of mercury can be re-volatilized from the snowpack back to the atmosphere shortly after deposition the proportion and biological significance of MeHg in the snowmelt runoff is indeed an important source to downstream ecosystems. To assess the seasonal contribution of MeHg in runoff to the overall annual load of MeHg, the tributaries of two lakes, Dickie (DE) and Harp (HP) in the Haliburton-Muskoka district of Ontario were sampled on a weekly basis for MeHg, dissolved organic carbon (DOC) and conductivity over two years. Stream discharge was monitored on a continuous basis. In order to assess the amount of MeHg in the snowpack, snow cores from the watersheds were sampled during early spring. Additionally, bulk precipitation samples were collected using a wet-dry automated precipitation collector in the mercury deposition network (MDN) operated station in St. Anicet, Quebec every 4-6 weeks, for 26 months. The samples were analyzed for MeHg, and an annual deposition rate was calculated. THg and MeHg data obtained from the MDN was used to calculate a deposition rate for THg, and the proportion of MeHg. THg in wet deposition was 5.29-6.88 $\mu g\ m^{-2}\ year^{-1}$, and MeHg was 0.15-0.19 $\mu g\ m^{-2}\ year^{-1}$ and equivalent to 2.7-2.9 % of THg. Although low MeHg concentrations were measured in runoff during spring freshet, the high discharge rates resulted in quantities which were up to 33.9% of the annual amount of MeHg. The seasonal contribution of MeHg in runoff was found to be: spring>summer>fall> winter for the wetland rich DE and fall> spring> winter> summer for the wetland dull HP. Multiple regression analysis illustrated that DOC was the most significant predictor of MeHg (r^2=0.32, $p<0.01$) across all data with a strong seasonal dependence of the DOC-

MeHg correlation. The strongest correlation was found during spring freshet (r^2=0.65, p=0.001) followed by summer, winter and fall (r^2= 0.37, 0.23 and 0.22 respectively, $p<0.05$ for all). The constant flow of water during the winter and strong correlation with DOC during snowmelt suggests a terrestrial source of MeHg even during the winter months, however, direct precipitation during spring and snowmelt were also found to contribute to the MeHg load during snowmelt runoff.

Résumé

Le méthylmercure (MeHg), connu comme étant la forme toxique du mercure ne constitue généralement que 1-3 % du mercure total (THg) dans les précipitations. De ce fait, les précipitations étaient jadis reconnues pour être une source négligeable pour les écosystèmes aquatiques. Cependant, étant donné que d'autres formes de mercure peuvent être revolatilisées dans l'atmosphère à partir de la couverture de neige peu après la déposition, l'importance biologique et la proportion du MeHg dans l'écoulement généré par la fonte des neiges est vraisemblablement une source importante aux écosystèmes en aval. Pour évaluer la contribution saisonnière du MeHg dans l'écoulement par rapport à la charge annuelle du MeHg, les tributaires de deux lacs, Dickie (DE) et Harp (HP) dans le district de Haliburton-Muskoka en Ontario ont été échantillonnés pendant deux ans sur une base hebdomadaire et des analyses de MeHg, de carbone organique dissout (COD) et de conductivité ont été effectuées. Le débit des cours d'eau a été suivi sur une base continue. Afin d'évaluer la quantité de MeHg dans la couverture de neige, des carottes de neige ont été échantillonnées tôt le printemps à l'intérieur de la limite des bassins versants. De plus, des échantillons de précipitation brute ont été récoltés à toutes les 4 à 6 semaines pendant 26 mois à l'aide d'un collecteur automatisé de précipitations humides-sèches par la station opérée par le *Mercury Deposition Network* (MDN) à Saint-Anicet, Québec. Le MeHg a été mesuré et un taux de déposition annuel a été calculé. Les données de THg obtenues du MDN ont été utilisées pour calculer le taux de déposition du THg ainsi que la proportion du MeHg. La concentration du THg était de 5.29-6.88 $\mu g\ m^{-2}\ an^{-1}$ et celle du MeHg était de 0.15-0.19 $\mu g\ m^{-2}\ an^{-1}$ dans les dépositions humides ce qui correspond à 2.7-2.9 % du THg. Bien que les concentrations de MeHg mesurées dans l'écoulement lors de la crue nivale printanière étaient basses, le haut débit a eu comme conséquence d'augmenter la

quantité annuelle de MeHg jusqu'à 33.9 %. La contribution saisonnière relative du MeHg dans l'écoulement était en ordre d'importance : printemps> été> automne> hiver pour DE, riche en milieux humides et automne> printemps> hiver> été pour HP, pauvre en milieux humides. Une analyse de régression multiple a démontré que le COD était le terme le plus significatif pour prédire le MeHg (r^2=0.32, $p<0.01$) à travers toutes les données avec une forte dépendance saisonnière de la corrélation COD-MeHg. La corrélation la plus forte a été trouvée pendant la crue nivale printanière (r^2=0.65, p=0.001) suivi par l'été, l'hiver et l'automne (r^2= 0.37, 0.23 et 0.22, respectivement ; $p<0.05$). L'écoulement constant de l'eau durant l'hiver et la forte corrélation avec le COD pendant la fonte des neiges suggèrent une source terrestre de MeHg et ce, même pendant les mois d'hiver. Cependant, les précipitations directes au printemps ainsi que la fonte des neiges ont aussi contribuées à la charge de MeHg pendant l'écoulement dû à la fonte des neiges.

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List of Abbreviations

BrCl- Bromine chloride

CAAA- Clean Air Act Amendments

CAMNet - Canadian Atmospheric Mercury Measurement Network

CV- AFS- Cold Vapor- Atomic Florescence Spectroscopy

DE- Dickie

DIW- De-ionized Water

DMeHg- Dimethylmercury

DOC- Dissolved Organic Carbon

EPA- Environmental Protection Agency

GEM- Gaseous Elemental Mercury

HAL- Hg Analytical Laboratories

HCl- Hydrochloric acid

HDPE- High Density Polyethylene

HP- Harp

MACT- Maximum Achievable Control Technology

MDN- Mercury Deposition Network

MDL- Method Detection Limit

MeHg- Methylmercury

NADP- National Atmospheric Deposition Network

OME- Ontario Ministry of Environment

POP- Persistent Organic Pollutant

QA/QC- Quality Control/ Quality Assurance

$SnCl_2$- Stannous chloride

SRB- Sulfate Reducing Bacteria

THg- Total mercury

TOC- Total Organic Carbon

UNEP- United Nations Environmental Program

USA- United States of America

UOttawa- University of Ottawa

UV- Ultra Violet

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1. Introduction

1.1. Background

Mercury (Hg), recognized internationally as a contaminant of concern (UNEP 2002; EPA 2006), has both the capacity for long-range atmospheric transport as elemental mercury (Hg^0) (Munthe and McElroy, 1992), and the ability to bioconcentrate and bioaccumulate through the aquatic food web (Lindqvist et al. 1991) as methyl mercury (MeHg). This results in high rates of mercury accumulation in the aquatic and marine food chains; such that the top predator animals including humans are exposed to potentially toxic levels.

MeHg can lead to adverse physiological and neurological effects that vary with the dose and exposure time. Low level chronic exposure has been shown to result in a decrease in attention, memory and language skills in humans (Grandjean et al. 2003; Castoldi et al. 2001; Davidson et al. 2004) and decreased reproductive success has been observed in wildlife species (Meyer et al. 1998; Wolfe et al. 1998). In humans, high exposure is known to cause symptoms such as trembling, ataxia, hearing and speech impediments and in severe cases even death (Harada, 1995). Such extreme poisoning has resulted in many deaths several times in modern history. The most well-known cases occurred in the 1950s-1960s in the Bay of Minamata, Japan (Harada, 1995), and in 1971-1972 in Iraq (Clarkson et al. 1976). These acute poisonings are rare and easily detected.

What is more difficult to assess, is the long term chronic exposure to MeHg. Recent epidemiological studies emphasize the importance of identifying the pathway leading to this persistent poisoning (Zahir et al. 2005), as its effects are widespread and severe.

Currently, mercury is one of only eight hazardous air pollutants for which the EPA set emission standards and is among the 189 hazardous air pollutants requiring

Maximum Achievable Control Technology (MACT) under Title III of the Clean Air Act Amendments (CAAA). Even with this effort to regulate and reduce emissions, and despite the fact that several studies have reported a decline in atmospheric mercury (Engstorm and Swain, 1997; Temme et al. 2003), MeHg levels found in pristine ecosystems and wildlife do not seem to be decreasing (Evers et al. 1998; Chase et al. 2001). This clearly illustrates that we have much to learn about the origin, fate and transport of mercury in the environment.

The work presented in this thesis is an attempt to identify the significance of inputs of MeHg arising from snow melt as an alternative source of MeHg to the aquatic ecosystem. Ironically, this source has previously been overlooked as MeHg in precipitation represents only 1% of THg (Grigal, 2002), and up until recently was considered insignificant. In order to establish the framework for the thesis and to quantify the importance of MeHg in snow, the first chapter is a literature review, presenting an overview of Hg cycling and some of its chemical interactions.

1.2. Rationale, hypothesis and objectives

In this study I focused on assessing the seasonal contribution of MeHg in runoff to the overall load of MeHg to two lakes in the temperate Haliburton-Muskoka district of Ontario, Canada. Based on recent findings of complex mercury chemical dynamics in the snowpack (discussed in detail in section 1.4.3), I hypothesized that after deposition and prior to snowmelt, much of the oxidized THg in the snow becomes photoreduced and is lost from the snowpack to the atmosphere. This process may have an effect on the relative amounts of THg and MeHg in the snowpack, increasing the relative importance of MeHg in snowmelt during the spring freshet, and making it a major contribution to the overall MeHg influx to temperate lakes.

Because wetlands are thought to be a major source of biological mercury methylation (as discusses in section 1.4), I predicted that the overall relevance of MeHg in spring freshet will be greater for lakes with fewer wetlands in their catchment than for wetland-rich lakes.

The objectives of this study were: 1) to measure MeHg concentration and deposition rate in precipitation, as well as to assess the proportion of THg in precipitation present as MeHg. 2) To assess the relative contribution of the MeHg during spring freshet to the annual budget of MeHg in runoff to Dickie and Harp Lakes. 3) To elicit the source of the MeHg in snowmelt runoff.

To achieve these objectives, I conducted two separate studies: The first, in the mercury deposition network (MDN) operated site of St. Anicet, bulk precipitation samples were collected using a wet-dry automated precipitation collector, and analyzed for the presence of MeHg. Using the data collected for the MDN I obtained the concentration of weekly precipitation samples, and calculated an annual deposition rate for both THg and MeHg in precipitation. Since the collected samples were stored in the dark until analysis, no photo induced chemical dynamics could occur, and the proportion of MeHg found represented the fresh deposition only.

The second study was designed to investigate the environmental relevance of the MeHg in snowmelt. The study was conducted in two lakes near the Dorset Environmental Science Center operated by the Ministry of the Environment (MOE). Ten tributaries to the lakes were sampled for MeHg DOC and conductivity on a weekly basis, and the discharge rate was recorded on a continuous basis. Using these data, I calculated the relative contribution of each season to the overall annual MeHg load, and used the DOC and conductivity temporal and spatial dynamics in an attempt to determine the origin of MeHg in the snowmelt. In the following thesis I will present the

details of this study in chapter 2, the results in chapter 3 and discuss the results and their implications in chapter 4. Chapter 5 will present a summary and conclusions from the study.

1.3 Sources and fate of mercury in the environment

Since the beginning of the industrial revolution, the global atmospheric reservoir of mercury has increased by a factor of 3 to 5 (Fitzgerald et al. 2005). According to estimates, human activities contribute 50 to 75% of the overall global input of Hg to the atmosphere every year (Lindqvist et al. 1991; Fitzgerald. 1995), primarily from fossil fuel combustion (Pacyna and Pacyna, 2002).

The ecological and toxicological effects of Hg, as well as its distribution and transport in the environment are strongly dependent on the chemical species present: Emission occurs primarily in the form of Hg^0, which is highly volatile and has a relatively long atmospheric residence time of 6 months to 3 years (Schroeder and Munthe, 1998). Long range transport of mercury in the atmosphere takes place as Hg^0 moves with wind currents but it is slowly oxidized to the mercuric state Hg^{2+}, mainly in the solid-liquid interface in fog and cloud droplets (Morel et al. 1998), with ozone the likely key oxidant in this process and sulfur dioxide as an important reactant (Munthe, 1992; Van Loon et al. 2000, 2001). Oxidized mercury and particulate mercury in emissions have much shorter atmospheric residence times (Morel et al. 1998).

The deposition of Hg occurs either in wet or dry form, primarily via scavenging of the oxidized form Hg^{2+} by rain or snow; High concentrations of THg tend to occur in low volume precipitation events. Adsorption of mercury to aerosols such as soot (Iverfeldt, 1991) also results in deposition of particulate Hg which is rarely quantified. As a result of the scavenging effect an inverse correlation between Hg concentrations in

precipitation with precipitation volume has been found in several studies (Iverfeldt, 1991; Lindqvist et al. 1991; Morrison et al. 1995). Across North America, total mercury (THg) is higher during the summer months (Ahmed et al. 1987; Sorensen et al.1994; Burek et al. 1995; St. Louis et al. 1995) due to soil derived particles in the atmosphere (St Louis et al. 1995). In Sweden, a different seasonal deposition pattern has been observed with higher concentrations of THg measured during the winter (Iverfeldt, 1991, Lindqvist et al. 1991). This was attributed to THg associated to soot particles (Lindqvist et al. 1991) originating from combustion of fossil fuels in Europe (Iverfeldt. 1991).

MeHg has been found in precipitation as well. Since it is only on average 1% of total mercury (THg) (Grigal, 2002), most authors have considered it to be unimportant. Once mercury is deposited, it undergoes several chemical and biological transformations as it cycles through the water column: In the aquatic environment, Hg can bind to dissolved organic carbon (DOC) (Hintelmann et al. 1995), inorganic ligands such as Cl^- or OH^-, or sorb to particulate matter. The chemical form of Hg in aquatic systems is strongly influenced by redox (Eh) and pH conditions as well as by the concentrations of inorganic and organic complexing agents (Ulrich et al, 2001). Mercury can also be reduced either under low redox conditions, by mercury reducing microbes or photoreduced by UV radiation to Hg^0. MeHg can also be photodegraded to Hg^{2+} and further transformed to Hg^0, allowing re-volatilization (Sellers et al. 1996; Mason et al. 1994). UV can also cause photooxidation of DOC, releasing bound metals into the water column and reducing the photoactivity of the DOC (Winch et al. 2002).

Sediments constitute the main reservoir of Hg in freshwater systems (Ulrich et al. 2001), due to transport of Hg by way of particle settling (Lee et al. 1998). Nevertheless, although the sediments and soils of Kejimkujik Park N.S contained 98%

of the mercury in the lakes studied (O'Driscoll et al. 2005), these forms did not participate in the flux of mercury through the ecosystem. Furthermore, the contaminated sediments at the Cornwall Area of Concern were not a significant source of mercury to the food web leading to fish. (Delongchamp, 2006), and Henry et al. (1995) found that only 0.4% of the annual Hg flux to an urban New York lake was from the sediments. This implies that contaminated sites will recover rapidly with reduced inputs.

1.4 MeHg sources and chemistry

Environmental MeHg concentrations reflect net methylation. Since both methylation and demethylation processes occur simultaneously (Ulrich et al. 2001), only net change is observed. Because methylation reactions require energy, they either are the result of photochemical processes or need to be catalyzed by microorganisms (Morel et al. 1998). Biological methylation of inorganic mercury is thought to occur primarily by sulfate-reducing bacteria (SRB) (Morel et al. 1998), and is believed to occur mainly in anoxic waters and sediments (Morel et al. 1998; Gilmour et al. 1991), in forest soils (Verta et al. 1994) and wetlands (Rudd, 1995). Organisms capable of Hg methylation have been found among anaerobes, facultative anaerobes, and aerobes, but it is believed that SRBs are the principal methylators of inorganic Hg in aquatic environments (Downs. 2001). Critical evidence of this hypothesis is provided by Eckley et al.(2006), who found positive correlations between decreasing sulfate concentrations to methylation activity in 5 lakes across Canada. Watras et al. (2005) found a strong positive relationship between the presence of SRBs and high methylation rates in a wetland dominated lake; and Gilmour et al. (1992) found that inhibition of sulfate-reducing bacteria blocked MeHg production in a water reservoir.

However, despite this large body of evidence, the ecological importance of SRBs in MeHg formation remains incomplete.

In-lake methylation has been identified as an important site of MeHg production, and has been found in several cases to be the most significant source of MeHg (as reviewed by Ulrich et al. 2001). The methylation rate of mercury in lakes varies from 0.5 to about 3 $\mu g\ m^{-2}$, but its importance relative to direct atmospheric deposition and runoff changes with different circumstances (as reviewed by Rudd 1995).

Recent studies suggest that the role of abiotic methylation by humic substances might be more significant than previously thought (Weber 1993; Celo et al. 2005). Abiotic methylation has been shown to occur in industrial wastewater and sewage effluent (Ulrich et al. 2001) or in humic compounds (Nagase et al. 1982; Nagase et al. 1984), when suitable methyl donors are present. Methylcobalamine is thought to be the most likely methylating agent in aquatic ecosystems (Ulrich et al, 2001), since it is prevalent in anaerobic environments and living organisms, and is capable of transferring a methyl group as carbanions.

As mentioned above, in the aquatic environment MeHg can be photodegraded to Hg^{2+} and further transformed to Hg^0, allowing re-volatilization (Sellers et al. 1996; Mason et al. 1994). This would assume that MeHg levels should decline in lakes during the sunlit hours of the day. However, Siciliano et al. 2006 found that MeHg actually increased in the water column of two lakes in Nova Scotia, with maximum values at mid-day. In subsequent incubation studies, they showed that MeHg could be *photoproduced*. Previous work on photodegradation of MeHg was done on samples enriched with MeHg, and this indeed may explain the discrepancy.

Still, little is known about the biochemistry of MeHg formation in the natural environment, and the mechanism has not been fully determined. Whatever the mechanism, all previous authors have considered that MeHg inputs through precipitation are not significant as MeHg typically constitutes approximately 10-15% THg in the water phase of non point contaminated aquatic ecosystems (Morel et al. 1998, Dennis et al. 2005)

1.4.1 Dissolved Organic Carbon (DOC): Effects on Transfer, Retention, and Bioavailability of Mercury.

Wetlands are considered to be one of the key sites for MeHg formation. Many studies have found a strong correlation between the percent of wetlands in a catchment to the MeHg concentration downstream (St. Louis et al. 1994; Watras et al. 1995), with an average 3- fold increase in MeHg flux with an increase of wetland area from 1 to 10 % (Grigal, 2002). Other studies indicate that the percent of near shore wetlands has a greater influence on the MeHg exported to a lake than the overall amount of wetlands in a catchment. (Driscoll et al. 2005) DOC is widely accepted as the chief transport vector of mercury from the watershed. The composition of DOC from different watersheds varies to a great extent depending on land composition land use and disturbance such as logging (O'Driscoll et al. 2004). The binding of mercury is controlled largely by a small fraction containing thiol groups, which form a strong ionic bond with mercury, and thus facilitate the transfer of Hg from soils (Ravichandran, 2004).

Once transported to the aquatic ecosystem, the fate of the mercury is again largely dependant on the DOC: Reduction of Hg^{2+} to Hg^{0} and subsequent evasion from the water has been observed in the presence of DOC (Xiao et al. 1994; Mason et al.

1995). Under certain circumstances this process may be of great importance: O'Driscoll et al (2005) found that the reduction rate of Hg^{2+} was equal to deposition rates on the lake itself. In exposure experiments with a fixed radiation source, mercury photoreduction rates were found to increase with DOC. In contrast, Amyot et al. (1997) and others observed higher mercury evasion rates in lakes with low DOC, and attributed it to the UV absorbance capability of DOC, which caused reduced light penetration and increased mercury complexion to DOC. The difference between results from these two groups may reflect the levels of DOC investigated as O'Driscoll et al worked on systems with low DOC (<7 mg L^{-1}) and Amyot et al. on systems with high levels (>7 mg L^{-1} DOC). Evasion of elemental mercury results in less mercury available for in-lake methylation processes, and thus higher DOC levels often result in higher mercury levels in the biota (Watras et al. 1998).

The bioavailability of mercury is also strongly dependant on DOC, due to differences in fractionation to the different size particles of organic material and DOC. Wallschlager et al. (1996) found that only 1% of all mercury in water from the Elbe floodplain soils can be truly dissolved in the water, and the rest was associated with humic acids. Hurley et al. (1995) found that in wetland and forested watersheds in Wisconsin, most of the total mercury was associated with the filtered phase, while in agricultural watersheds the total mercury flux was principally due to particulate loading. Balogh et al. (2005) also found similar results in two contrasting watersheds in Minnesota. Since food is the most dominant pathway of MeHg uptake by fish (Hall et al. 1997), the mercury levels in fish are ultimately determined by MeHg accumulation in the base of the foodchain (Clarkson, 1997), and the uptake of the MeHg by microorganisms, phyto and zooplankton that feed on the dissolved and particulate phases.

1.4.2 Mercury in precipitation

MeHg in precipitation was measured as early as 1987 (Lee et al. 1987; Ahmed et al. 1987) with reported concentrations of 0.01 to 9.4 ng L^{-1} (as summarized by Downs, 1998). MeHg concentrations in precipitation do not show the same scavenging pattern as THg (Bloom and Watras, 1989), or increased deposition during summer (Mason et al. 2000). Furthermore, MeHg does not seem to be influenced by proximity to industrialized areas (Ahmed et al. 1987). The increased ratio of MeHg: THg in less polluted areas suggests that anthropogenic activities enhance inorganic mercury species, but not MeHg (Bloom and Watras 1989 and Lee and Iverfeldt 1991).
Until recent years, measurements of MeHg in snow were sparse but recent studies report levels of 0.01 to 0.2 ng L^{-1} (Fitzgerald et al. 1991; St. Louis et al. 1995: St Louis et al. 2007).

Since MeHg is not a very volatile compound (Ethier et al. 2008), its pathway to the atmosphere and subsequent deposition with precipitation is perplexing. Several studies have attempted to answer this question: In a review of the available literature, Downs (1998) suggests that the source of low levels of MeHg measured from the equatorial Pacific is terrestrial. Conversely, Mason et al. (1995) found that dimethylmercury (DMeHg) in the North Atlantic Ocean increased with depth, suggesting up-welling from deep ocean layers. Based on modeling calculations, the authors concluded that DMeHg either evades the surface waters, or is decomposed to MeHg. Following this, in a study of mercury species in the snowpack of the Canadian Arctic, St. Louis et al. (2005) found a significant correlation between concentrations of Cl and MeHg in snow deposited in the spring, and speculated that this indicated a marine source. The authors hypothesize that MeHg is produced by photolysis of dimethylmercury (DMeHg) fluxes from the ocean to the atmosphere. In an earlier study

in Lake Hoare in Antarctica Vandal et al. (1998) examined the major solutes in the streams entering the lake in order to establish the origin of the mercury in the meltwater. The conclusions from this study were similar to those of St. Louis et al. (2005).

However, Hammerschmidt et al. (2007) point out that if the source of MeHg is upwelling of DMeHg, we would expect to find higher concentrations of MeHg in areas where the upwelling of oceanic water is greater such as near the equator. Mason et al. (1992) and Lamborg et al. 1999 found that rain samples from the equatorial region generally had undetectable levels of MeHg, suggesting the hypothesis presented by Vandal et al (1998) and St. Louis (2005) was incorrect.

Hammerschmidt et al. (2007) also compiled measurements of MeHg and reactive mercury (RHg, an operationally defined fraction of Hg that is reduced readily with $SnCl_2$) in precipitation from studies across North America and found a strong correlation (r^2=0.98, p=0.0001) between the two forms. He concluded that MeHg in precipitation results from methylation of RHg in the atmosphere, and that the methylating agent is either terrestrial, or that MeHg decomposition is enhanced in the marine troposphere, potentially by reactive halogens.

1.4.3 Mercury dynamics in the snowpack

In 1998, Schroeder et al. published the surprising discovery that during the early springtime frequent episodic depletions resulted in unexpectedly low concentrations of gaseous elemental mercury (GEM) in the arctic air. This phenomenon was termed Mercury Depletion Event (MDE) and it was later discovered that GEM is converted to a more reactive species that is subsequently associated with or converted to particles in the air and/or deposited to the snowpack (Lindberg et al. 2002, Ariya et al. 2004). This

discovery had great implications to the arctic marine ecosystem, and it triggered a large number of related studies.

However, subsequent work, especially later in the warm season when the sun was stronger (May-June), revealed that a large part of the mercury deposited to the snow during the MDEs was later re-emitted to the atmosphere: Lalonde et al. (2002) found that on average 54% of deposited Hg was reduced within the first 24 hours by way of photoreduction of Hg^{2+}, and Ariya et al. (2004) observed a rapid reduction of 20-21% of the mercury in the snow back to Hg^0, which then volatilized quickly. Also in the arctic region, St. Louis et al. (2005),not only found similar dynamics of inorganic mercury, but also that the MeHg concentration in the snow stayed constant throughout the experiment and with depth. Moreover, the percent of MeHg in the snowpack showed a negative exponential relationship with the concentration of inorganic Hg, which supported the hypothesis that the concentration of MeHg in the snow will not be altered because Hg^0 deposited during MDEs is not oxidized directly to MeHg. This finding has great significance to the relative importance of MeHg in the snowpack: if 50% of the inorganic mercury is volatilized, the proportion of MeHg, which was only approximately 1%, will increase. This hypothesis is supported by the results of a 2005 study by St. Louis et al., which found that when inorganic mercury concentrations were low, MeHg composed up to 100% of mercury in the snow.

In order to understand the importance of this phenomenon on an ecological scale, the dynamics of mercury during the snowmelt must be examined.

One of the first to study the importance of the springmelt was Dommergue et al (2003), who estimated that up to 90% of THg in Arctic snow surface is released with meltwater during the first day of snowmelt. This observation is supported by the conclusions of a literature review on organic contaminant amplification during

snowmelt (Meyer and Wania, 2008). In a subsequent study by Loseto et al. (2004b), arctic drainage basins with and without wetlands were examined. When MeHg export was monitored throughout the season, they found that MeHg concentration in runoff peaked with flow volume and that there was no difference between drainage basins with and without wetlands. Subsequently, Lahoutifard et al. 2005 found that although mercury depletion events resulted in high concentrations in the arctic snow, much of it was lost prior to snowmelt. Conversely, MeHg in snow persisted until the first melt and concentrations similar to that found by Loseto et al. 2004 were exported.

These studies on the dynamics of mercury during snowmelt have presented a growing body of evidence showing that the MeHg in the arctic snowpack might be of more significance to the aquatic ecosystems than previously thought.

The scientific response to these new findings has been focused mainly on arctic regions, and reports of mercury dynamics in snow in temperate regions are sparse. Lalonde et al. (2002), who measured THg in the snowpack above a frozen lake in Quebec, Canada, was the first to discover that in temperate regions, THg levels decrease after deposition at rates that averaged 54% within 24 hours. This finding was confirmed by incubation experiments showing an increase in Hg^0 from snowmelt and solid snow exposed to UV radiation, and by a subsequent study in a more remote area with similar findings (Lalonde et al. 2003). These results were also supported by the work of Poulain et al. (2007) who studied the dynamics of a snowpack under different types of forest canopies near Montreal. They found that the mercury concentration in snow deposited under conifers was approximately twice as high as the concentration under deciduous trees. They argued that the photoreduction of Hg^{2+} and subsequent evasion of Hg^0 from the snowpack was significant in open areas, but was greatly reduced by light attenuation under winter canopies.

A recent study by Nelson et al. (2008) illustrates the difficulty in accurately assessing the actual content of mercury in the snow. In this study Hg in snow in open areas and under mixed forest canopies was measured and compared with four alternative collection methods. As in the study by Poulain et al. (2007), here too the snow under the canopies was found to have higher levels of THg than open areas, indicating either higher deposition rates or less re-volatilization. However, the team also found a significant difference in the deposition rates for the different collection methods. Snow collected from under canopies on event basis had the highest deposition rate (5.6 $\mu g\ m^{-2}$ cold $season^{-1}$). Furthermore, the deposition rate for the snowpack samples was less than 50% of the event throughfall rate (2.38 $\mu g\ m^{-2}$ cold $season^{-1}$) and the deposition rate for season- long samples was even lower: 1.8 $\mu g\ m^{-2}$ cold $season^{-1}$.

The work presented here is one of the first studies designed to evaluate the contribution of MeHg in the snowmelt to temperate aquatic ecosystems. In the following thesis I will present the details of this study and discuss the results and implications.

2. Materials and Methods

2.1 Study Site

2.1.1. St Anicet

Samples were collected from an environmental monitoring site (45°07' North latitude and 74°17' West longitude), 3 km southeast of the town of St. Anicet, Quebec. The station is located about 3 km inland on the south shore of the St. Lawrence River, between Cornwall (Ontario) and Montreal (Quebec). This station is part of both the Canadian Weather Network and the Mercury Deposition Network (MDN). The topography is flat and suitable for mostly as pasture and row crops with some wooded areas, consisting mainly of deciduous maple trees.

2.1.2 Dorset

Harp and Dickie Lakes are two small lakes (71.4 and 93.6 ha, respectively) in the Muskoka –Haliburton area of south-central Ontario (Mierle and Ingram, 1991), which have been the focus of a long term study of the impacts of long range atmospheric transport of contaminants, climate change, and cottage development on the water quality in forested headwater catchments and lakes. Being in close proximity to each other, the two lakes are affected by the same geology of predominantly granite Precambrian shield covered with thin to occasionally deep till (Mierle and Ingram, 1991) and are also affected by the same meteorological conditions. Moreover, the two lakes have roughly the same catchment area (Dickie: 406.4ha, Harp: 470.7ha), and both receive water inputs mainly from well defined stream runoff and precipitation while groundwater inputs seem to be negligible (Dillon et al, 1986). Both catchments are primarily forested second or third growth forests (Dillon et al. 1994) and there is no point source mercury contamination to either lake. However, the two lakes differ in

depth and slope of the drainage basin: Dickie is a shallow lake (mean depth 5m) with a mild watershed slope (average 6%) (Dillon and Molot, 2005) which gives rise to wetlands covering about 20% of the watershed area (Mierle and Ingram, 1991). Conversely, Harp Lake is deeper (mean depth 13.3 m) with an average 12% slope, and only 6.3% wetland in the catchment area (see Table 2.1). The morphometry, chemistry and geology of the lakes and watersheds are described in detail by Dillon and colleagues (Dillon et al. 1986).

This study focuses on 6 streams (HP3, HP3A, HP4, HP5, HP6, HP6A) draining Harp Lake catchment (Fig 2.2), and 4 streams (DE5, DE6, DE8, DE10) draining Dickie Lake catchment (Fig 2.1). The sampling of an additional station, DE11 stopped in 1995 at the request of the owners of the property. This stream is likely a major contributor of mercury in runoff to Dickie Lake; it is the second biggest sub-catchment, and ranks third in % wetland. Based on 15 year historic discharge data and using the percent wetland to estimate the MeHg concentration, an annual MeHg load was estimated for this station (see calculations). The physical and chemical characteristics of the 10 streams and the partial characteristics of DE11 are summarized in Table 3.2 in the results section.

2.2 Sample Collection

2.2.1 St. Anicet

MeHg samples in wet deposition were collected by the author from November 2003 to April 2006, using automated wet-dry deposition collectors. Volume-weighted annual concentrations (ng L^{-1}) and annual depositions ($\mu g\ m^{-2}$) of total mercury were obtained from the national atmospheric deposition program/ mercury deposition network (NADP/MDN) (http://nadp.sws.uiuc.edu/mdn/), a cooperative research support

program designed to measure THg in precipitation on a weekly basis from over 100 sites across North America. THg sampling for this program follows a strict QA/QC protocol, that is described in detail in Lindberg et al. (1995), Vermette et al. (1995) and Welker et al. (1996), and can be found in the operating manual available from http://nadp.sws.uiuc.edu/QA/ . Briefly, a modified Aerochem Metric collector model 301 (Aerochem Metrics, Inc.,Bushnell, FL) was used to collect bulk samples of wet deposition for THg analysis. Inside the collector, the sample was collected on a weekly basis in acid washed glassware, and was sent to *Hg Analytical Laboratory* (HAL) at Frontier Geosciences in Seattle, Washington for analysis by cold vapor atomic fluorescence.

During the winter months, a heater placed inside the collector was set to maintain an internal temperature of 21°C, in order to keep the sample from freezing and to melt the snow deposition allowing it to flow into the collection bottle.

A MIC® type B1 automatic rain sampler with a Teflon® coated stainless steel funnel (0.3m 0.3m) (Richmond Hill, Ontario) was used to collect larger samples of wet deposition for MeHg analysis. This collector was originally designed for collection of persistent organic pollutants (POPs) (W. Strachan, National Water Research Institute Burlington, Ontario, personal communication with D. Lean). The Teflon funnel was found to cause adsorption of the POPs but was ideal for collection of the larger volumes needed for MeHg analyses. Inside the collector, the funnel was connected to a 12 Liter high density polyethylene (HDPE) bottle, using a Teflon® tube. The collecting bottle contained 0.6.L of 10% HCl to preserve the maximum volume expected to a minimum concentration of 0.05% HCl. During the winter months a heater placed inside the collector was set to maintain an internal temperature of 21°C, in order to keep the

samples from freezing and melt the collected snow which was collected as deposition. The melted water was then able to flow into the collection bottle containing acid.

In order to determine if any of the MeHg was adsorbed to the equipment, the old funnel and tubing were rinsed with 2L of 0.05% HCl solution, followed by 2L of DIW. The rinses were collected using pre-acid washed 1L Nalgene©- high density polyethylene (HDPE) bottles, stored in a cooler and transported to the University of Ottawa for fixing with 10 mL of concentrated HCl and stored in a cold room at 4°C until MeHg analyses within 30 days (see methods described in details in section 2.3.2). Samples were collected once every 4 to 6 weeks. The 12L collection bottle was transported in a cooler to University of Ottawa, where immediately after arrival the precipitation collected was transferred into 3 1liter acid washed Nalgene© HDPE bottles and stored in a cooler in a cold room held at 4o C until analysis within 30 days of collection. The remaining sample was poured into a graduated cylinder to measure volume, and then discarded.

2.2.2 Dorset

The water samples were collected in duplicates and analyzed on a weekly basis by members of the Dorset Center of Environment Canada, as part of a long term monitoring program run by the Ontario Ministry of Environment (OME). All samples from one drainage basin were taken on the same day, but Harp streams and Dickie streams were sampled on different dates. Samples were analyzed at MOE for the following parameters: sulfate, dissolved organic carbon (DOC), color, iron, conductivity, silicate, alkalinity, pH, total phosphorus, nitrate, and on some occasions for total mercury (THg). MeHg analyses were conducted at the University of Ottawa.

Analytical methods and quality assurance protocols used for all but MeHg are documented in the Ontario Ministry of the Environment Analytical Methods/Quality Assurance Manual (Teresi, 2003) and in the Handbook of Analytical Methods for Environmental Samples (OMOE, 1981)

Stream discharge was calculated as described by Hutchinson (1994). In short, stream discharge was determined from stage – discharge equations with a minimum of 95 % explained variance. Stage height was logged using continuous stage recordings and calibrated from two-stage weirs located on each stream.

MeHg samples were collected on a weekly basis at the 12 stations of Dickie and Harp lakes using "clean" sampling methods (Bloom, 1995) into 1L Nalgene©-high density polyethylene bottles (HDPE) that were previously washed with 10% HCL followed by rinsing 5 times with distilled water. The bottles were double bagged using ZIP-LOCK® bags and transported to the MOE station where the samples were preserved with 5 ml of concentrated hydrochloric acid (HCL) (EM Science, ACS grade 99%), to a preservation capacity of 0.5%. The bottles were then re- bagged using ZIP-LOCK® bags and stored in a cooler until transfer to the University of Ottawa, where they were stored in a cold room (4°C) in the dark until analysis.

Water samples were collected from March 2005 to May 2007. The streams are often dry during the summer, thus making sampling during the summer sparse and irregular. There was no sampling between July 2005 and October 2005, a period when the streams were largely dry, and between December 2005 and March 2005, when the streams were largely frozen.

Snow samples were collected on two occasions, shortly before spring snowmelt, on March 30, 2005 and March 9th, 2006. In both sampling events, snow was collected

from 3 locations: Dickie 8, mostly spruce and balsam forest, Harp 4, mostly hardwood forest and Harp Outflow, open cover.

All sampling locations were adjacent to the water collection points, in an undisturbed area and the person sampling was located downwind from the location site. An acid washed polyethylene trowel was used to homogenize the top 10 cm of the snow surface and to fill a 2 liter HDPE bottle with the homogenized snow. In order to get a large volume of water in every sampling bottle the snow was packed in to the bottle by hand, using clean nitrile gloves. The samples were collected in duplicates from every site, bagged in ZIP-LOCK® bags and transported to the University of Ottawa in a cooler. Immediately after arrival at the University laboratory the samples were melted in room temperature in the dark and acidified with concentrated HCl to a preservation capacity of 0.05%. The samples were then re-bagged using ZIP-LOCK® bags and stored in a cold room (4°C) in the dark until analysis.

2.3 Analytical Methods

2.3.1. THg analytical methods

THg samples were analyzed using pre-oxidation by BrCl, and $SnCl_2$ reduction with pre-concentration by two-stage gold amalgamation, followed with detection using cold vapor atomic fluorescence spectroscopy (CV-AFS). This analysis was conducted using a Tekran 2600 system, following the modified US EPA method 1631 guideline for mercury analysis (US EPA 2001). The detection limit was estimated to be 0.2 ng L^{-1}. Analysis of procedural blanks consisting of de-ionized water revealed no mercury contamination during THg analysis. The mean recovery of spiked samples was 101.78$\pm$ 9.6% (n=50).

2.3.2. MeHg analytical methods

The MeHg samples were analyzed using a two step method described by Cai et al. (1996). First, a solid phase extraction on sulfide columns was conducted using acidic-potassium bromide elution, followed by extraction using dichloromethane to obtain the organic layer of the solution, then the sample extracts were analyzed using standard capillary gas chromatography paired with atomic fluorescence spectrometry (GC-AFS) (Analytical Mercury System Model PSA 10.723) (Cai et al. 1996). The Method Detection Limit (MDL) was estimated to be 0.02 ng L^{-1}. Analysis of procedural blanks consisting of de-ionized water revealed no mercury contamination during MeHg extraction and analysis. The mean recovery of spiked samples was 97.72+ 6.29% (n=40). Further QA/QC was successfully conducted as part of the inter-laboratory comparison program under the Collaborative Mercury Research Network (COMERN) of Canada.

2.4. Climate data

Daily minimum, maximum and average temperatures, as well as amount of precipitation were obtained from Environment Canada's website (Environment Canada, 2008. http://www.climate.weatheroffice.ec.gc.ca/climateData/canada_e.html).
The data for 2005 was from Dwight station (45°22.8'N, 78°45'W, within 25 km from Dorset), and the data for 2006-7 was from Beatrice2 station (45°78'N, 79°24'W, within 50 km of Dorset), as Dwight station data was not available for that time frame.

2.5. Calculations

Annual deposition rate ($\mu g\ m^{-2}\ year^{-1}$) was calculated using the precipitation volume and mercury concentration measured weekly in St. Anicet:

$$D=\Sigma\ (CV/A) \qquad [1]$$

Where D is deposition rate, C is the concentration of the mercuric species (THg or MeHg), V is the volume of precipitation collected (measured either by the respective collector: THg or MeHg), and A is the collector area. Annual deposition rate was calculated by summing over 365 days. Annual deposition rate over the entire sampling period was calculated by normalizing to 365.

The annual deposition rates of THg and MeHg were used to calculate the percentage of MeHg of THg in precipitation:

$$\%\ MeHg=100\ D_{MeHg}/\ D_{THg} \qquad [2]$$

Where D is deposition rate for the chemical species.

MeHg flux rates in runoff were calculated using the water discharge and MeHg concentration data for each stream:

$$F = Ca,\ t\ Va,\ t \qquad [3]$$

Where F is the flux rate ($ng\ sec^{-1}$), C is the MeHg concentration ($ng\ L^{-1}$) in stream *a* at time *t*, and V is the discharge rate of stream a ($L\ sec^{-1}$) at time *t*.

MeHg Yield for a given time interval was determined by calculating the geometric area of the trapezoid under the curve and between two sampling intervals:

$$Y = [(T(F_{ti} + F_{ti+1})/2)]\ 10^6 \qquad [4]$$

Where Y is yield (mg), T is the time between consecutive sampling events *ti* and *ti+1* (sec), F_{ti} is the flux rate ($ng\ sec^{-1}$) at time i and F_{ti+1} is the flux rate ($ng\ sec^{-1}$) calculated for the same location on a consecutive sampling event. The result was multiplied by 10^6 in order to convert ng to mg. In order to assess the proportional

contribution of each season to the annual MeHg load (mg $year^{-1}$), the yield was summed over all sub-catchments for each sampling date, and divided into seasons. To calculate the annual yield (mg m^{-2} $year^{-1}$) of a sub-catchment the individual yields of all time, intervals were summed over a one year period, and normalized to the drainage basin area:

$$Ya = \Sigma (Ya,ti + Ya,ti+1)/A \quad [5]$$

Where Y is the annual yield for sub-catchment *a* (mg), Ya,ti is the yield for sub catchment a for a given time interval *ti* , $Ya,ti+1$ is the yields calculated for the subsequent time interval, and A (m^2) is the area of the drainage basin.

Statistical analyses were performed using Microsoft Excel, and SAS/STAT version 9.1.

2.6. Missing data

Several estimation and interpolation methods were used to overcome data gaps and missing information. During the summer of 2006, when the majority of the streams were dry no water chemistry samples were collected, and the discharge data were not recorded. Due to technical difficulties, this data gap continued until the end of September (Dickie Lake) or mid- October (Harp Lake). Historic precipitation records from the region show that the precipitation during the summer does not vary greatly from year to year. The data from the following sampling year (March-2006-Feb 2007) were used to calculate the relative contribution of the summertime discharge, and it was found that between July 19th and October 11th (the missing data period) the runoff amounted to 1.93% and 3.06% of the annual amount of runoff to Dickie and Harp lakes, respectively. Based on this information, the missing discharge values for summer

2005 were substituted with the discharge values from the corresponding dates from summer 2006 (July 19th- September 20th in Dickie, July 24th to October 11th in Harp).

For several smaller data gaps which were largely due to lost samples or technical difficulties, the missing data were filled by calculating the mean of the data points from the previous and following sampling events. This was done only if the previous and following sampling events were within a week of the missing sample, and the providing interpolated data points consisted of no more than 10% of the original data.

The annual MeHg yield for the large sub-catchment not sampled, DE11, was estimated using an approximation of the average annual discharge rate, and the average annual MeHg concentration. The average annual discharge rate for DE11 was calculated as a mean of daily discharge rate measurements from 1979 to 1995 (Dorset MOE, unpublished data).

The average annual MeHg concentration was calculated as:

$$ln\,[MeHg\ (ng\ L^{-1})] = -1.95 + 0.25[ln(\%\ Wetland\ ] \qquad [6]$$

Adapted from Grigal, (2002) and based on a compiling of MeHg flux in 49 rivers and streams from moderate-sized watersheds from Wisconsin, Ontario, New York, and Scandinavia.

Table 2.1- Physical characteristics of 4 tributaries to Dickie (DE) Lake, and 6 tributaries to Harp (HP) Lake, in the Muskoka- Haliburton region of Ontario. Streams were monitored and sampled from March 2005 to February 2007.

Sub catchment	Station Longitude	Station Latitude	Drainage basin area	Percent Peatland	Slope
DE5	45°08'41"	79°05'22"	299800	25.4	1
DE6	45°08'46"	79°05'13"	218000	22	1.6
DE8	45°09'09"	79°05'26"	669600	8.2	1
DE10	45°09'18"	79°04'51"	788900	17.1	1
All DE	--	--	**2739000**	**13.9**	--
HP3	45°22'28"	79°08'26"	260000	9.3	4
HP3A	45°22'29"	79°08'33"	196500	2.9	8
HP4	45°22'49"	79°08'28"	1190900	0	5
HP5	45°22'60"	79°07'55"	1905300	13.3	3
HP6	45°22'40"	79°07'37"	99700	0	8
HP6A	45°22'46"	79°07'42"	152800	8.5	10
All HP	--	--	**3805200**	**6.3**	--

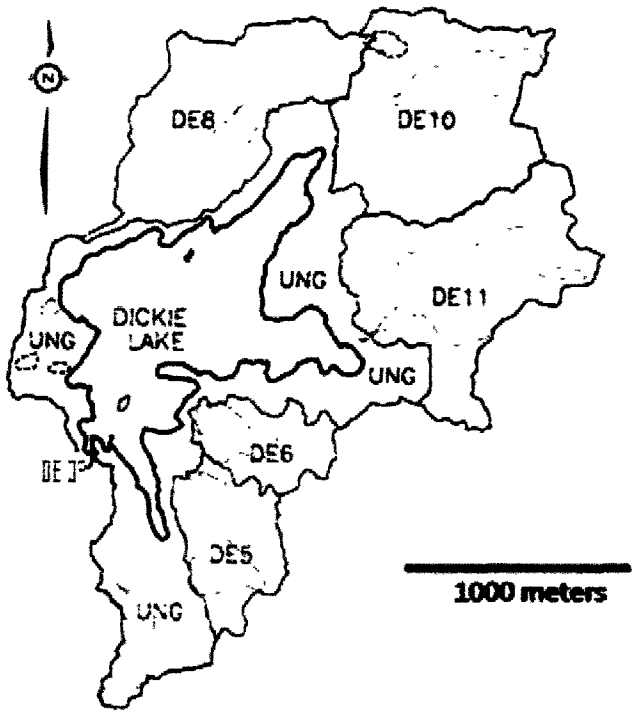

Figure 2.1: Map of Dickie Lake located in the Haliburton Muskoka district, south central Ontario (45°09', 79°05'), and its sub-catchments. The shaded areas represent wetlands. 4 inflowing streams (DE10, DE5, DE6 and DE8) and the outflow (DE OF) were sampled weekly from March 2005 to February 2007. The stream draining DE11 was not sampled during the study.

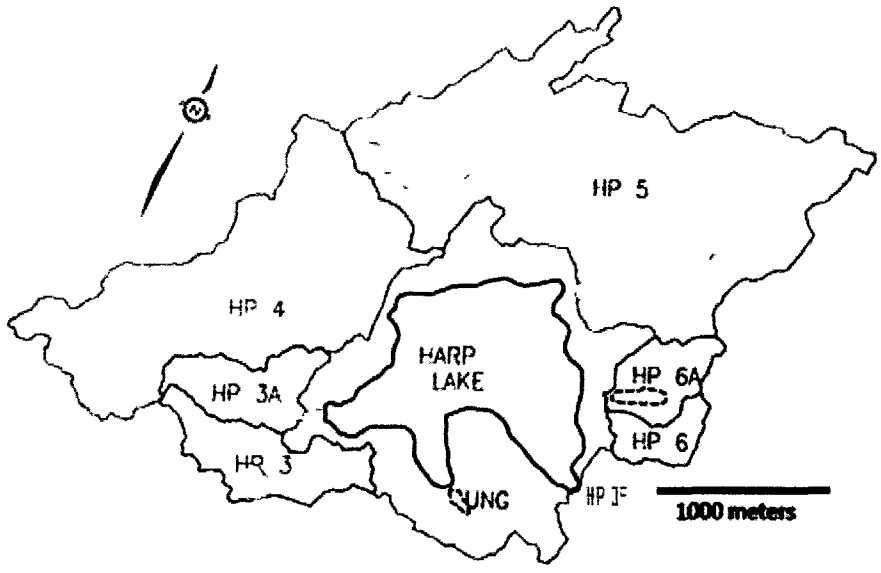

Figure 2.2- Map of Harp Lake which is located in the Haliburton-Muskoka district, south central Ontario (45°23', 79°08'), and its sub-catchments. The shaded areas represent wetlands. 6 inflowing streams (HP3, HP3A, HP4, HP5, HP6 and HP6A), and one outflow (HP OF) were sampled weekly from March 2005 to February 2007.

3. Results

3.1. St. Anicet

THg in all samples ranged between 2.88 ng L^{-1} and 17.5 ng L^{-1} with a mean of 9.64 ng L^{-1}. MeHg levels were detectable in all samples, and ranged between 0.02 ng L^{-1} and 0.31 ng L^{-1} with a mean of 0.11 ng L^{-1}. The annual deposition rate for the sampling year November 2003-2004 was calculated to be 5.29 μg m^{-2} $year^{-1}$ THg, of which 2.91% was MeHg, 0.15 μg m^{-2} $year^{-1}$. In the past when deposition rates were measured at Dorset, similar concentrations were found: 10.2 ng L^{-1} THg (Mierle, 1991), but the deposition rates for THg in Dorset were greater than those measured in St. Anicet, 8.5 μg m^{-2} $year^{-1}$ (Mierle, 2007)

For the sampling year November 2004- November 2005 the annual deposition rate was calculated to be 6.88 μg m^{-2} $year^{-1}$ THg and 0.19 μg m^{-2} $year^{-1}$ MeHg, which amounts to 2.7% . The annual deposition rate for the duration of the experiment (November 2003- January 2006) was calculated to be 6.46 μg m^{-2} $year^{-1}$ THg of which 2.87% was MeHg, 0.19 μg m^{-2} $year^{-1}$. The average concentration of collector rinses was 0.4 ng L^{-1} MeHg. This concentration yielded on average 5.2 percent of the amount of MeHg collected during the preceding time interval.

3.2. Dorset

3.2.1. MeHg concentration

The MeHg concentrations measured in the tributaries to the two lakes varied greatly both spatially and temporally, by over three orders of magnitude (0.02 ng L^{-1} – 7.52 ng L^{-1}). Generally, the highest MeHg concentrations were measured during the summer and the lowest during the winter and spring. A summary of descriptive

statistics of the physical and chemical characteristics and graphic representation of temporal changes are presented in Table 3.2 and Figures 3.1- 3.17.

The mean MeHg concentration in all measured Dickie tributaries was 0.72 ng L^{-1} and the median was 0.5 ng L^{-1} (n=356). Both values were roughly double the values for the Harp streams sampled (average 0.38 ng L^{-1}, median 0.17 ng L^{-1}. n=480), illustrating that the MeHg concentration in runoff is profoundly influenced by features of the drainage basin and less by direct inputs from precipitation.

The seasonal pattern in MeHg concentrations was consistent in all sub-catchments (Fig 3.1 and 3.2) with some exceptions. With the onset of snowmelt, the relatively low concentrations of MeHg (0.15-0.75 ng L^{-1}) in both catchments were further reduced to a range of 0.05 ng L^{-1} to 0.3 ng L^{-1}. From the end of April to the end of August, MeHg concentrations constantly increased in a fluctuating pattern. The magnitude of these peaks varied greatly with values from a maximum of 7.5 ng L^{-1}, (HP5 on June 28, 2005) to a low of 0.3-0.6 ng L^{-1} in HP, and 0.5-1.1 ng L^{-1} in DE. The fall brought generally lower MeHg concentrations (0.1-0.3 ng L^{-1} in DE, 0.05-0.2 in HP), with occasional higher peaks. During the winter the MeHg levels dropped further to near limit of detection (0.02 to 0.5 ng L^{-1}). The range and variability in MeHg concentration measured in Harp sub-catchments was greater than that measured in DE sub catchments.

Annual average MeHg concentration was highly correlated with the percent of wetlands in a catchment explaining 24% and 36% of the variance in the average MeHg concentration in 2005-6 and 2006-7, respectively, though this correlation was not statistically significant (p=0.06 and p=0.15, respectively) (fig 3.3). When the annual yield of MeHg was plotted against percent wetland, the correlation was similar to that found with concentration in 2005-6 (r^2= 0.21). In sampling year 2006-7, percent

wetland could only explain 23% of MeHg yield, less than the explanatory power of the % wetland on MeHg concentration for that year. These correlations were not statistically significant (p= 0.18, p=0.16, respectively). This illustrates the complex dynamics of MeHg export from the watersheds. Although wetlands can be sites of MeHg production and thus explain at least partially the variability in MeHg concentration, each sub catchment responds to the changing environmental conditions in a different way, resulting in relative yields that may vary from the relative concentrations.

3.2.2. Seasonal Hydrograph

The seasonal hydrograph for all streams (Fig 3.4 and 3.5), measured over the duration of the sampling period) and the major precipitation events during that time illustrates the patterns of water export from each of the drainage basins. This information will provide a background for the identification of specific features that distinguish the drainage basins or sub-catchments.

Although the amount of runoff varied from stream to stream (see Table 3.2), and the annual yield of discharge (L m^{-2}) also varied between the streams (not shown), they all followed a similar seasonal pattern. There was an initial period in early spring when the snow began to melt and flow rates increased rapidly to the yearly peak maximum. This occurred within a few days in April and continued in May. Apart from a few large peaks observed in some of the drainage basins which occurred during intense precipitation events, there was little flow in most of the streams over the summer. During the fall as precipitation increased, and especially after the leaves had fallen and transpiration losses were reduced the stream flow increased. The rate of

discharge continued to decline into the winter and during the coldest months after the streams froze over the flow rate was the lowest of the year.

During April, discharge rates were higher in all streams: in 2005 the discharge rate in DE reached a peak as high as 91.9 L sec^{-1} (DE10, Aril 7th). During the same period of time a peak of 115.7 L sec^{-1} occurred in HP5, on April 11th. In spring 2006 the discharge rate in DE peaked on April 5th, with a maximum of 89.6 L sec^{-1} in DE10. In Harp streams the maximum flow was measured on April 11th, with a staggering 138.5 L sec^{-1} in DE5 station. The magnitude of the spring freshet peak was dependant largely on the sub-catchment area (r^2= 0.94, not shown).

The importance of this annual snowmelt event becomes clearer when the relative contribution of each time period to the annual amount of runoff is calculated. The accumulated percent of annual runoff to each one of the lakes is shown on Figures 3.6 and 3.7. In the year beginning in March 2005 the spring freshet occurred between March 30 and May 30, and was identified using both the seasonal hydrograph and temperature data. It accounted for 56.6 and 59.2 % of the annual runoff to Dickie Lake and Harp Lake, respectively (fig 3.6). The percent accumulated discharge graph for 2005-6 was calculated by re-using the summer discharge data from summer 2006 (fig 3.7). This likely does not reduce the accuracy of the calculation, as the contribution of the 2006 summer discharge to the annual amount was almost negligible (about 3% of 2006 discharge), and the amount of precipitation during summer 2005 was similar to that measured in 2006: In 2006 the spring freshet (March 20- May10) was 48.1% of the annual runoff to Dickie Lake, and 36.0% to Harp Lake (fig 3.7).

The summer and early fall discharge rates measured seem to contribute very little to the annual amount of runoff to the lakes. From June to September 2005, a total of 4.6% of the annual amount of runoff entered Dickie Lake (increase from 75.8% to

80.5%), and a total of 3.6% of annual runoff amount entered Harp Lake (from 59.8% to 63.4%). However, one extreme precipitation event on June 14th, 2005 had a major impact on the hydrograph of Dickie Lake: the runoff following this precipitation event alone accounted for 20% of the annual amount of measured runoff to Dickie Lake. The effects of this major event are not seen in the runoff to Harp Lake, which was sampled on June 14th and June 21st.

In the summer of 2006 the amount of runoff was virtually insignificant. Most streams were either dry or not flowing over large parts of the season. From mid May to the end of September both lakes received only 8.5% of the annual runoff.

In 2005 the fall runoff contributed 4.46% and 11.8% to the annual amount in Dickie and Harp, respectively. An increase in accumulation rate was observed in Dickie streams from November to the end of the sampling year in February, resulting in 12.4 % of the annual load during the winter (Dec-Feb). In Harp streams an increase in accumulation rate was measured in mid October, and continued throughout the winter, resulting in 20.2% of annual discharge.

In 2006, the fall runoff amounted to 12.4% and 20.2% of the annual runoff to Dickie and Harp, respectively. In both lakes an increase in accumulation rate was measured in early to mid October, a trend which continued throughout the remaining fall and winter. The winter runoff accounted for 21.5% and 23.3% of annual discharge in Dickie and Harp, respectively.

In both years, the snowmelt period in the spring coincided with a number of precipitation events: In the spring of 2005 there was 25.6 mm rain on April 7th and 21 mm rain on April 20th. In the spring of 2006 there also were 2 major events: on April 12th, 16.7 mm, and on April 23rd, 16.4 mm.

There was a small difference in precipitation between 2005-6 (1199.6 mm) and 2006-7 (1073.2 mm), both slightly above a 20 year average for the region (1067.8 mm) (http://www.climate.weatheroffice.ec.gc.ca/climateData/canada_e.html). Unfortunately, the relative amount of snow and rain is not determined for these calculations as it is recorded only as total precipitation.

3.2.3. MeHg Flux rate

While concentration is the variable that is most often monitored, the product of concentration times volume of flow provides the overall flux rate. The overall flux rate of MeHg for all the Dickie streams, averaged over the duration of the sampling period was 3.70 ng sec^{-1}, and the average for Harp was 2.97 ng sec^{-1} (Table 3.2). In general, the tributaries from Harp Lake show a greater range in MeHg export than Dickie Lake tributaries. In Harp Lake, the average MeHg in the different tributaries varied by over an order of magnitude from 0.3 ng sec^{-1} in HP3A station to 8.4 ng sec^{-1} in HP5, a 28 fold difference. In Dickie streams the averages are higher and vary from 2.4 in DE5 ng sec^{-1} to 7.7 ng sec^{-1} in DE10, a 3-fold difference.

Despite the great differences in the catchment characteristics, the MeHg export rate from the watershed in all streams seemed to follow roughly the same temporal trends (fig 3.8, 3.9 and 3.10), which differs substantially from the pattern seen in the MeHg concentration graphs. Early spring began with elevated rates of MeHg export (roughly 1-6 ng sec^{-1}). As the spring freshet reached its climax in mid to late April, the amount of MeHg exported from the watersheds to the lakes also reached a monumental peak (between 2 and 25 ng sec^{-1}).

As the spring freshet declined, the rate of MeHg export from the watershed decreased as well. During late spring and early summer (mid May to late June) new

peaks were observed. The export rate then fluctuated between very high (up to 67 ng sec^{-1}) and short-lived peaks, to very little or no export at all over the summer. In late July and the month of August 3 peaks were observed: on July 26th, August 2nd, and15th, with MeHg export rate ranging from 1.7 ng sec^{-1} to 20.9 ng sec^{-1} (HP6A and DE8 respectively, August 2nd). During the rest of the late summer period, the MeHg export rate was near zero. During the fall, the MeHg export increased again and stayed relatively constant over the period. Over the winter was the only time that the two years sampled seem to differ in trend and not magnitude: While in 2005-6 the MeHg export rate decreased throughout December and then increased over January and February, in 2006-7 the MeHg export decreased in a steady pattern from December to February. However, this change in trend did not seem to affect the overall pattern of MeHg loading to the lakes. In both watersheds the MeHg export diminished to near zero only in a few of the tributaries for a short period of time when the streams were frozen.

3.2.4. Cumulative Percent MeHg

The flux rate of MeHg was integrated over time in every drainage basin, (see methods: 2.5 for calculation), and the calculated amount was summed over all sub-catchments for every time interval to describe the amount of MeHg exported during each sampling time interval to each lake. The relative contribution of MeHg exported during each time interval to the annual load was calculated, and plotted on a cumulative scale (Fig 3.11). Due to MeHg data gaps during the low flow periods of summer 2005 and winter 2006, this calculation was possible only for the second sampling year, from March 2006 to February 2007.

During 2006-7 the accumulation pattern of percent MeHg through runoff to both lakes was almost identical, and resembled the pattern of accumulated discharge.

Early spring began with a relatively moderate slope, indicating low accumulation rate. By April 3rd this rate increased in both watersheds and by the end of spring freshet, on May 11th, resulted in 34% of annual MeHg in DE, and 25.5% in HP. Between the middle of June and the end of September, both watersheds showed a remarkable decline in the slope of accumulation rate, decreasing to zero over several weeks (HP) or months (DE). During this low accumulation time, there were two short- lived but dramatic increases in percent MeHg with both pronounced in DE watershed but much less in HP watershed: Between June 13th and June 20th there was an increase from 46.1% to 53% in DE. In Harp Lake this increase was hardly visibly distinguishable from the overall slope, likely because of the shorter duration of the runoff events in steeped sloped Harp drainage basin, and also because of different sampling dates. By June 26th the accumulation rate in both lakes decreased to 0 (indicated by flat line). The second summertime increase was seen in DE between July 24th (55.5%) and August 9th (62.2%). In HP watershed this increase lasted over a slightly longer period of time (July 11th- August 15th), and resulted in a less prominent amount of MeHg: from 39.5% to 47.4%. By the second week of August both watersheds exported very little MeHg, a trend that ended in the first week of October. From October to January, a large percentage of the annual amount of MeHg in runoff was exported to both lakes, resulting in 97.6% by January 23rd in DE, and 95.2% by Jan 11th in HP. Over the end of January and the remainder of February, the accumulation rate decreased again, as the remaining 2-5% of MeHg was exported to the lakes.

3.2.5. MeHg yield

Table 3.2 summarizes the yield calculations for both catchments. Based on the MeHg concentration and discharge rate, the annual yield of MeHg in runoff was calculated for each catchment by dividing by area (See methods for calculations).

In the year 2005-6, the annual yield from runoff in Harp catchment was 0.06 μg m^2 yr^{-1}, and the annual MeHg yield calculated for runoff in Dickie catchment was 0.17 μg m^2 yr^{-1}.

In 2006-7 Harp runoff yielded 0.14 μg m^2 yr^{-1}, and DE runoff yielded 0.18 μg m^2 yr^{-1}.

3.2.5.1. Expected and observed MeHg in snowmelt

Snow core samples taken shortly prior to spring melt were used to calculate expected values of MeHg yield in the snow covering both drainage basins. In 2005-6 the snow samples, averaged over 9 cores taken from both drainage basins yielded 0.003 μg m^{-2}, and in 2006-7 the snow yielded 0.005 μg m^{-2} (n=10). The expected values were compared to the calculated values of methylmercury in runoff during spring freshet. In 2005-6 runoff to Dickie Lake during spring freshet yielded 0.07 μg m^{-2} MeHg, while in Harp Lake the spring freshet runoff yielded 0.04 μg m^{-2} MeHg. In 2006-7, 0.06 μg m^{-2} MeHg was measured in runoff to Dickie Lake, while 0.04 μg m^{-2} was measured during the same period of time In Harp Lake.

3.2.6 Net MeHg flux

In order to estimate how much of the MeHg exported from the watershed was retained in the lake, discharge and MeHg concentration were measured in the outflow of both lakes over the sampling duration, at the same weekly intervals as the inflow

sampling. A net flux was calculated by subtracting the MeHg outflow flux from the sum of the integrated MeHg flux over all the sub-catchments. Fig 3.12 shows the result of these calculations: A time when the lake acted as a net sink is indicated by positive values, while negative values correspond to a time when the lake was a net source of MeHg.

For the majority of the year Dickie Lake acted as a net source of MeHg to downstream waters, with little MeHg retained in the lake and short intermittent intervals in which the lake acted as a net sink, mainly during the summer. The greatest negative values were observed during the spring time and the early winter. In 2005 a net amount of over 41 mg of MeHg was measured in the outflow between April 14th and April 20th. In 2006 the greatest negative values were seen between March 28th and April 5th (-32.5 mg MeHg), and between November 29th and December 5th (-37.26 mg MeHg). In 2005 a large positive peak was observed during the summer: a net amount of +63.83 mg of MeHg was exported into Dickie Lake between June 9th and June 16th. In 2006 a less prominent amount of +10.8 mg MeHg was exported into the lake between July 24th and August 2nd. Although this calculation was made without assessing the temporal dynamics of MeHg export from DE11, it is likely that the MeHg from this watershed would change the magnitude of the peaks, and not the trend.

The annual sum of net MeHg flux in Dickie Lake (including an annual estimate for DE11) amounted to 103.15 mg for the partial year of 2005-6 (calculated without missing summer and winter data). The complete annual sum of net MeHg was -157.34 mg for 2006-7 (not shown).

The pattern of net MeHg export in Harp Lake is quite different than that observed in Dickie Lake. During the greater part of the year, the lake acted as a net sink for MeHg in both years sampled, and the contrast between net source to net sink

periods was less dramatic. From March to June 2005 the net export fluctuated roughly between +3 mg to +20 mg MeHg, reaching a peak of +22.7 mg between June 21st and June 28th. During October and November, the MeHg export to the lake and the amount of MeHg exiting the lake was roughly balanced, with small fluctuations around zero.

The pattern of net MeHg export from Harp Lake in 2006-7 was similar to the partial pattern seen in 2005-6, with some differences. From April to August the export rate stayed roughly between +1 to +13 mg. During much of August and September the export dropped to near zero, increasing to the maximum annual peak of +26.09 on October 3rd. Following this peak the export rate decreased throughout October and November, but rose again for a short period of time in December (Dec18th, +14.8 mg). Throughout January and February the export was almost balanced, with fluctuations in the range of + 3 mg.

The sum of annual net MeHg influx for Harp Lake amounted to 161.9 mg MeHg for 2005-6, and 292.6 mg MeHg for 2006-7 (not shown).

3.2.7. DOC

3.2.7.1 DOC in snow and temporal dynamics in runoff

Two other water chemistry variables that were measured for this experiment are DOC and conductivity of the water, both known to be substantially different in pure snowmelt and in runoff.

The two lakes and corresponding watersheds are very different in the DOC content; Dickie Lake is a brown water system, with high DOC levels in all tributaries, rarely going below 10 mg L^{-1}. On the other hand Harp Lake on is generally a clear water system, and its tributaries display high variability in the DOC content of the water: from average 3.3 mg L^{-1} in HP3A to average 17.7 mg L^{-1} in HP5 (Table 3.2).

Snow core samples collected from both lake catchments shortly prior to snowmelt in spring 2006 were found to have an average of 0.56 (±0.15) mg L^{-1} TOC, (n= 12). These values were generally substantially lower than DOC concentration in runoff during the spring freshet, which varied greatly from one sub-catchment to another, but as the other water chemistry variables measured, followed roughly the same seasonal trend (Fig 3.13, 3.14): During early snowmelt the DOC concentration was low (13-19 mg L^{-1} in DE tributaries, 5-13 mg L^{-1} in HP tributaries), and further decreased within a few weeks to a low of 5-7 mg L^{-1} in DE and 3-6 mg L^{-1} in HP (April 11-13 in spring 2005, April 3-11 in spring 2006). Over the rest of the spring and the majority of the summer the DOC levels rose constantly, reaching a peak in early August. Over this time some fluctuations were observed: On June 1st 2005 DOC levels decreased to near zero in DE6, DE8 and DE10, but not inDE5 or Harp streams (DE5 had highest % wetland). Fluctuations were also observed in Harp streams on the rising limb of the DOC curve: Roughly from mid June to mid July DOC levels dropped in all Harp streams, then rose from late July to the August peak. Throughout the month of August and the fall season the DOC levels in both watersheds decreased with many fluctuations, reaching a relatively steady level in mid November (fall 2006) or early December (Fall 2005)(approximately 4-10 mg L^{-1} in HP, 17-17 mg L^{-1} in DE). These levels were maintained throughout the remaining of the winter.

3.2.7.2 Multiple regression analysis

In order to determine how the variables of DOC, conductivity, discharge and the seasonality of MeHg concentration are related, a stepwise multiple regression analysis was performed. DOC, conductivity, and the dummy variables representing season were all significant predictors for Log transformed MeHg concentration and were kept in the

model as determined by stepwise regression ($p<0.01$ for all). Discharge was not found to be a significant predictor for the overall model. The highest percent of variability was explained by DOC ($r^2=0.32$), followed by seasonality (spring-summer $r^2=0.07$, spring-fall $r^2=0.05$, spring-winter $r^2=0.01$) and conductivity ($r^2=0.01$).

Seasonal correlation

In order to determine how the above variables are related to seasonal MeHg concentrations, a regression analysis was performed for data from individual seasons. DOC was found to be the most significant predictor for MeHg in all seasons; therefore it was chosen to be the focus of further investigation. The results from this analysis are summarized in Fig 3.5 and Table 3.1.

DOC across all samples was found to be a strong predictor for MeHg in spring freshet ($r^2=0.65$, $p<0.001$). In spring freshet of 2005 DOC was found to explain 50% and 45% of variability in MeHg concentration measured in runoff from Dickie and Harp catchments, respectively. In spring freshet 2006 DOC also had a positive correlation with MeHg concentration ($r^2=0.30$, $r^2=0.50$ for Dickie and Harp, respectively) (Fig 3.15a and Table 3.1). Conductivity was also significant and kept in the model, but it was found to have less significance than the DOC ($r^2=0.03$, $p=0.02$).

In the summer DOC was found to be the only significant predictor of MeHg concentration, though to a lesser extent than in the spring ($r^2=0.37$, $p<0.001$).

In the partial data collected during summer 2005 DOC was found to explain 22% and 16% of variability in MeHg in Dickie and Harp tributaries respectively. In summer 2006 it was found to explain 19% of variability and 34 % of variability in MeHg concentration in runoff to Dickie and Harp lakes, respectively (Fig 3.15b)

The fall model found conductivity to be the most significant predictor for MeHg concentration (r^2=0.25, p<0.01). DOC was also found to be significant (r^2=0.22, p=0.01).

In fall 2005 DOC had a positive weak correlation with MeHg (r^2=0.09 and r^2=0.04 for DE and HP, respectively). In 2006 the correlation increased for both catchments: (r^2=0.17 for DE and r^2=0.25 for HP (Fig 3.15c).

During the winter DOC was also found to be the most significant predictor of MeHg in runoff (r^2=0.23, p<0.01), and discharge was found to be also significant, but less (r^2=0.04, p=0.04). During winter 2006-7 DOC was found to have a positive correlation with MeHg concentration, with an intermediate correlation strength (r^2=0.43 for both) (Fig 3.15d).

No MeHg samples were collected during winter 2005-6.

3.2.8. Conductivity

The average conductivity of the snow was 24.2 $\mu s\ cm^{-1}$ (based on the average conductivity of precipitation collected in the months of January and February in Harp Lake, between 1984 and 2004, n=158). (Dorset environmental science center, MOE Unpublished data)

The temporal trends of conductivity measured in runoff from Harp Lake and Dickie Lake sub catchments over the duration of the sampling period varied greatly from stream to stream (Fig 3.16, 3.17). During the spring of 2006-7 some streams were found to have low but increasing conductivity levels (HP6: increased from 9 $\mu s\ cm^{-1}$-50 $\mu s\ cm^{-1}$ from March 28th to April 11th, DE8 from 39.4 $\mu s\ cm^{-1}$ to 49 $\mu s\ cm^{-1}$), while others exhibited decreasing levels of conductivity (HP3 decreased from 48 $\mu s\ cm^{-1}$ on March 27th to 29.2 $\mu s\ cm^{-1}$ on April 11th, DE10: 37 $\mu s\ cm^{-1}$-29.4 $\mu s\ cm^{-1}$). Some of the

streams increased in conductivity throughout the spring and into mid-summer (DE8, HP4), while others (DE5) stayed nearly constant or slightly decreased from shortly after peak snowmelt to late summer (HP6A). The trend in conductivity during the fall and winter is somewhat more uniform. During the month of September 2006 there is a data gap, and no conductivity measurements are available. The month of October began with increased levels of conductivity (range 20-100 $\mu s\ cm^{-1}$ in Dickie, 30-75 $\mu s\ cm^{-1}$ in Harp), decreasing rapidly until the end of November. Over the winter of 2006-7 the conductivity dropped occasionally, even reaching levels near zero (DE10, January 2, 2007, 0.4 $\mu s\ cm^{-1}$), but generally stayed constant in the majority of the streams (roughly 20-50 $\mu s\ cm^{-1}$ in both catchments). In DE8, HP6 and HP4 a mild constant increase in conductivity was measured over the winter.

There was only partial data for the year of 2005-6. Here, although the range of the data is greater, the conductivity levels in all sub-catchments decreased constantly from October to February.

Table 3.1-Summary of results for analysis of correlation between dissolved organic carbon and methylmercury in the seasonal runoff to Dickie and Harp Lakes, using a stepwise multiple regression. r^2 and p values under the season (column heading) represent the overall model, the statistics in the table represent the seasonal model. The duration of spring freshet was determined by the seasonal hydrograph and climate data. No MeHg samples were collected during winter 2005-6.

	Statistic/ model	Spring freshet (r^2=0.65, p=0.001)		Summer (r^2=0.37, p=0.02)		Fall (r^2=0.22, p<0.01)		Winter (r^2=0.23, p<0.01)	
		DE	HP	DE	HP	DE	HP	DE	HP
2005-6	r^2	0.51	0.47	0.22	0.16	0.09	0.04		
	p	<0.001	<0.001	0.02	0.05	0.13	0.25		
	n	36	60	26	25	27	38		
2006-7	r^2	0.30	0.50	0.19	0.34	0.17	0.25	0.43	0.43
	p	<0.01	<0.001	<0.01	<0.001	<0.01	<0.001	<0.001	<0.001
	n	27	42	43	68	39	62	35	59

Table 3.2- Physical and chemical characteristics of the 6 tributaries to Harp Lake (HP) and the 5 tributaries to Dickie Lake (DE). All streams were monitored and sampled weekly from March 2005 to February 2007.

Station	Catchment area m^2	Percent peatland	Mean Discharge L sec^{-1}	Mean DOC mg L^{-1}	Mean MeHg ng L^{-1}	MeHg yield[a] $\mu g\ m^{-2}\ yr^{-1}$	n[b]
DE5	299800	25.4	5.7	15.4	0.48	0.17 (0.16)	79 (68)
DE6	218000	22	4.3	21	0.67	0.34 (0.32)	80 (70)
DE8	669600	8.2	10.7	22.8	0.88	0.09 (0.14)	80 (68)
DE10	788900	17.1	15.3	22.7	0.82	0.20 (0.19)	77 (59)
DE11	762700	20.9	13.2[c]	-	0.3[c]	0.16[c]	-
All DE	2739000	13.9	8.04	21.3	0.72	0.17 (0.18)	402 (350)
HP3	260000	9.3	4.3	12.3	0.27	0.06 (0.1)	80 (66)
HP3A	196500	2.9	3.8	3.3	0.35	0.03 (0.04)	82 (72)
HP4	1190900	0	18.9	7.05	0.15	0.04 (0.07)	86 (76)
HP5	1905300	13.3	28.2	17.7	1.05	0.08 (0.2)	80 (70)
HP6	99700	0	1.9	9.95	0.19	0.03 (0.06)	80 (65)
HP6A	152800	8.5	2.8	13.4	0.3	0.02 (0.06)	71 (55)
All HP	3805200	6.3	9.6	10.5	0.39	0.06 (0.14)	479 (405)

[a] - MeHg yield is presented for both years sampled: numbers with no brackets are from 2005-6; numbers in brackets are from 2006-7.
[b] - n- number of discharge samples used for analysis. In brackets- the number of MeHg samples used for analysis.
[c]- Discharge, MeHg concentration and yield for DE11 represent estimations. See calculations for details

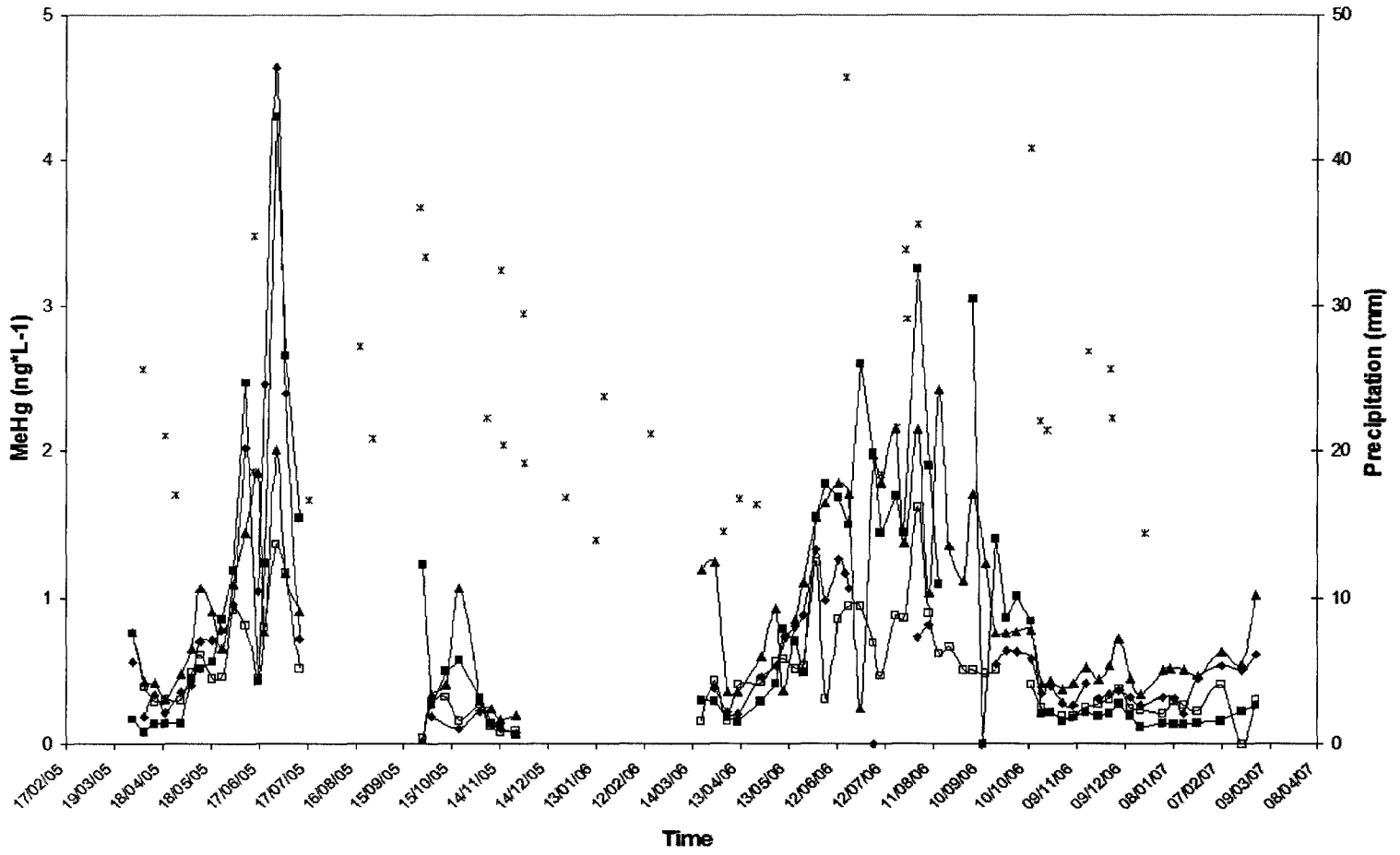

Figure 3.1- Temporal changes in MeHg concentration in 4 tributaries of Dickie (DE) Lake. Each sample represents an average of two replicates. Closed diamonds – DE10, open squares- DE5, closed triangles- DE6, open squares- DE8. Precipitation events over 15 mm are presented for reference as asterixes.

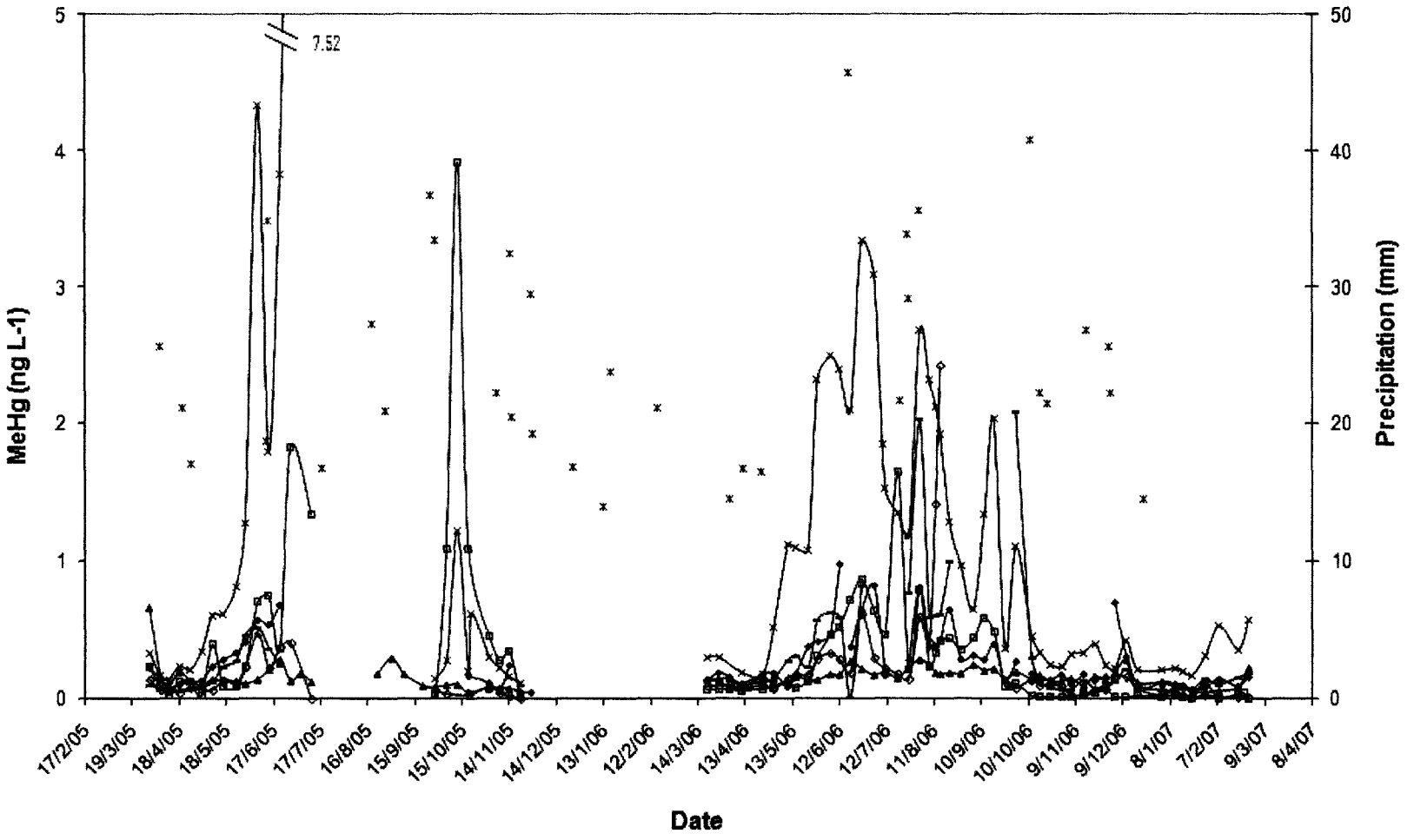

Figure 3.2- Temporal changes in MeHg concentration in 6 tributaries of Harp Lake (HP). Each sample represents an average of two replicates. Closed diamonds- HP3, open squares- HP3A, closed triangles- HP4, exes- HP5, open diamonds- HP6, horizontal lines- HP6A. Precipitation events over 15 mm are presented as asterixes for reference.

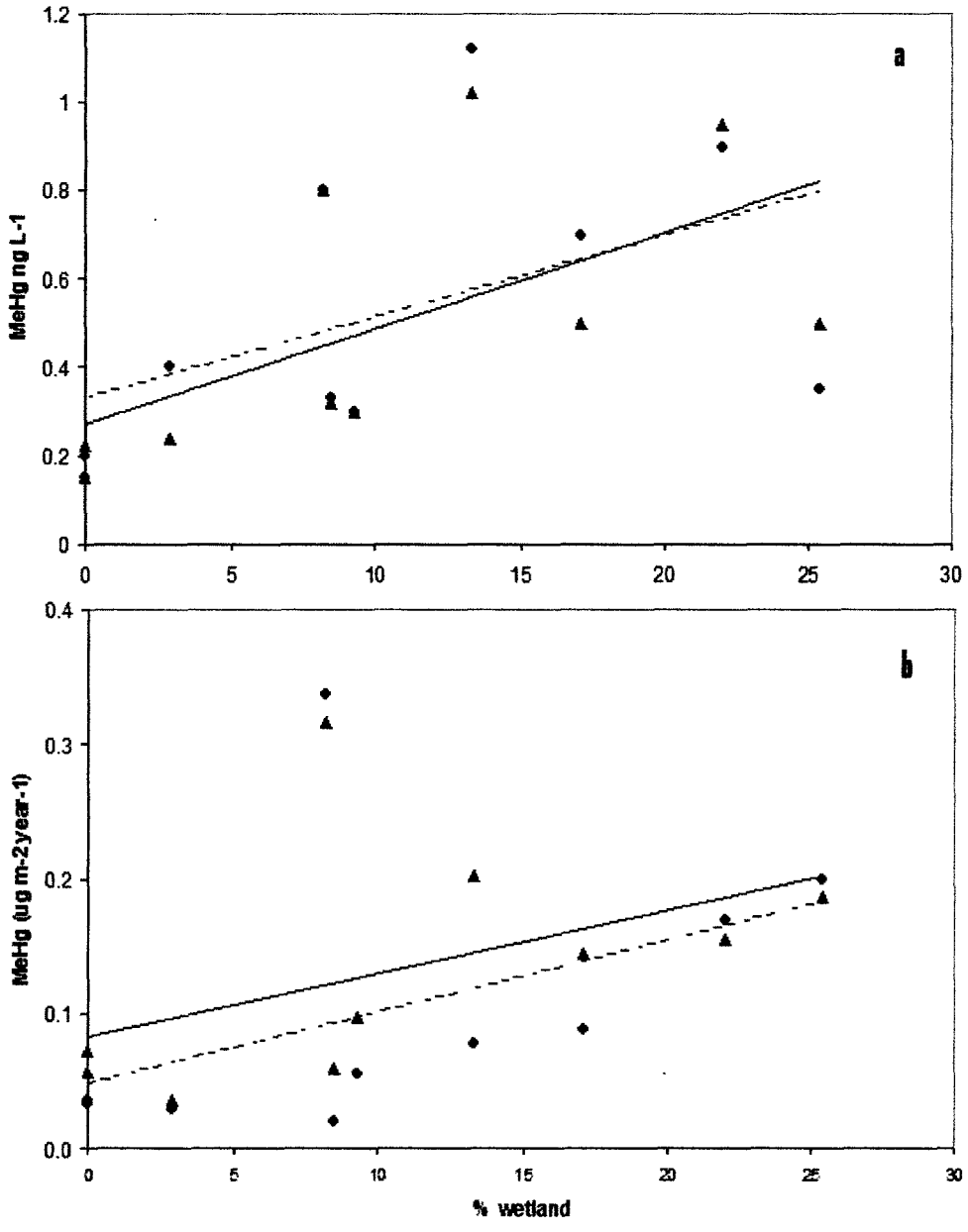

Figure 3.3- Correlation between % wetland in a sub-catchment and (a) the annual mean MeHg concentration (ng L^{-1}) or (b) annual MeHg yield (μg m^{-2} $year^{1}$) measured in tributaries to Dickie (DE) and Harp (HP) Lakes between March 2005 and February 2007. Circles and dashed line represent measurements made during sampling year 2005-6 (% wetland/ MeHg conc: r^2= 0.24, p=0.06. % wetland/ MeHg yield: r^2=0.21, p=0.18). Solid line and triangles represent measurements made during sampling year 2006-7 (% Wetland/ MeHg conc: r^2=0.36, p=0.15. % Wetland/ MeHg yield: r^2= 0.23, p=0.16).

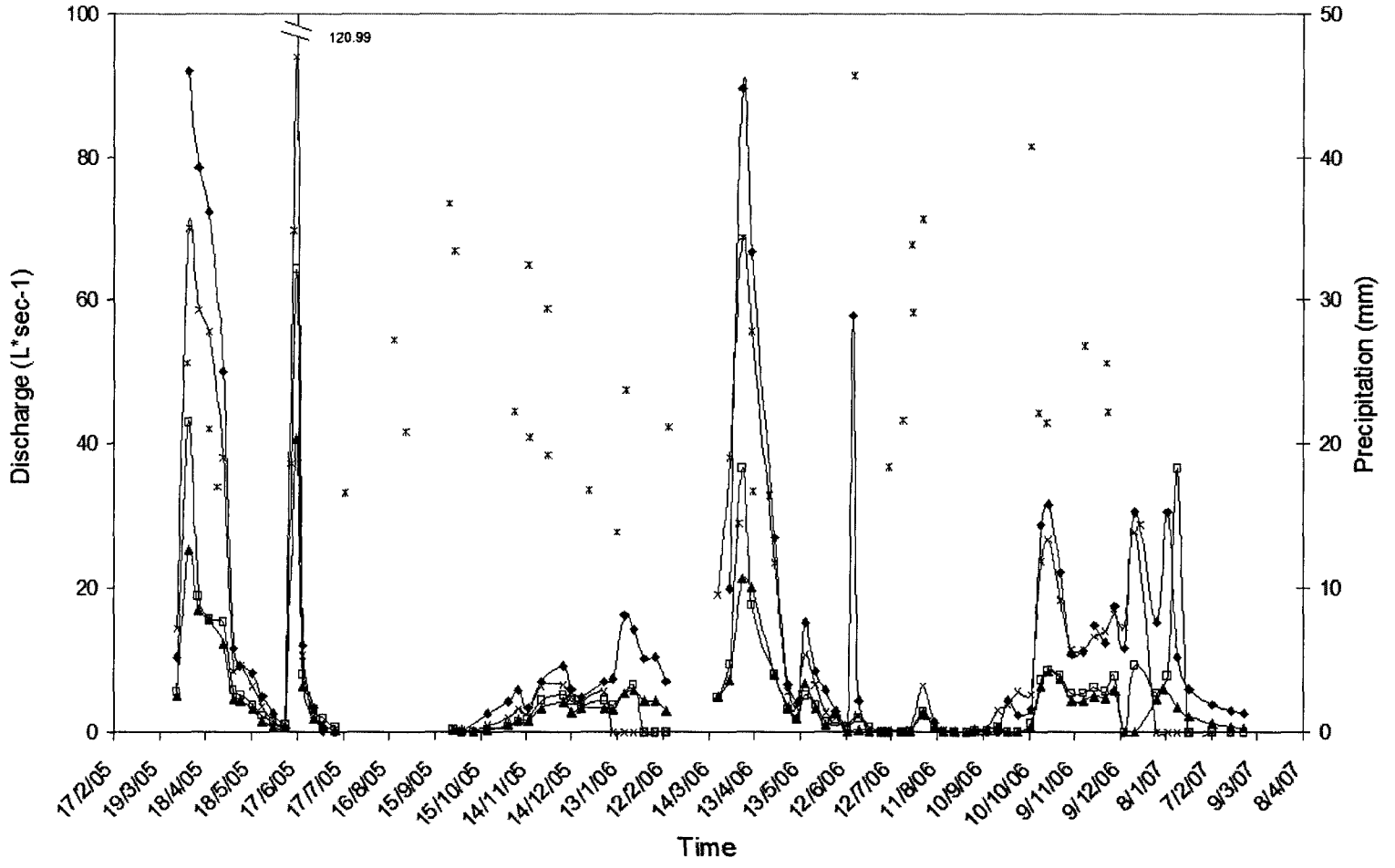

Figure 3.4- Temporal dynamics of discharge rates for 4 tributaries to Dickie (DE) Lake. Closed diamonds- DE10, open squares- DE5, closed triangles- DE6, exes- DE8. Precipitation events over 15 mm are presented as asterixes for reference.

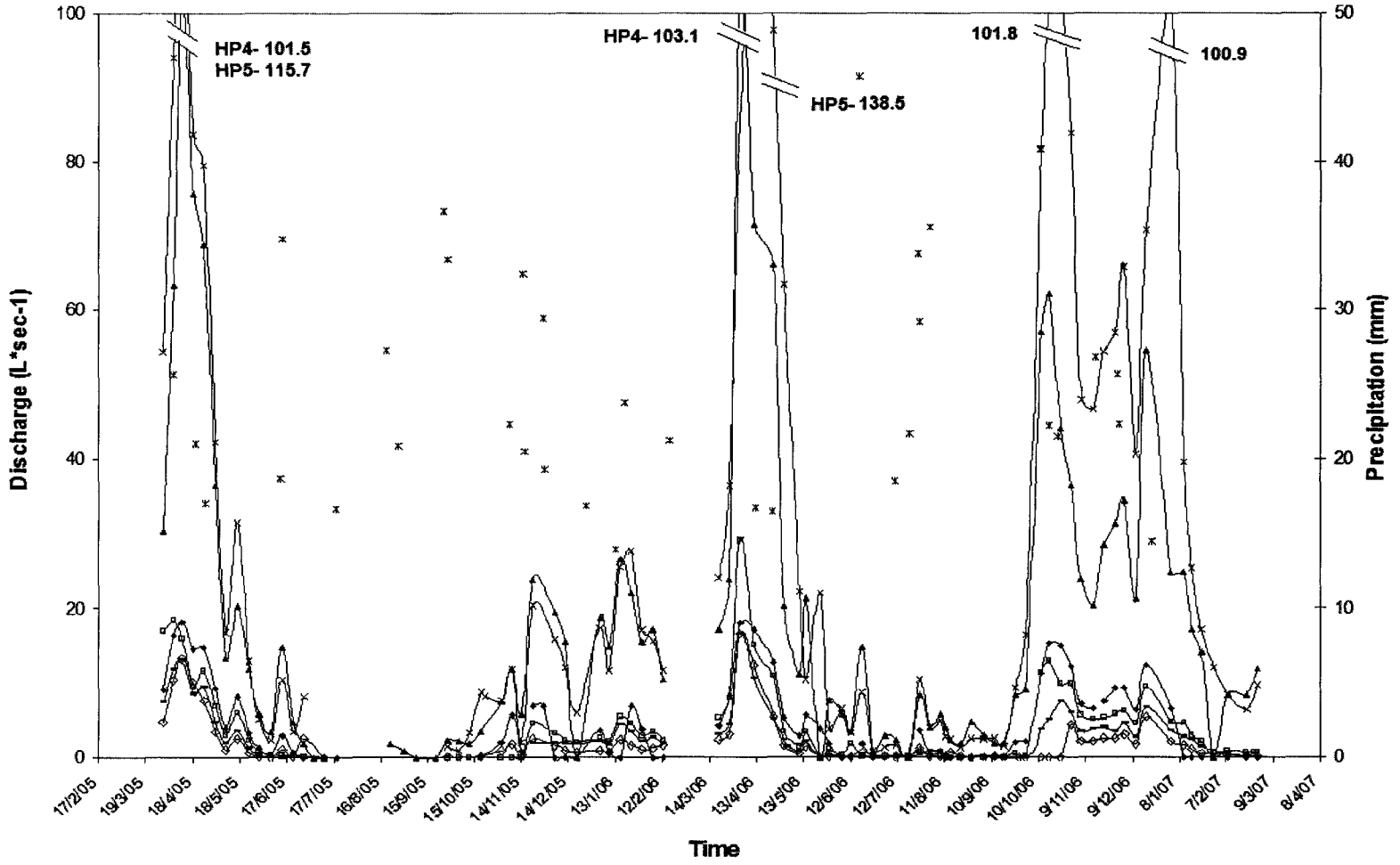

Figure 3.5- Temporal dynamics of discharge rate for 6 tributaries to Harp (HP) Lake. Closed diamonds- HP3, open squares- HP3A, closed triangles- HP4, exes- HP5, open diamonds- HP6, horizontal lines- HP6A. Precipitation events over 15 mm are presented as asterixes for reference.

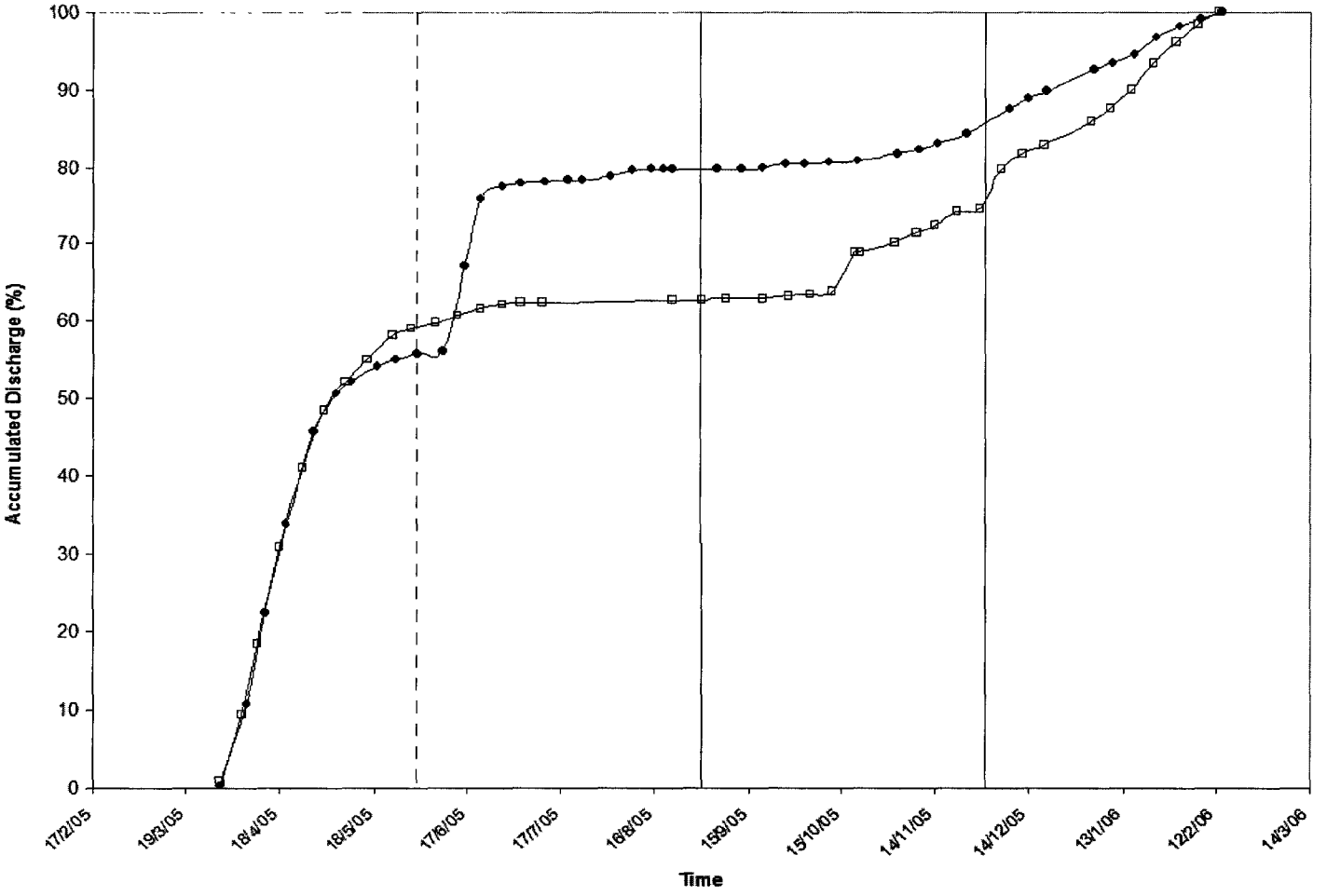

Figure 3.6- The cumulative percent of annual discharge (liters) to Harp and Dickie Lakes, accumulated over sampling year 2005-6. The calculation was made by summing the discharge (L) from all sub catchmets for a given time interval, and dividing that number for every time interval by the annual amount of water flowing into the lake. Closed circles- Dickie, open squares- Harp. The dashed line represents the end of spring freshet which coincided with the end of the spring. The solid lines represent the end of the summer and fall.

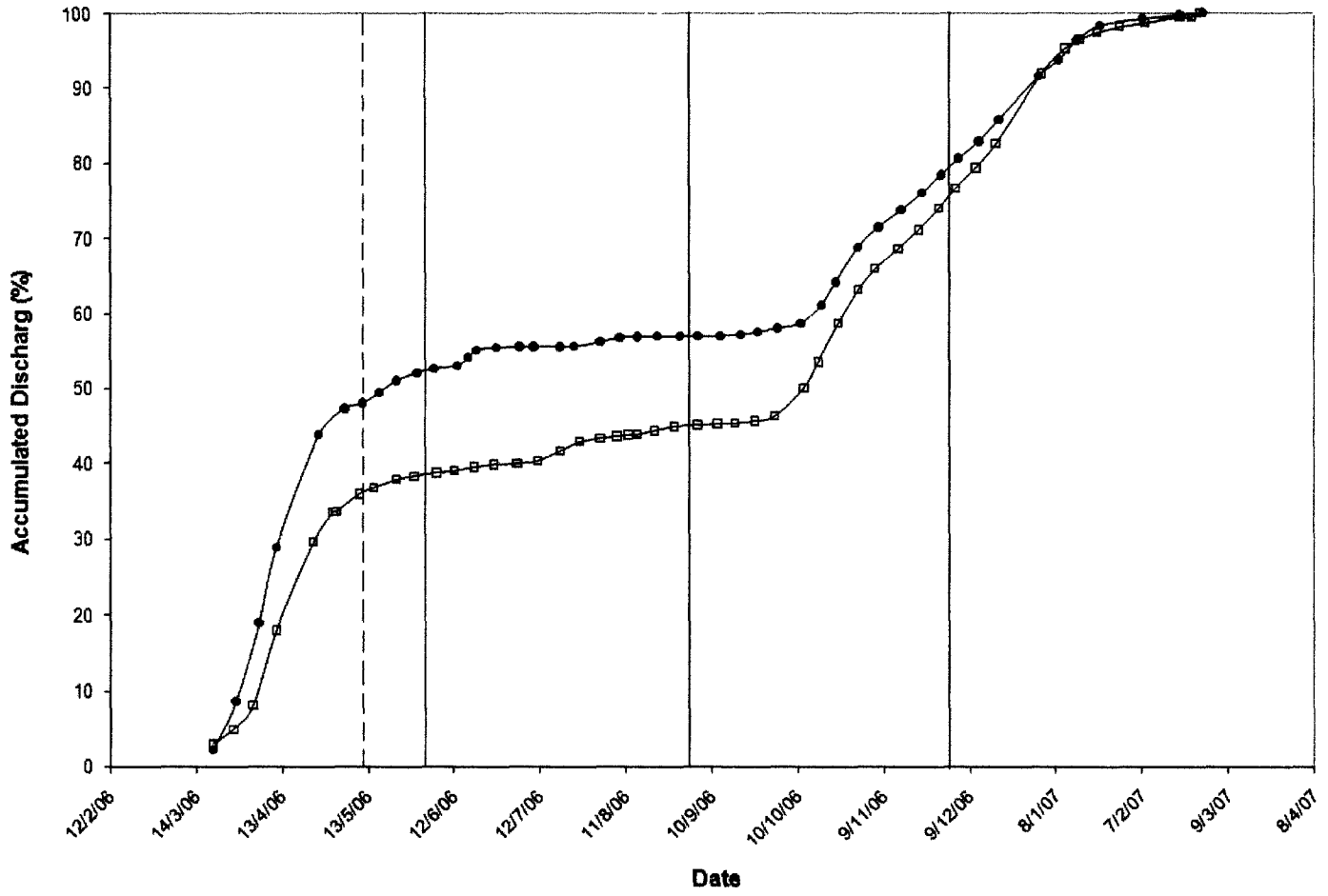

Figure 3.7- The cumulative percent of annual discharge (liters) to Harp and Dickie Lakes, accumulated over sampling year 2006-7. The calculation was made by summing the discharge (L) from all sub catchmets for a given time interval, and dividing that number for every time interval by the annual amount of water flowing into the lake.Closed circles- Dickie, open squares- Harp. The dashed line represents the end of spring freshet. The solid lines represent the end of the spring, summer and fall.

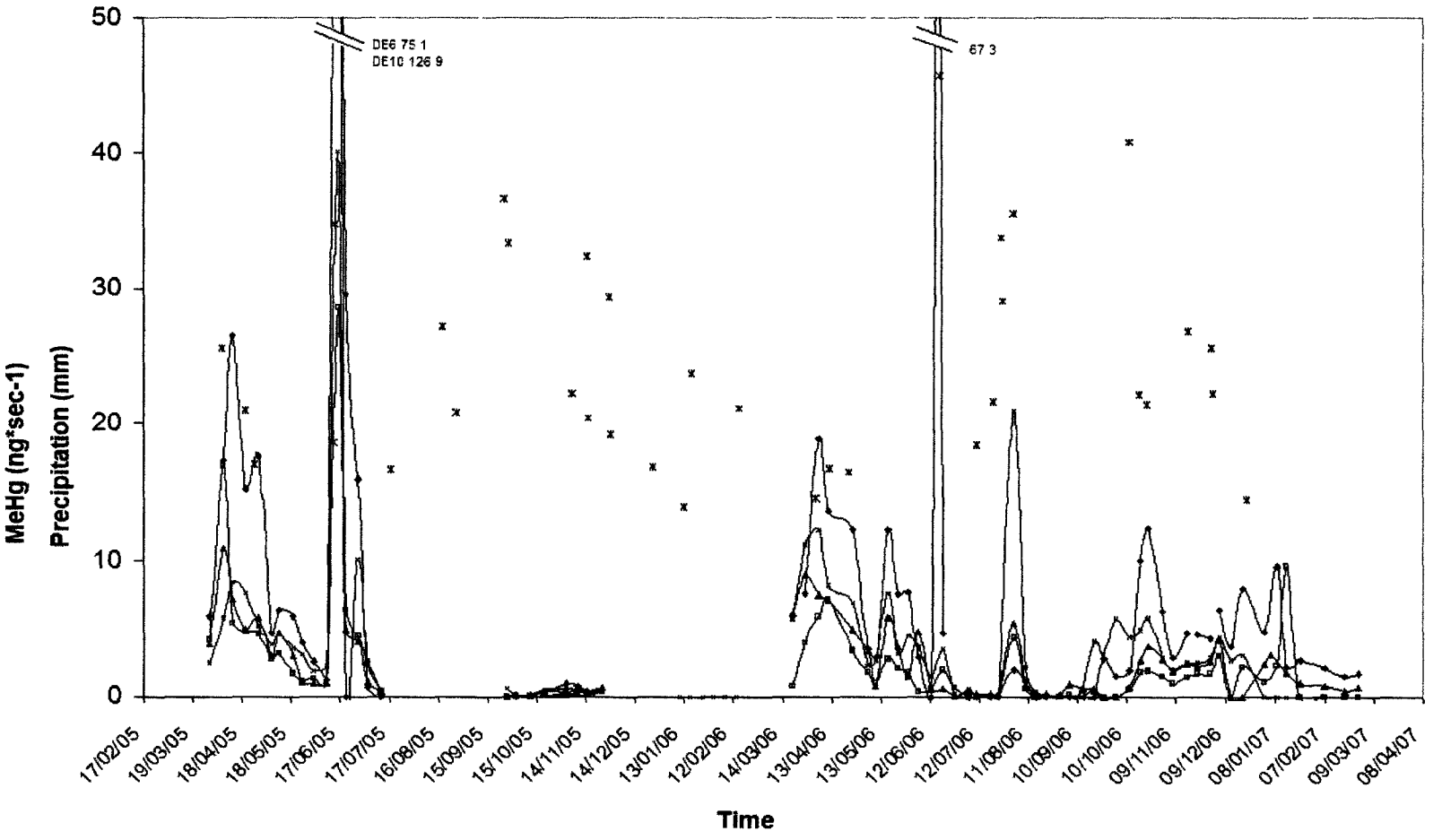

Figure 3.8- The Temporal dynamics in MeHg flux rate (calculated as concentration times discharge rate) from 4 tributaries to Dickie (DE) Lake. Closed diamonds- DE10, open squares-DE5, closed triangles- DE6, exes- DE8. Precipitation events over 15 mm are presented as asterixes for reference.

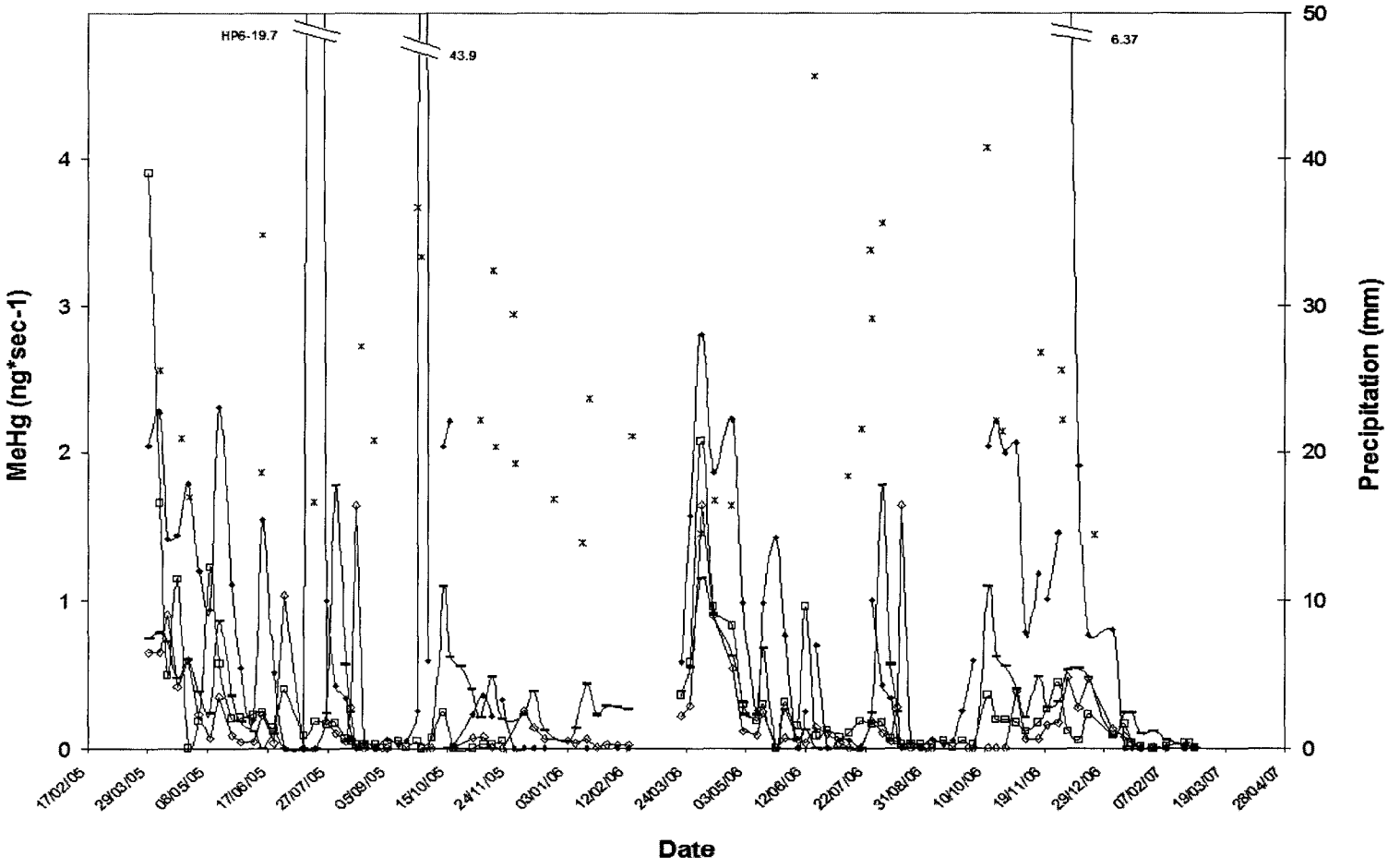

Figure 3.9- Temporal trends in lower scale MeHg flux rates (calculated as concentration times discharge rate) from 4 tributaries to Harp (HP) Lake. Closed diamonds- HP3, open squares-HP3A, open diamonds- HP6, horizontal lines- HP6A. Precipitation events over 15 mm are presented as asterixes for reference.

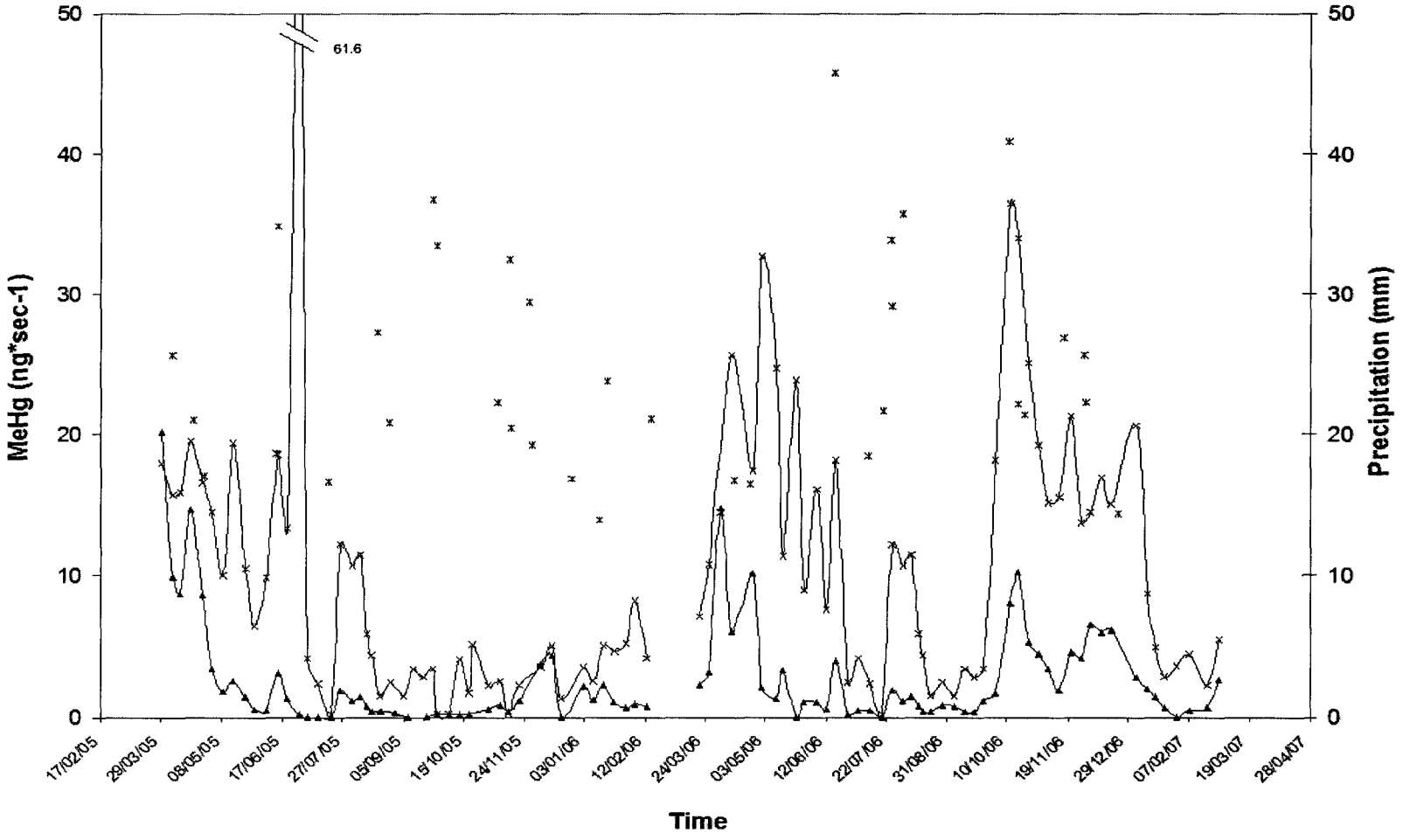

Figure 3.10- Temporal trends in higher scale MeHg flux rates (calculated as concentration times discharge rate) from 2 tributaries to Harp (HP) Lake. Closed triangles- HP4, exes, HP5. Precipitation events over 15 mm are presented as asterixes for reference.

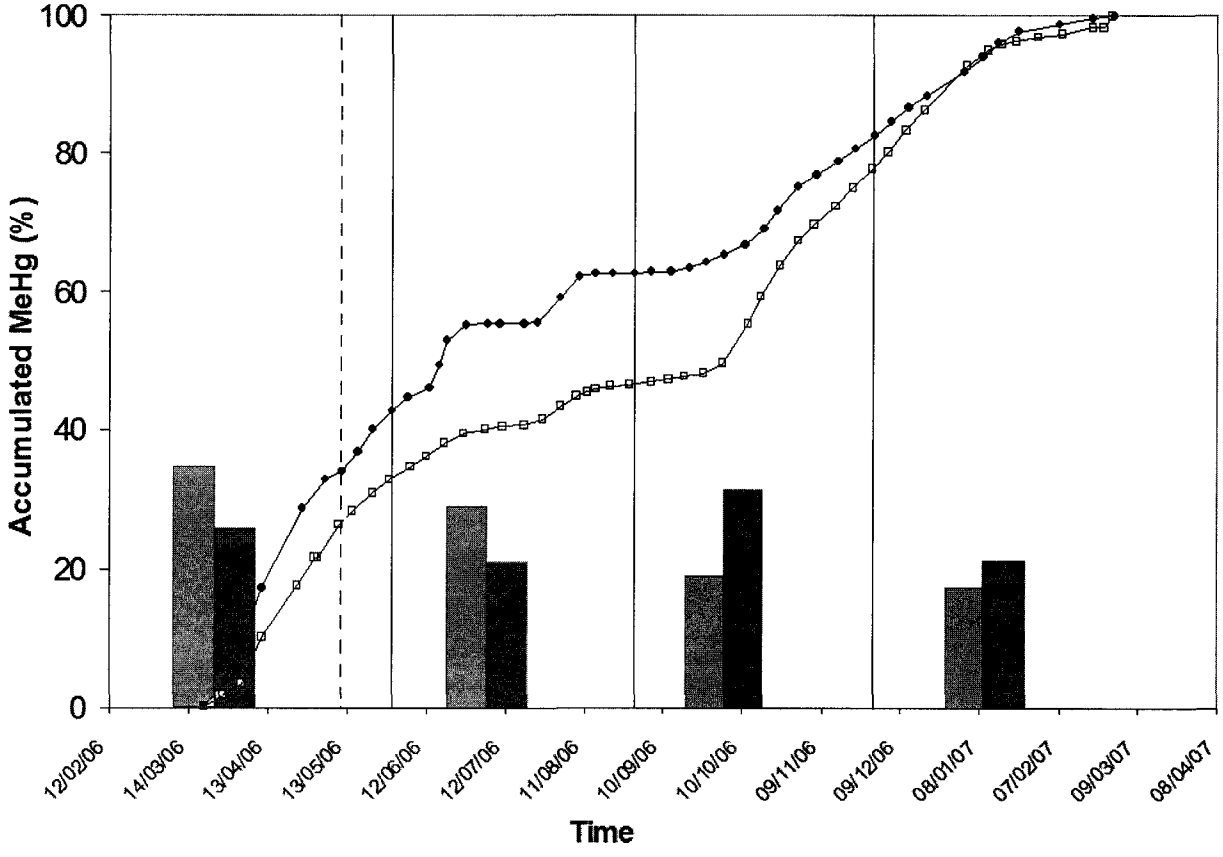

Fig 3.11- Lines- the cumulative percent of annual MeHg load (mg) in runoff to Harp and Dickie Lakes, summed over all respective streams for sampling year 2006-7. Closed circles- Dickie, open squares- Harp. **Bars-** the total (non cumulative) proportion of MeHg in runoff to Harp and Dickie Lakes, summed over the respective streams and transported to the lakes during each season of the sampling year 2006-7. Dark bars- Harp streams, light bars- Dickie streams. The dashed line represents the end of spring freshet on May 10th, estimated based on the seasonal hydrograph and climate data. The solid lines represent the end of the spring, summer and fall.

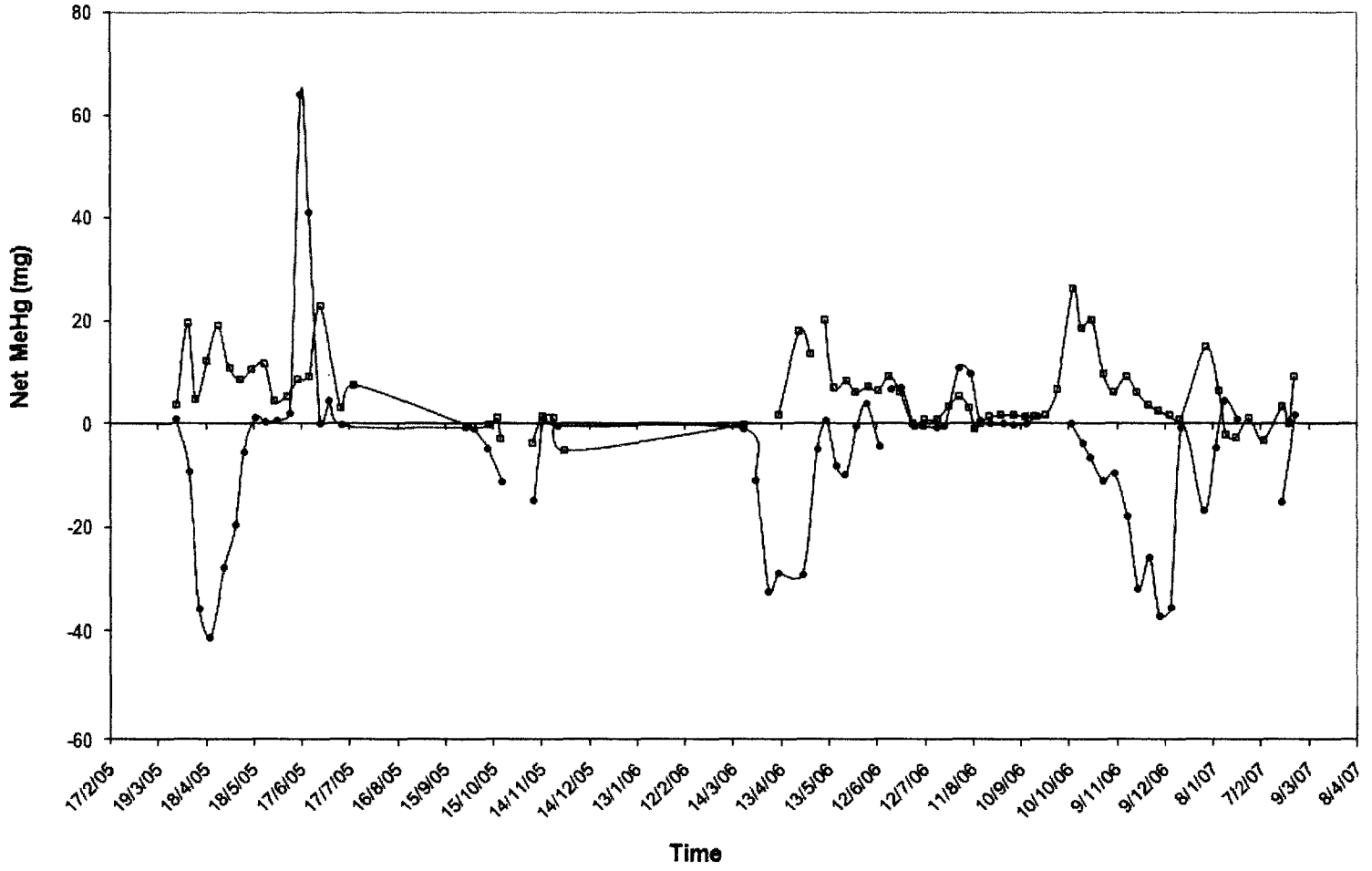

Figure 3.12- Net MeHg flux in Dickie (DE) and Harp (HP) Lakes. A net flux was calculated by subtracting the MeHg outflow flux from the sum of the integrated MeHg flux over all the sub-catchments. Negative values represent a time where the lake acted as a net source to downstream waters. Closed circles- DE, open squares- HP.

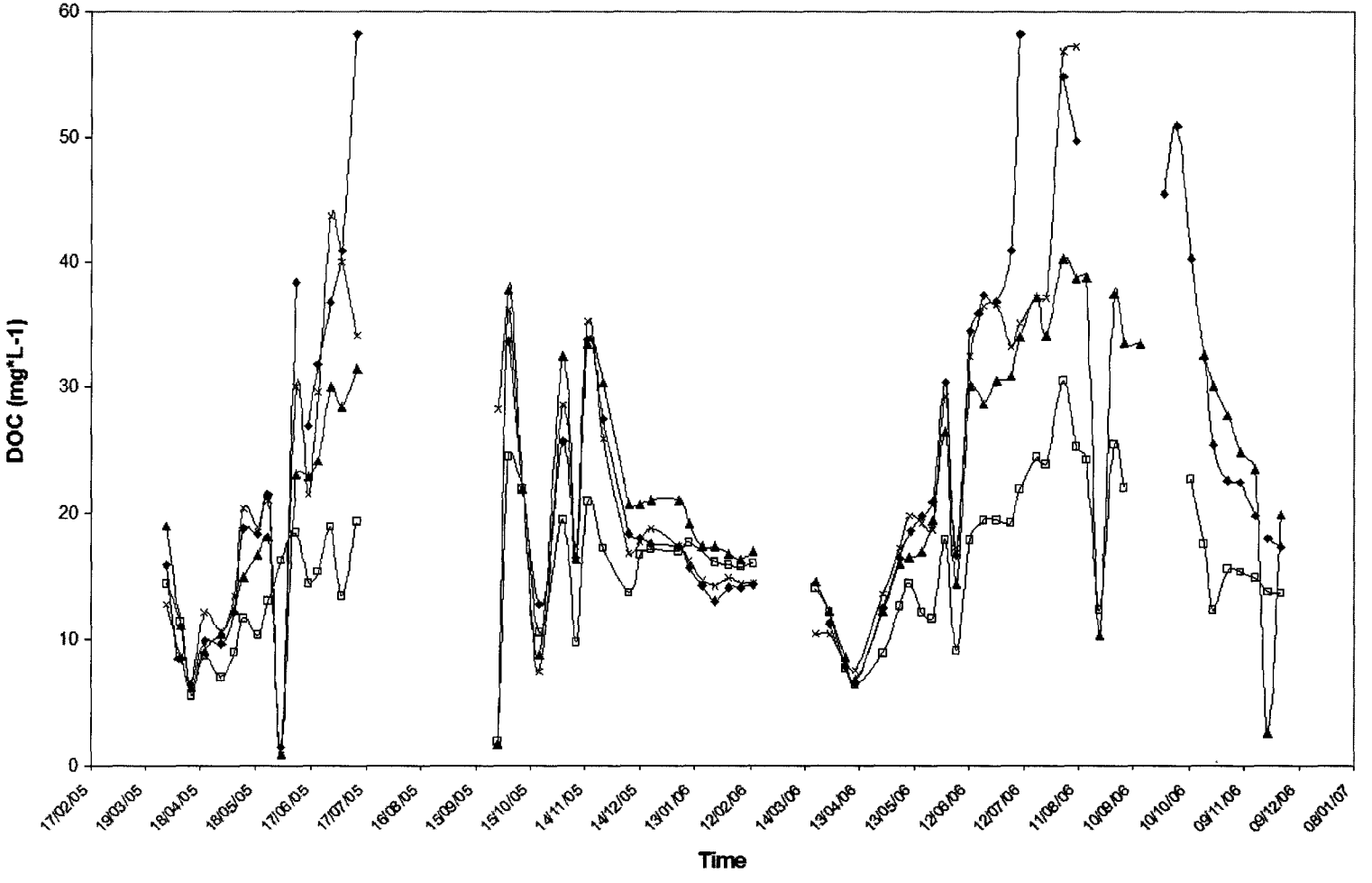

Figure 3.13- Temporal dynamics of DOC from 4 tributaries to Dickie (DE) Lake March 2005 and February 2007. Closed diamonds- DE10, open squares- DE5, closed triangles- DE6,exes- DE8.

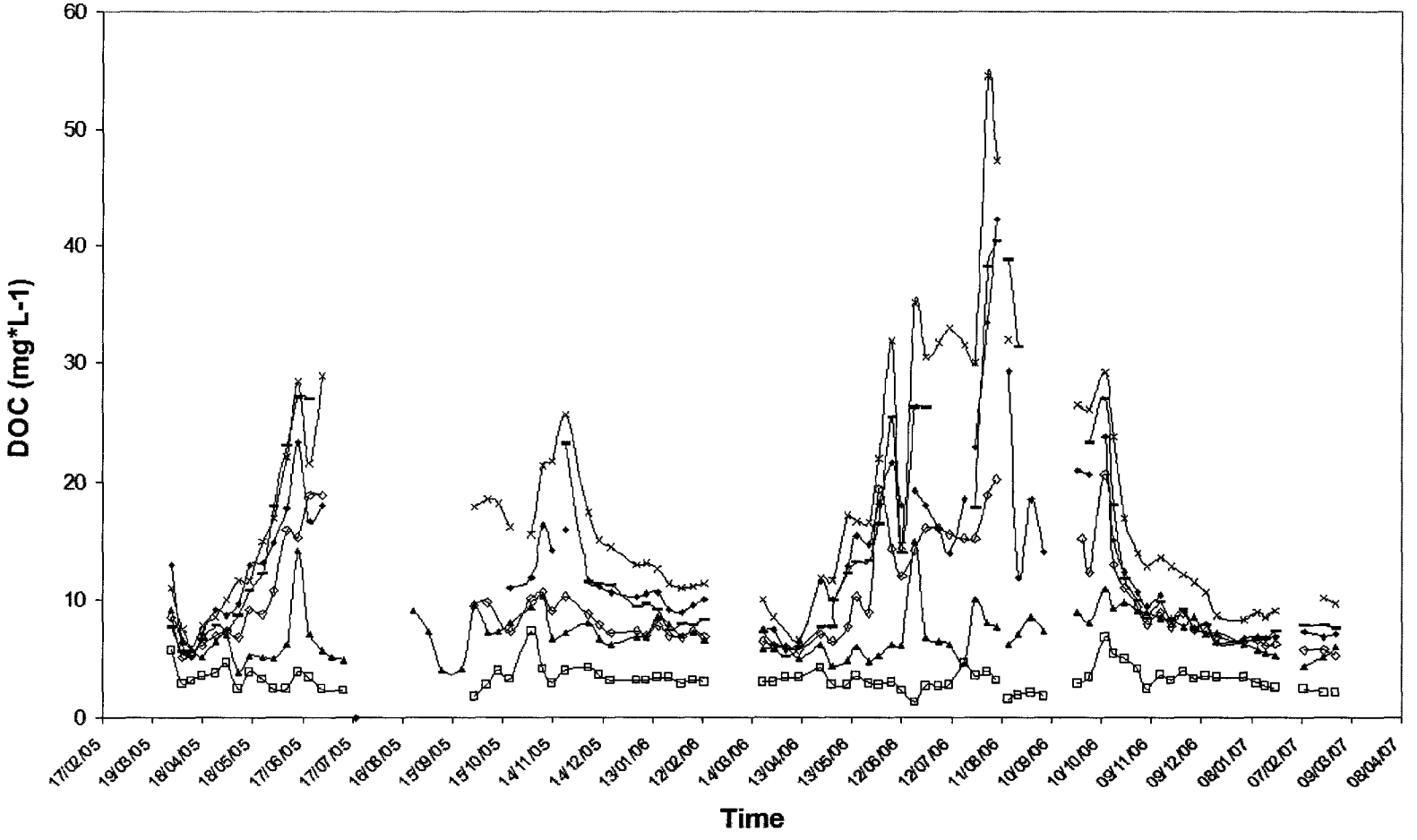

Figure 3.14- Temporal dynamics of DOC for 6 tributaries to Harp (HP) Lake between March 2005 and February 2007. Closed diamonds- HP3, open squares- HP3A, closed triangles- HP4, exes- HP5, open diamonds- HP6, horizontal lines-HP6A.

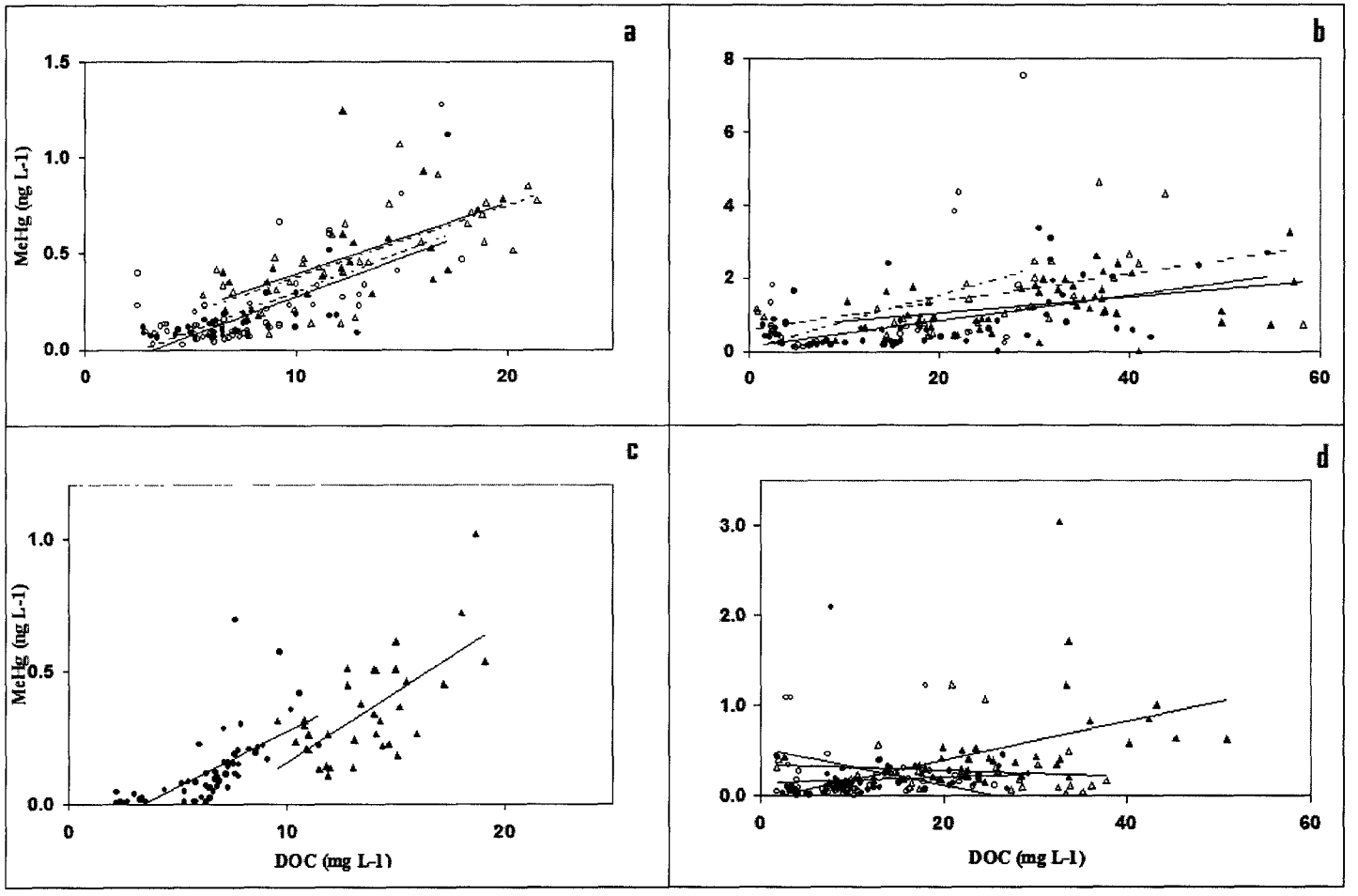

Figure 3.15- Seasonal variations in the relationship between dissolved organic carbon (DOC) and methylmercury (MeHg) measured in tributaries to Dickie (DE, triangles) and Harp (HP, circles) Lakes between March 2005 and February 2007.Dashed lines and open symbols represent regressions for data from sampling year 2005-6, complete lines and closed symbols represent regressions for data from sampling year 2006-7. In winter 2005-6 no MeHg samples were collected. a- spring, b- summer, c- winter, d-fall

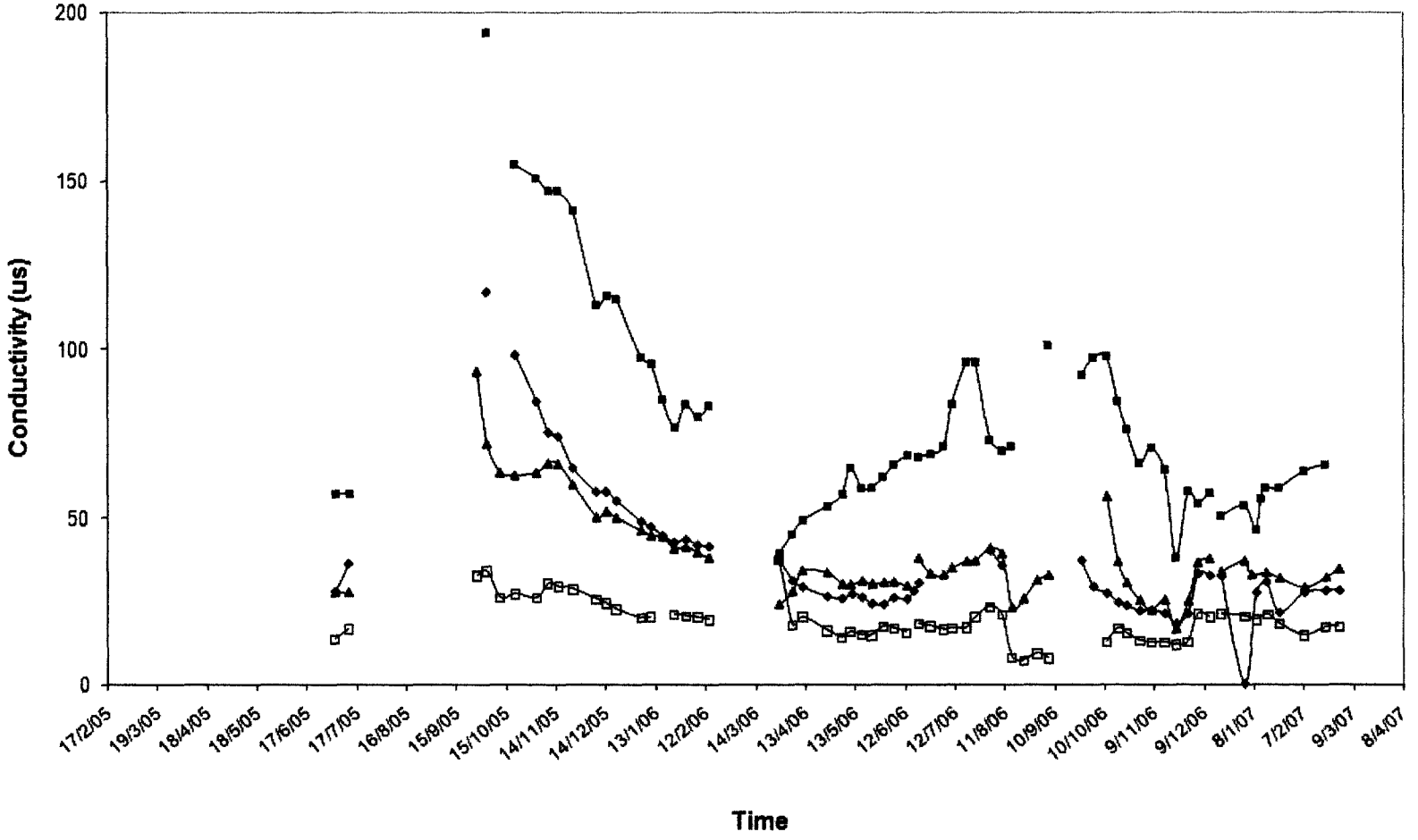

Figure 3.16- Temporal dynamics of conductivity from 4 tributaries to Dickie Lake, between June 2005 and March 2007. Closed diamonds- DE10, open squares-DE5, closed triangles- DE6, closed squares- DE8.

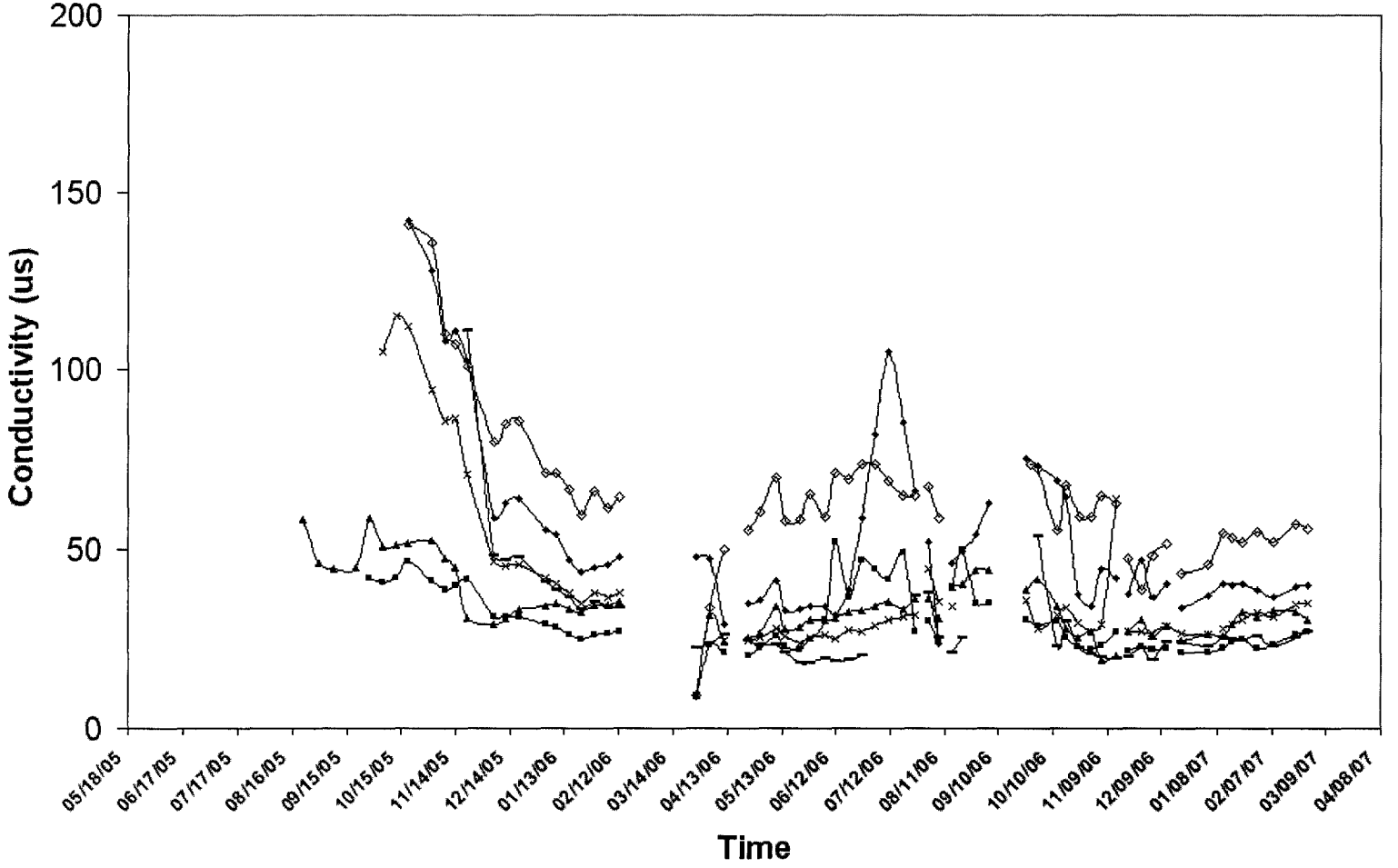

Figure 3.17- Temporal dynamics of conductivity for 6 tributaries to Harp Lake, August 2005 to March 2007.Closed diamonds- HP3, closed squares- HP3A, closed triangles- HP4, exes- HP5, open diamonds- HP6, horizontal lines-HP6A.

4. Discussion

4.1. St. Anicet

4.1.1. Mercury concentration and yield

The concentration of THg measured in precipitation in St. Anicet is similar to other values reported in this region. Hall et al. (2005) measured THg in precipitation in the Experimental Lake Area in Ontario and found concentrations to be between 10 and 60 ng L^{-1}, with few samples exceeding that number, measuring as high as130 ng L^{-1}. Glass and Sorensen (1999) found between 4.3 and 28.9 ng L^{-1} in the upper Midwest of the USA (Table 4.1). In a study of data collected for the MDN over 7 years, Vanarsdale et al. (2005) stated that the site at St. Anicet along with two other sites received higher concentrations of THg than other sites in the network, probably as a result of the lower precipitation volumes in this location. In the same study it was found that these higher concentrations did not result in higher deposition rates compared to the other sites, as can be seen in Table 4.1.

Temme et al. (2007) who analyzed total gaseous mercury (TGM) measurements from various stations across USA and Canada, found a decreasing trend in TGM in St. Anicet, at a rate of about -1.5% a year. The researchers also compared their findings with precipitation data from MDN, and found a similar decrease in THg in precipitation at a rate of -1.5% to -1.8% over 8 years. A similar decrease in THg levels was found in several atmospheric studies and lake/wetland core studies, but the magnitude and rate of the change seems to vary; Temme et al (2007) found a decrease by 14.7% near Toronto between 1995-2005, at a rate of 1.8% a year. Watras (2000) measured THg concentration in precipitation in Wisconsin from 1994 to 1999, and reported a decrease rate of about 1.2 ng L^{-1} $year^{-1}$, which resulted in a 50 percent decrease in annual deposition rate from 11.2 μg m^{-2} yr^{-1} to 5.5 μg m^{-2} yr^{-1}. Watras and Morrison (2008)

reported a decrease in THg in precipitation measured in Wisconsin at a rate of 0.04 ng L^{-1} yr^{-1} from 1988 to 2007. Between 2002 and 2004 they recorded a 38% decrease in annual atmospheric THg deposition. These decreasing THg levels likely reflect the ongoing national and international effort to decrease emissions of mercury globally, since the Clean Air Act was enforced in early 1990, resulting in decreased emissions of Hg from power plants in the USA and Canada. From 1991 to 1995 Canada reduced its anthropogenic mercury emissions by 70% from an estimated 38.8 t in 1990 to 11.2 t in 1995. The United States has also reduced its anthropogenic mercury emissions by 36% from 220 tons in 1990 to 144 tons in 1995 (Pilgrim et al. 2000).

Despite this, the data presented here shows no evidence of the global trend of decreasing atmospheric mercury. In a comprehensive analysis of long term data collected by the Canadian Atmospheric Mercury Measurement Network, (CAMNet), Temme et al (2007) concludes that the observed changes of THg in the atmosphere and wet deposition are driven by local or regional Hg emissions. It is possible that the chemistry of the air and precipitation measured in the St. Anicet station is highly influenced by the relative proximity to the large urban area of Montreal, masking the more subtle global changes.

Measurements of MeHg in precipitation are sparse, and usually represent the concentration in a single event or over a short period of time. However, the data presented here agrees with data recorded in the literature (Table 4.2).

The calculated annual deposition rate for THg falls within the expected range in this region (Table 4.1).

The annual deposition rate for MeHg measured in the investigation presented here is somewhat higher than the rate reported in North America (Table 4.2), but similar to the deposition rates reported in Sweden and Norway, 0.1-0.29 $\mu g\ m^{-2}\ year^{-1}$, (reviewed by St. Louis et al. 1995). This deposition rate may even be an underestimation, as the analysis of the collection funnel rinses revealed that some MeHg adsorbed to the instrument. Although the MeHg adsorbed represented on average only 5% of MeHg collected, further research is needed in order to understand the dynamics of this process and its implications.

The percent of THg present as MeHg reported in the literature varies from less than 1 % (St. Louis et al. 1995, Mason et al. 1997) to 18% in single rain events (Hall et al. 2005). Based on a review of the published literature, the annual average in North America seems to be around 1.2% (Table 4.3), about half as much as measured in St. Anicet. The variation in % MeHg reported in the literature may stem from the short sampling periods generally used to measure MeHg in precipitation. To my knowledge, this project was the most comprehensive investigation of MeHg in precipitation to date, and as such it likely represents the proportion of MeHg in precipitation more accurately than ever done before.

The low proportion of MeHg measured in precipitation has led the scientific community to believe that at large, MeHg in precipitation does not have an important role in aquatic ecosystems. This is reflected in the low number of scientific publications reporting MeHg in precipitation, and also the absence of a large scale and long term monitoring program for MeHg in precipitation, as is done for THg by the MDN. However, the dynamics of the mercury speciation in the environment may lead to the amplification of the proportion of MeHg after deposition, increasing its significance.

Due to the uneven sampling intervals for THg and MeHg it is difficult to accurately evaluate the temporal dynamics of the change in proportion of MeHg and seasonal effects. However, as in other North American studies (Slein et al. 2008, Guentzel et al. 2001, Lamborg et al. 1995), a scavenging pattern (Poissant and Pilot, 1998) and increase spring and summer deposition of THg have been reported at the St. Anicet site in the past. The seasonal trend and difference between urban and rural areas do not seem to effect MeHg concentration and deposition to the same extent (Mason et al. 2000).

4.2. Dorset

Although the MeHg concentration varied greatly over the sampling period and peaked during the summer, the rate of discharge was found to be an important determinant of the MeHg load to the lakes. The high discharge rate during the spring freshet compensated for the low MeHg concentration, resulting in transport of over a quarter of the annual MeHg load in runoff to the lakes during this time.

4.2.1 Seasonal Hydrograph

The importance of both the seasonal hydrograph and percent accumulated discharge graphs lies in the visualization of the relative contribution of each season to the overall input of runoff to the lakes. In temperate and more northern regions, spring freshet can account for more than half of the annual runoff (Mielko and Woo. 2006, Prowse et al. 2006, Schuster et al. 2008). According to Environment Canada website the annual average distribution of precipitation in this region is 26% snow and 74% rain (based on annual average of at least 15 years). Here too, we find that the spring freshet brings to both lakes a large percent of the annual amount of runoff, though the

percentage is quite higher: 56.6% and 59.2% in 2005-6, 48.1% and 36% in 2006-7, for Dickie and Harp Lakes, respectively (fig 3.6, 3.7).

Two seasonal differences could explain this discrepancy between our measured data and the literature, and also between the two years: Spring showers and mid- winter snowmelts: The amount of precipitation measured is nearly identical in both years sampled (1199.6mm in 2005-6 and 1073.2 in 2006-7, (Environment Canada), and although we do not have the climate data to determine the relative amounts of snow and rain during the sampling period, the depth of the snow on the ground prior to snowmelt is quite different in the two springs: In February 2005, just before the spring sampling started there was 69 cm of snow on the ground, while in February 2006 there was only 38 cm, probably resulting in less snowmelt which accounted for a smaller percentage of the annual runoff. The reduced snow depth could be caused by less snowfall during the winter, and/or by warm periods during the winter, resulting in mid- winter snowmelts and reduced amounts of runoff during spring freshet.

Unfortunately, the climate data for this period is not available to determine which of these climate conditions is responsible for the difference in the amount of snow, as the data available from Environment Canada does not distinguish between the different forms of precipitation.

The higher proportion of runoff we measured in springtime relative to the Environment Canada data can probably be accounted for in the rain events measured during early spring: 164.6 mm of rain were measured during spring freshet in 2005, and 84.3mm rain were measured during spring freshet of 2006. Although this precipitation added to the snowmelt is substantial in terms of the amount of runoff, the contribution of these events on the MeHg flux is less pronounced. The average THg concentration in this region is 10.2 ng L^{-1} (Mierle, 1991), of which approximately 1-3% is MeHg (based

on Table 4.3). This will be discussed in more detail in section 4.2.3.1: Methylmercury yield in snow and snowmelt.

Since discharge values were near zero during the summer, discharge values were not recorded in summer 2005. Consequently, discharge values were used from summer 2006 to calculate the percent accumulated discharge (fig 3.7). However, this had a minor effect on the quality of the dataset: the amount of precipitation that fell during the entire summer season in 2006-7 was 8.2 percent less than the amount that fell during the same period of time the following year (188.8 mm rain in 2005, 205.6 mm in 2006), making the contribution of the latter even less significant. In relation to the total annual runoff, the amount of runoff to both lakes that was re-used represented a fraction of the annual sum of runoff in 2006-7: 1.69 % and 3.7% of annual runoff to Dickie and Harp, respectively.

An examination of graphs 3.6 and 3.7 reveals the importance of the time interval between sampling events, and the timing of the sampling. The sampling in DE catchments on June 18th and June 21st captured the major rain event (34.8 mm) that occurred on June 14th, and the result is a large peak in the hydrograph (fig 3.4), which alone accounts for almost 20% of the annual amount of runoff to Dickie Lake. In the steep- sloped Harp Lake, this rain event was missed by sampling early on the 14th of June, then again on June 21st by which time the runoff had subsided.

4.2.2. MeHg flux and Seasonal contribution of MeHg

The MeHg concentration in streams varied over the year. The pattern was almost inverse to the discharge: low concentration during the spring (roughly 0.05 to 0.7 ng L^{-1}) increasing over the summer (0.2 – 7 ng L^{-1}), then decreasing over the fall and winter (0.03 – 1.5 ng L^{-1} and 0.05 to 0.5 ng L^{-1}, respectively) (fig 3.1 and 3.2). The

lowest MeHg concentrations were observed during the spring freshet, while the discharge rate was at its peak (fig 3.4 and 3.5), suggesting a source of low MeHg concentration, or a dilution effect by the high volume of water. The highest concentration was measured at the same time that the runoff to both lakes was minimal, during the peak of summer.

While other studies provide MeHg concentration in runoff (Lee and Iverfeldt, 1991, Hines and Brezonick, 2007, and many more) measurements of MeHg concentration coupled with discharge rates are less common. Since the MeHg export rate is determined by both these factors, evaluating the seasonal contribution of MeHg is impossible without both. The percent accumulated MeHg and temporal MeHg flux rate graphs allow a visualization of the seasonal pattern of export rate and reveal the importance of the individual seasons to the annual MeHg flux to the lakes.

4.2.2.1 Spring

In Dickie Lake the MeHg export rate peaks during the spring freshet were second in magnitude only to very short lived peaks generated by isolated rain events during the summer (fig 3.8). These spring peaks were moderately high, but continued over a longer time span, resulting in large amounts of MeHg in runoff. For Dickie Lake, this period of time represents the largest seasonal contribution of MeHg to the annual load: 33.9% (fig 3.11). Moreover, if we add to this figure the MeHg that was transported to the lake during the second part of the spring (between the end of the spring freshet and the beginning of the summer; May 15th to May 30th), the proportion increases to 42.7% of the annual load. In Harp tributaries the MeHg export rate during the spring freshet alone was also high (25.5% of annual load), but somewhat less than the proportion of MeHg that was exported during the fall (30.4%) (Fig 3.11).

In one of the only studies designed to assess the seasonal variation in MeHg yield, Bishop et al. (1995) measured THg and MeHg in snow and snowmelt runoff from a small watershed in Northern Sweden, and found that it accounted only for 12% of the annual MeHg flux. However, the dynamics of the MeHg export from this Bishop study are likely very different from the ones observed in Dorset. While I found an order of magnitude more MeHg in the runoff than in the snow, the Swedish team found that the MeHg concentration measured in snow cores was much higher than the MeHg concentration in runoff during peak snowmelt. Moreover, in the Dorset data a strong decrease in DOC concentration during peak snowmelt was observed, while Bishop and colleagues found an increase in both THg and TOC concentrations during this time. The authors suggested that higher volumes of flow would have more of a dilution effect of THg and TOC. It is also possible that the difference between the two studies can be accounted for in the shift of the dominant form of carbon from dissolved to particulate (Grigal, 2002).

Among the few studies on the seasonal effect on MeHg in meltwater is a study by Babiarz et al. (1998). In this study, THg and MeHg were measured in streams of different watershed characteristics during different seasons. It was found that the snowmelt carried mostly inorganic species of mercury, and contrary to the findings presented here, the daily yield during this time was low compared to other seasons in all streams sampled. Conversely, Hurley et al. (1995), who measured the mercury concentrations in 39 rivers in Wisconsin during the spring and fall reported over a 3 fold increase of daily yields from fall to spring. Although comparable THg data were not available for this study and the proportion of MeHg cannot be determined, it is clear that the MeHg yields in the Dorset streams were very high during the spring. One factor that might explain the discrepancy is the sampling interval: during the spring freshet

there are great temporal changes in MeHg yield even on the weekly scale. The 1998 study, although valuable in other respects, cannot accurately capture these dynamics based on a monthly sample.

Although both lakes exhibited similar MeHg yields during the spring, they differed in term of net export. In Harp Lake, spring is a time where the lake acted as a sink for great amounts of MeHg. In contrast, for Dickie Lake the spring is a time when the lake is a great source of MeHg to downstream waters (Fig 3.12). The difference between the two lakes could possibly be attributed to the difference in the depth of the lakes. In the shallow Dickie Lake the storage capability is limited and the strong flux of water can possibly reach and disturb the sediments. This may cause re-suspension of MeHg binding particles, resulting in a greater outflow than inflow of MeHg. In the deeper Harp Lake the strong flux of water during spring freshet might not be strong enough to disturb the sediments. While the lakes do have a similar size and outflow discharge rates (averaged over all data: 140 L sec^{-1} and 137 L sec^{-1} for Dickie and Harp outflow, respectively), Harp lake has a longer hydraulic residence time of the water (3.5 years and 1.9 years for Harp and Dickie, respectively (Law et al. 2001), allowing the MeHg in the water to settle or become cycled, resulting in a total net inflow to the lake.

Although the net flux data was calculated without the contribution of DE11 catchment, the addition of the contribution of MeHg from the missing catchment (DE11) would reduce the magnitude of the net peaks for Dickie, but the overall pattern would remain very similar to the pattern shown here. The MeHg contribution of DE11 sub- catchment to the overall net flux was estimated by using the discharge rates from DE10 and the MeHg concentration measured in DE5 (the two sub-catchments that bare the most resemblance to DE11 in terms of average annual discharge rate and MeHg concentration, respectively. See Table 3.2). When these flux rates were added to the net

MeHg calculation, the magnitude of the peaks was slightly reduced, but the overall trend did not change (not shown).

In spring 2005 the MeHg export rate in runoff exhibited peaks of similar magnitude and width to those measured in spring 2006. Although the dataset for this year is partial, there is still valuable information that can be extracted. Given that the significance of the missing summer data is negligible (see 4.2.1), and also that the fall export rates in 2005-6 are substantially lower in all sub-catchments than those measured in fall 2006-7 (fig 3.8-3.10), we can estimate that in 2005-6 the MeHg exported to the lakes during the spring freshet represented a greater proportion of the annual load than that measured in 2006-7.

In conclusion, the massive amounts of runoff during spring freshet have an immense impact on the MeHg export from the watersheds, as indicated by the similar pattern of MeHg export observed in all sub-catchments during this time. However, the great differences in magnitude of the export rates between individual sub-catchments suggests that even during early spring the snowmelt is not the only source for MeHg.

4.2.2.2 Summer

Although the MeHg concentration was at its peak over the summer period in both years sampled and in both watersheds (fig 3.1 and 3.2), the export rate from the watersheds was usually low during this time (fig 3.8-3.10), dropping frequently to zero when the streams ran dry. Despite the higher MeHg concentrations, the summer time runoff (June to August) in 2006-7 contributed only 20% and 16.3% of the annual MeHg flux to DE and HP respectively, which can be seen in the almost flat line in the graph describing percent accumulated MeHg (fig 3.11).

Large rain events during early summer in both years resulted in extreme MeHg export rate peaks in the streams that were sampled shortly after the rain events. Though the discharge produced by these rain events seems minute in comparison to the spring freshet (fig 3.4 and 3.5), a high concentration of MeHg (likely produced in the wetlands during the summer anoxic conditions) was flushed out of the catchments, resulting in prominent amounts of MeHg.

The large storm on the 14th of June 2005 alone accounted for 20% of the annual flux of MeHg to Dickie Lake. Branfireun et al. (1996) found an even greater proportion. 53% of the annual flux of MeHg from a watershed in the Experimental Lakes area in Ontario occurred during one summer storm. The response of the different sub-catchments to this precipitation event can be largely explained by the % wetland in the catchment: the sub catchments with a higher proportion of wetlands produced more runoff (r^2=0.62, not shown), suggesting that the degree of soil saturation or height of the water table, and not the slope, was the main driver for the runoff in this event. This leads to the hypothesis that the rainwater in this event did not penetrate deep into the soil, but rather flowed through the organic horizon and entered the lakes. This alternative hypothesis offers an explanation to the massive flux of MeHg during this flushing event. This hypothesis is also supported by other findings reported in the literature. In terrestrial soils, highest contents of THg and MeHg are usually found in the organic material of the forest floor (Lindqvist et al. 1991; Schwesig et al. 1999; Grigal, 2002), with MeHg decreasing with depth and THg showing an inverse pattern (Schwesig et al. 1999). MeHg flux through the various horizons has also been shown to correlate with the flux of the water during heavy rain events, but not in annual streamflow (Schwesig et al. 2001), emphasizing the importance of superficial flow during intense precipitation events.

This phenomenon of extreme flushing events through high flow paths has been observed by others. Allan et al. (2001) who studied the response of different catchments in the Experimental Lakes Area in Ontario to individual precipitation events found patterns of flushing followed by dilution effect in forested watersheds. Similarly, Lee and Iverfeldt (1991) and Lee et al. (1998), who measured Hg transport from the Svartberget watershed in Sweden, found that during periods of high flow, the flow paths were superficial and passed through soils layers rich in Hg.

The importance of these summer events was noted by Babiarz et al. (1998), who found that the flushing of the late summer pore water (usually during precipitation events) had an important role in the MeHg load of wetland-dominated streams. Interestingly, in the same study Babiarz et al. (1998) also found that MeHg yield under base and medium flow conditions, but not during event flow was highly correlated to percent wetlands. However, these conclusions were made based on a set of 9 watersheds of varying characteristics which were sampled only 9 times throughout the year, only few of which were actually high flow conditions. Hurley et al. (1995) reported similar findings in 39 Wisconsin rivers: MeHg daily yields were found to be positively correlated to % wetland, with a steeper slope in spring than in fall.

During the big rain event in June 2006 the only station that was sampled was DE10. As a result it is impossible to evaluate whether this large amount of MeHg is being retained in the lake. In 2005 all DE stations and outflow were sampled shortly after the event. The net MeHg flux graph (3.12) shows a large positive peak despite the missing DE11 data, indicating that this MeHg was retained in Dickie Lake.

4.2.2.3 Fall

The initially high but decreasing MeHg concentration, combined with increasing discharge rates in the fall resulted in a substantial amount of MeHg in runoff, amounting to 19.8% and 30.4% of the annual amount of MeHg in runoff to Dickie and Harp lakes, respectively (Fig 3.11). This amount was, in effect equal to the proportion of MeHg in runoff entering Dickie Lake during the spring freshet. For Harp Lake this was the most substantial seasonal contribution of MeHg. These elevated MeHg export rates are comparable to other findings reported in the literature: Babiarz et al. (1998) found elevated MeHg export rates resulting in high yields (0.09- 0.59 $\mu g\ m^{-2}\ day^{-1}$) during the fall, and especially during large volume events.

Despite similar fall MeHg concentrations in both years (fig 3.1 and 3.2) the fall MeHg export rates of all streams in 2006-7 were much higher than those measured in 2005-6. The cause for this is the substantially higher discharge rates in 2006-7 (fig 3.4 and 3.5), which occurred despite nearly identical amounts of precipitation during the both seasons (330.7 mm and 332.7mm in fall 05-06 and 06-07, respectively).

The slower discharge input in 2005-6 resulted in a roughly balanced net MeHg flux in both lakes during this season. The following year the elevated discharge rates resulted in a net negative flux (meaning the MeHg is retained in the lake) for Dickie Lake and the highest annual positive net flux (meaning the lake acted as a source) for Harp Lake.

4.2.2.4 Winter

In many studies in temperate regions, MeHg is not measured over the winter season due to the technical difficulties of sampling under winter conditions and also because the frozen ground and snowpack are assumed to produce little to no flow and

MeHg during this time. Recent studies have shown that soils from high Arctic wetlands were capable of producing significant amounts of MeHg even at temperatures as low as 4°C (Loseto et al., 2004a). In lake sediments, which are known to be sites of MeHg formation (Grigal, 2002, Morel, 1998), the temperature often does not exceed 4°C, even during the summer.

In this study we found that during the winter season a surprisingly large amount of MeHg was transported in runoff to the lakes: 17.4 % and 21.4 % of the annual amount of MeHg in runoff to Dickie and Harp, respectively. The majority of this MeHg was exported during the first part of the winter (December to mid January), as can be seen in the both the MeHg export rate and percent accumulated MeHg graphs (fig 3.8-3.11). These export rates seem to be an extension of the fall export, which ends with decreasing discharge rate (fig 3.4-3.5) as the streams freeze. This surprising amount of MeHg is even greater than the proportion Harp Lake receives during the summer, and just slightly less than the proportion of MeHg that Dickie Lake receives during the fall.

In a review of factors affecting organic contaminant amplification during snowmelt, Meyer and Wania (2008) present two types of mid winter snowmelt: Surface melting and bottom melting. Surface melting is when the upper layers of the snow melt as a result of increases in ambient temperatures, and it often results in an amplification of contaminants in the meltwater. This meltwater can travel vertically, but often freezes again in lower layers, forming an impermeable ice structure that can significantly delay the first meltwater flush. The second type of mid-winter snowmelt illustrates the effect of ground heat: higher soil temperatures can be caused by a deep, low density snow cover that is developed early in the fall, insulating the soil and resulting in small but constant snowmelt over the entire winter season. Because the source of meltwater is the base of the snowpack, it usually does not contain high levels of organic contaminants.

The upper layer of the soil, which is not entirely frozen, is often permeable to water, with lateral flow being sub-surface or overland, depending on the soil infiltration rate.

The early release of MeHg during the early spring freshet (fig 3.1-3.2), the nearly constant flow and the relatively stable concentration of DOC over the winter all suggest a bottom melting pattern in Dickie and Harp lakes. Hence, it is likely that the source for the MeHg in the winter flow is not directly from the snowpack, but from the great storage or production capability of the forest floor or wetlands.

Over the majority of winter 2006-7 the MeHg exported into Harp Lake was retained in the lake, while in Dickie Lake more MeHg was transported out of the lake than was received in runoff. This too might be due to the difference in retention time, as discussed in section 4.2.2.1. Due to missing data a net flux was calculated only for winter 05-06.

The MeHg flux data for 2005-6, although partial, provides important support to the findings from the 2006-7 data. The temporal flux rates of the spring, early summer and late fall are all very similar to those observed in the following year, showing that the seasonal contribution of MeHg in runoff repeats itself on larger time scale.

4.2.3. MeHg Yield and percent wetland

In both years sampled the calculated annual MeHg yield (normalized to area) in runoff from Dickie catchment was greater than that calculated for Harp catchment. These values compare well with the literature (Babiarz et al. 1998; Driscoll et al. 1998; Watras and Morrison, 2008) and are attributed mainly to the relative proportion of the wetland in the drainage basin (St. Louis et al. 1994; Hurley et al. 1995; Watras et al. 1995, Grigal, 2002) (Dickie: 13.9%, Harp: 6.3 %).

These values are all similar to the annual MeHg deposition rate measured in St. Anicet deposition over the duration of the sampling (0.19 μg m^{-2} $year^{-1}$). Some individual sub- catchments, however, did have higher MeHg export rates than the deposition rate measured in St. Anicet, notably DE6 and DE10 (Table 3.2). These high rates can only be partially explained by % wetland: Although DE10 had the highest percent wetlands of all sub-catchments, DE6 has the least amount of wetlands of all DE streams.

The difference between the yields calculated for the drainage basins, varied with the years. In 2005-6 Harp yield was only about a third of the MeHg yield from Dickie basin, while in 2006-7 Harp yield represented more than 3/4 of Dickie yield. One big difference between the two years is the amount of data used to calculate the yield: while 2006-7 yield was calculated based on a complete set of weekly samples, the 2005-6 data was very partial, missing the majority of the summer and winter data.

The great increase in Harp MeHg yield from 2005-6 to 2006-7 cannot be attributed to any one sub-catchment. All sub-catchments exported more MeHg per area in the second year sampled. This indicates that in Harp drainage basin the environmental conditions in 2005-6 were favorable for more MeHg production or export during the summer or winter. For Dickie drainage basin, the environmental conditions had less of an influence on the MeHg export, or were favorable for production or export during the spring or fall.

The spatial and temporal geochemical features of the watershed influencing MeHg export in streams are a very complex matter, and cannot be discussed in detail in this thesis. Sosso-Kolle (2008) discussed the issue. Briefly, she concluded that MeHg concentration and yield are affected by environmental variables such as iron, DOC,

color and pH, and geophysical parameters like percent wetland and, most importantly, percent slope.

4.2.3.1 MeHg yield in snow and snowmelt

The measured values of MeHg yield from both catchments in both springs (0.04-0.07 μg m^{-2} $season^{-1}$) were at least an order of magnitude higher than the values expected based on the MeHg levels in snow cores (0.003 μg m^{-2} - 0.005 μg m^{-2}), but were similar to the MeHg deposition rate measured in St. Anicet during the winter months alone, 0.04 μg m^{-2} snow $season^{-1}$. Comparing these values to the known literature is extremely difficult, as very few studies in the region focus on MeHg in snow and snowmelt. In one of the few studies to measure MeHg in runoff during spring melt, Hurley et al. (1995) measured MeHg during spring time in 39 rivers from Wisconsin. 12 of the rivers, characterized mainly by forests and wetlands in their catchments, yielded a mean of 0.5 ng m^{-2} day^{-1}. When converted to the same units, the spring export rates measured in this study were found to be much higher than the mean daily export rates measured in the 1995 study (2.35 and 2.91 ng m^{-2} day^{-1} for DE, 1.25 and 1.71 for HP for 2006-7 and 2006-7, respectively). However, the data for the 1995 study was obtained by analyzing filtered MeHg samples, and likely represents an underestimation of the MeHg in stream water, as acknowledged by the authors. This discrepancy may also stem from the different design of the projects: the Hurley et al. data were collected during one springtime sampling while the data presented here are based on weekly samplings, and likely better represents the seasonal contribution of MeHg.

The great difference between the MeHg snow core yields and MeHg runoff yields is surprising, but can be explained by one of the two options: either the snow

cores taken represent an underestimation of the MeHg levels in the snow, or there are additional sources of MeHg to the snowmelt. Bales et al. (1989) found that chemical species within the snowpack are released from the base of the snowpack, and also determined that 80% of solutes in the top layer of the snowpack are removed with the first 20% of the snowmelt. It was demonstrated by Dommergue et al. (2003) that up to 90% of mercury eludes the snow pack with early snowmelt. If the first spring sampling in these lakes occurred after the onset of snowmelt, the snow cores taken on these dates could possibly represent a small fraction of the MeHg in the snow pack. Examining the maximum daily temperature data for this location confirms that the first spring sampling in both years occurred after the maximum daily temperatures rose above zero. In 2005, the maximum daily temperature started rising above freezing point on March 14th, more than 2 weeks before the first spring sampling and snow cores were taken. Also in 2006 there were several warm days where the air temperature rose above zero before the first spring sampling on March 20th: the maximum daily temperature rose above zero from March 4th to March 14th, and then decreased to sub-freezing for several days. On March 23rd the air temperature rose again to positive values and remained so for the rest of the season. This information suggests that the calculation of the MeHg yield in snow is a gross underestimation of the actual amount that the snow held prior to snowmelt. The similar values of MeHg yield in snow from Dorset and the MeHg deposition rate in St. Anicet during the winter months supports this postulation. However, it is also possible that there are additional sources of MeHg to the snowmelt. These could be direct deposition of MeHg, and MeHg washed out from the soil by runoff.

As discussed in section 4.2.1, the amount of water in precipitation that fell during spring freshet was considerable; a total of 162 mm and 85.7 mm of rain fell

during spring freshet of 2005-6 and 2006-7, respectively. Assuming that the snow cover prevented soil penetration, this amount of rain translated into a tremendous amount of runoff, accounting for roughly 88 and 64 percent of the spring freshet runoff measured to Harp and Dickie lakes in 2005-6, respectively, and 40% and 36% of the spring freshet runoff measured to Harp and Dickie lakes, respectively in 2006-7.

However, these rain events had a lesser impact on the amount of MeHg in runoff. Multiplying the calculated amount of water in the spring rain events by an annual deposition rate of 10.2 ng L^{-1} in this region (Mierle, 1991) results in approximately 6.3 and 3.3 grams of THg to Harp and Dickie drainage basins respectively in 2005-6. In 2006-7, the spring rain resulted in 3.3 g and 1.7 g of THg to Harp and Dickie lakes, respectively. Assuming MeHg represents approximately 1.3% of THg in precipitation in this region (St. Louis et al. 1995), the drainage basins received an amount of 24 to 80 mg of MeHg in the spring showers. This amount accounts for approximately 54% and 29.5 % of the amount of MeHg measured in spring freshet runoff in Harp and Dickie lakes respectively in 2005-6, and 31.5% and 18.5% of the MeHg measured in spring freshet runoff in Harp and Dickie lakes respectively in 2006-7 which can explain, at least partially, the higher levels of MeHg in runoff relative to the snow. Using the data from St. Anicet (average of 0.11 ng L^{-1} MeHg) to estimate the contribution of MeHg from direct deposition gave similar results, but slightly lower.

However, these calculations might not be an accurate representation of the amount of MeHg in spring showers. Though the concentration of MeHg in spring and summer has been shown to be significantly higher than the MeHg concentration in the winter precipitation (Hall et al. 2005), the average deposition rate of MeHg in precipitation measured in St. Anicet during the winter months (0.004 μg m^{-2}) was on an order of magnitude lower than the deposition rate of MeHg averaged over one year

(0.02 μg m^{-2}). This suggests a strong seasonal variation in MeHg deposition pattern, which makes it difficult to accurately evaluate the contribution of MeHg in spring showers to the MeHg export from the watershed during snowmelt runoff.

Another possible source of MeHg in snowmelt is a terrestrial contribution. These sources will be discussed in the following section.

4.2.2. DOC and conductivity

DOC and conductivity were measured in order to assist in identification of the source of MeHg to the runoff measured in the streams. Since DOC is known to be a vector of MeHg, and since snow is known to be low in DOC, I expected the correlation between the two to be weak during the spring, but strong during the summer when low flow rates allow longer complexion time.

The correlation between DOC and MeHg in runoff has been reported so frequently it has almost become axiomatic (Krabbenhoft et al. 1995, Watras et al. 2005, Schuster et al. 2008). Still, this correlation may not always exist (Hurley et al. 1998a; Hurley 1998b; Watras, 2000). In a review of the interactions between Hg and DOC, Ravichandran (2004) suggested that a positive correlation between DOC and mercury concentration happens when the source of mercury is primarily wetlands and soils, and mercury is released and transported along with the organic matter. However, a lack of correlation does not necessarily imply different sources. The structural and chemical characteristics of the organic matter can affect the reactivity of DOC with mercury (Babiarz et al., 2001), and so the binding properties of DOC can change from one drainage basin to another, and over time.

The conductivity of pure water is 0.055 μS cm^{-1}, and as stated in the results section, the average conductivity of freshly deposited snow in the region is 24.5 μS cm^{-1}, while the conductivity of the stream water (not from snowmelt) measured in 2006-7 varied greatly between approximately 20- 65 μS cm^{-1} in Harp streams, and 9-80 μS cm^{-1} in Dickie streams. Even during the short snowmelt period, the differences between the streams are great and the trends sometimes opposite, which makes it extremely difficult to draw any conclusions regarding the source of the runoff.

The concentration of TOC in the snowpack was even lower than other reported values. Boyer et al. (1997) and Lafreniere et al. (2004) measured an average of 0.9 mg L^{-1}, in the snowpack of the Rocky Mountains.

4.2.2.1 Seasonal variations in DOC and MeHg correlation

The extraordinary seasonal variation in MeHg concentration and the tight coupling between the seasonal changes in the dynamics of MeHg export from the watershed and DOC, clearly illustrate the linkage between these variables.

Spring and winter

Many studies have investigated the relationship between DOC and THg, but few looked at the correlation in different seasons. One such study was done in Kejimakujik, Nova Scotia, where Meng et al. (2005) found a strong correlation between the two in the summer (r^2= 0.53), and a very low positive correlation during the spring (r^2=0.06). Similarly, during a 6 year study in Sweden, Lee et al. (2000) found that during the spring melt DOC and THg exhibited similar trends, but DOC and MeHg were not coupled. In a recent publication by Selvendiran et al. (2008), DOC and MeHg were found to be weakly correlated during the growing season in wetland stream water

(r^2= 0.2), but this correlation was slightly decreased for the non growing season (r^2= 0.17).

In the data presented here, the correlation between DOC and MeHg across all data was strongest during the spring (r^2=0.65), and much lower during the summer (r^2= 0.37) (Fig 3.15 and Table 3.1). During the spring freshet the concentration of DOC even was even able to explain up to 96% of variability in MeHg levels in individual streams (not shown). The slopes of the correlation in both catchments during the spring were similar, (0.03-0.04), suggesting that during this time the DOC of both catchments was of similar quality and origin. The near zero intercepts (-0.1 to +0.01) suggest that the snowmelt reaches the lake with minimal soil contact (Schuster et al. 2008), and that the source of source of MeHg during spring freshet is snowmelt.

Despite these observations there are contradictory reports in the literature and evidence in the data suggesting a terrestrial source for MeHg and DOC in snowmelt. In a review on the factors affecting Hg export to and from a watershed, Grigal (2002) concluded that when the soils are saturated such as during the snowmelt, the flow pathway of the water is through the organic layer (interflow), which is likely to mobilize particles. Schuster et al. (2008), who measured THg and MeHg during supersaturation of snowmelt and summer storms, found that THg and MeHg associated with particulates were highly correlated (r^2=0.84), and suggested that the source for both is in-stream or near-stream particulate organic carbon eroded or re-suspended during spring snowmelt and summer storms.

Although the lowest annual DOC concentrations measured in both years coincided roughly with the peak of snowmelt runoff, the lowest DOC values measured in runoff were twice as high as the TOC levels measured in snow cores, suggesting an additional carbon source. Additionally, the peak of the DOC during the snowmelt event

occurred during the rising part of the hydrograph, implying a flushing sequence. The source of these elevated levels of DOC is likely terrestrial. When investigating seasonal changes in snow and stream water chemistry in a Michigan watershed, Stottlemyer and Toczydlowski (1999) discovered that the most significant DOC reservoir contributing to stream water output during the winter was the forest floor. They found that the snowpack insulated the soil on the forest floor from freezing, which permitted over-winter mineralization and other biological processes to maintain shallow subsurface ion and DOC reservoirs. Furthermore, they concluded that DOC is mobilized by percolating snowmelt and particularly by lateral flow of saturated soil water at shallow depths. Likewise, Boyer at al. (1997) and Lafreniere et al. (2004) found that the path that provides the bulk amount of DOC to stream flow during snowmelt, was subsurface flow in the upper soil horizon of an alpine lake in the Rocky Mountains.

Although the climate in the sampling site for the Stottlemyer and Toczydlowski study is affected by Lake Superior and is somewhat milder than the climate in Dorset, in our sampling sites we observed a low but constant flow of water in all streams throughout most of the winter (see fig 3.4 and 3.5, discharge). Furthermore, since groundwater inputs to these lakes appear to be negligible (Dillon et al. 1986), and the mid winter snowmelt pattern appears to be bottom melting (see above: MeHg flux and Seasonal contribution of MeHg, winter), it is safe to conclude that the source for the DOC and MeHg measured in it is at least partially from the ground.

The conductivity was also found to be a significant predictor for MeHg spring model ($p= 0.02$), although it could only explain 3% of variation in MeHg. Stottlemyer and Toczydlowski's findings (1999) that the snowpack solute content had a minor role in determining stream water ion concentration during and following peak snowmelt

offers an explanation to the low explanatory power of the conductivity on MeHg concentration.

Summer

During the summer, and excluding large precipitation events, the discharge rates in all streams were low, allowing more contact time with DOC. This has been shown to allow mercury to complex with DOC, resulting in a stronger correlation (Kolka et al. 1998). Despite this, in the data presented here I found that following the transition from spring to summer, the correlation between DOC and MeHg was substantially reduced in both watersheds. Although the strength of the correlation during the summer was still moderately high (r^2 = 0.16-0.34), it was less than the strength during springtime runoff. These findings are contradictory to numerous reports of a strong positive correlation between mercury and DOC during the hot season (Mierle, 1991; Balogh et al. 2008; Shanley et al. 2008).

As Ravichandran (2004) suggested, a lower correlation does not necessarily stem from different sources for the variables. Hurley et al. (1998) who found a correlation of less than 0.01 between DOC and MeHg in the everglades, attributed the results to the DOC quality (i.e.: available MeHg binding sites), or non organic complexion of the MeHg. Kolka et al (1999) found decreasing total mercury to DOC ratio with increasing DOC concentrations, and suggested a super saturation of DOC compared to the mercury available for complexion. These are all possible explanations to the reduced co-transport. However, there is another explanation for the seasonal change which is related to changes in the depth of the flowpath.

The flowpath depth of the runoff decreases as the evapotranspiration rates increase in the growing season (Stottlemyer and Toczydlowski, 1999). The runoff depth

has a strong effect on the fractionation of the organic material in the runoff; while an elevated flowpath (usually during high volume events) is likely to cause suspension of particulates, a lower one usually results in a higher proportion of the organic carbon being present as dissolved (Grigal, 2002). This can have a profound influence on the fractionation of MeHg in runoff as well: As the concentration of MeHg decreases, its distribution coefficient (K_d, a measure of the affinity of a compound to the particulate phase) increases (Babiarz et al. 1998), meaning the fraction of MeHg bound to particulates will be higher when there are fewer particulates.

It is to be expected that the higher evapotranspiration rates and reduced discharge of Dorset streams during the summer resulted in a drop in the runoff flowpath, and consequently a higher proportion of mercury binding humic and fulvic acids in the dissolved phase. Fewer particulates would cause more of the MeHg to be bound to them, and a reduction in MeHg bound to the dissolved phase, explaining the weaker than expected correlation between DOC and MeHg in this season.

In an investigation of mercury speciation in four Minnesota streams, Balogh et al. (2008) found that the DOC-MeHg relationship in some of the streams varied greatly between high flow events and baseflow events, while in other streams the differences were much less pronounced. In the streams that did exhibit variability with flow conditions, the concentration of MeHg present in the particulate form did not show any variability with increase in total suspended solids (TSS, a measure of particulates), meaning more particulates did not result in more MeHg being in the particulate phase. Also in these streams, up to 95% of the MeHg was in the dissolved phase during the high flow event, presumably bound to DOC. The authors attributed the differences between the rivers to watershed characteristics that may or may not allow access to different sources of DOC and MeHg during high flow conditions. These findings

support the postulation regarding the weak correlation between DOC and MeHg in the summer, and offer strong evidence for the great importance of the discharge rate and flowpath on MeHg load.

Another possible explanation for the seasonal variations in MeHg-DOC correlations is that the higher concentration of DOC measured in the summer resulted in a supersaturation of DOC relative to the MeHg available for binding (Kolka et al. 1999), masking the transport coupling.

Fall

Though they fluctuate to a great degree, the DOC levels in all streams during the fall were roughly equal to those measured in the summer, representing a mirror image of the rising limb of the temporal DOC graph (Fig3.13 and 3.14). Even so, there is yet another decrease in the predictive power of DOC (r^2=0.22) with the shift from summer to fall, when the conductivity was found to be the most significant predictor of MeHg (r^2=0.25). The fall conditions of decreased temperature, increased precipitation and lower evapotranspiration rates likely disrupted the summer anoxic conditions which are ideal for methylation, causing reduced MeHg concentrations and re-suspension of weathering products. This also led to increasing discharge rates and probably an increase of the water table and water saturation degree of the soil. This could, in turn, lead to a shift in MeHg fractionation, as the increase in particulate matter would cause a higher proportion of MeHg to bind to the dissolved organic carbon. The climatic difference between the two falls sampled supports this postulation. Fall 05-06 was very dry, which is reflected in the very low discharge rates of the season, likely resulting in a sub-surface flow path, and consequently a very weak correlation between DOC and MeHg concentrations (r^2=0.09 and r^2= 0.04 for Dickie and Harp,

respectively), whilefall 06-07 had more precipitation, causing higher discharge rates, and likely a higher flow path and more suspended organic matter. This is reflected in an increase in the correlation between DOC and MeHg concentrations (r^2=0.17, r^2=0.25 for DE and HP, respectively). It is also possible that the gradual nature of the seasonal changes reduced the homogeneity of the flow conditions, and consequently the homogeneity of the relationship between DOC and MeHg.

Table 4.1- Mean Total mercury (THg) concentration and annual input in wet deposition from North America, Japan and Sweden. Values represent either a mean (when available) or a range, taken from the cited references.

Reference	*Location*	*Year*	*Mean THg* ($ng\ L^{-1}$)	**THg** $\mu g\ m^{-2}\ year^{-1}$
Mierle. (1990)	Dorset, Canada	1987-1989	10.2	10.2
Lee and Iverfeldt. (1991)	Sweden	1988-1989	7-20	--
St. Louis et al. (1995)	ELA	1992-1994	0.95-9.3	2.5-3.4
Glass and Sorensen. (1999)	Upper Midwest USA	1990-1995	4.3-28.9	7.4
Mason et. al. (2000)	Maryland, USA.	1997-1998	10.4	8.2-17.2
Hall et al. (2005)	Great lakes region, Canada	1997-2003	10-130	
Sakata & Marumoto (2005)	Japan	2002-2003	--	5.5-17.7
O'Driscoll et al. (2005)	Kejimkujik park, Nova Scotia, Canada	1997-2000	5.3	6.6
Watras and Morrison, 2008	Wisconsin, USA	2002-2004	0.9-12.1[a]	6.6-9.7[a]
This study	St. Anicet, Quebec, Canada	2005-2007	2.88- 17.5	6.46

[a]- Values represent a range of annual averages or deposition rates from different years sampled

Table 4.2- Mean Methylmercury (MeHg) concentration or range and annual deposition rate in wet deposition from North America, Sweden and Finland. Values in brackets represent either a range or one standard deviation.

Reference	*Location*	*Type of sample*	*MeHg(ng L^{-1})*	**MeHg µg m^{-2} $year^{-1}$**
Bloom and Wataras, 1989[b]	Wisconsin	Snow	0.05 (0.08)	--
Fitzgerald et al. 1991[a]	Wisconsin	Snow	0.058 (0-0.08)	Rain and snow: 0.09
Munthe and Iverfeldt, 1994[a]	Northern Sweden	Rain/Snow	--	0.7
Munthe and Iverfeldt, 1994[c]	Eastern Sweden	Rain/Snow	--	0.2
St. Louis et al. 1995	ELA, Ontario	Snow	0.028-0.179	
M. Vera, cited by St. Louis et al, 1995	Southern Finland	Rain/Snow	<0.005-0.36	0.1
Glass and Sorensen, 1999	Upper Midwest USA	Rain/Snow	0.18 (0.04-0.48)	3.37 (0.37-9.58) [d]
St Louis et al. 2001	ELA, Ontario	Rain/Snow	0.12 + 0.06	0.09
Hall et al. 2005	Great Lakes Region	Rain/Snow	0.01-0.85	--
Johnson et al. 2007	Maine	Rain, throughfall	0.025-0.63	0.05-0.1
This study	St. Anicet, Canada	Rain/Snow	0.11 (0.02-0.31)	0.19

[a]- adapted from St Louis et al. 1995.
[b]- Adapted from Hammerschmidt, et al. 2007.
[c]- Adapted from Rudd, 1995.
[d]- Deposition rate per week

Table 4.3- Mean concentration of THg, MeHg and the proportion of MeHg in wet deposition from sites in North America.

Reference	*Sample, Location*	*THg(ng L^{-1})*	*MeHg (ng L^{-1})*	**% MeHg**
Bloom and Wataras (1989)a	Snow, Wisconsin	4.06	0.05	1.23
Fitzgerald et al. (1991)[a]	Snow, Wisconsin	7.2	0.06	0.83
Lamborg et al. (1995)[a]	Snow, Wisconsin	7.2	0.03	0.9
Lamborg et al. (1995)[a]	Rain, Wisconsin	7.9	0.11	1.4
Mason et al. (1997)	Rain & Snow, Maryland	10.8	0.04	0.39
St. Louis. (2001)	Rain & Snow, NW ON	10	0.13	1.3
Balcom et al. (2004)	Rain & Snow, Connecticut	6.7	0.2	2.9
St. Louis. (2005)	Snow, Ellesmere Island	3.16	0.06	1.9
Watras and Morrison (2008)	Rain, Wisconsin	9-12[b]	0.06-0.11[b]	0.5-1.8[c]
This study	Rain and snow	2.88-17.5	0.02-0.31	2.87

a- Adapted from Hammerschmidt et al. 2007 b- Values represent a range of averages from different years sampled.
c- Re -calculated based on annual deposition rate.

5. Summary and conclusions

5.1 General conclusions

In this study, I found that although MeHg concentrations were very low in the snowmelt runoff, the high discharge rates during this time transported large amounts of MeHg to the downstream lakes of Dickie and Harp, accounting for up to 33.9% of the annual amount of MeHg in runoff. The source of the MeHg in runoff during this season is unclear, with evidence suggesting atmospheric, terrestrial and snowpack origin. These findings come despite MeHg representing only about 2.8 percent of THg in precipitation, implying important dynamics of THg and MeHg in the snowpack, changing the relative proportion of the chemical species.

5.2. Seasonal dynamics

In summary, I observed that the seasonal contribution to annual MeHg in runoff to Dickie lake was spring > summer > fall > winter, and in Harp Lake it was fall > spring > winter > summer.

These findings are surprising considering highest MeHg concentrations were measured during the summer period, based on reports in the literature that spring runoff accounted for approximately 12% of the annual amount of MeHg (Babiarz et al.1998). Although the discharge was not found to be a significant predictor for MeHg concentration, it seems to have an important role in determining the MeHg yield from a catchment, as the yield was highest during high flow periods in spring freshet and during large precipitation events in the summer season.

A surprisingly high amount of MeHg was transported to both lakes during the winter. For the wetland-dull Harp Lake this amount represented even a greater proportion of the annual MeHg budget than the summer runoff, which is widely accepted by the

scientific community as the season in which the majority of MeHg is produced and transported to lakes. These findings suggest that the importance of MeHg in snow increases for lakes that have fewer terrestrial methylation sites in their catchment, but cannot be neglected even for catchments with an abundance of wetlands.

The annual yield of MeHg in runoff from both catchments for both years measured (0.06-0.18 $\mu g\ m^{-2}\ year^{-1}$) was less than the annual deposition rate of MeHg measured in St. Anicet (0.19 $\mu g\ m^{-2}\ year^{-1}$), suggesting that overall, both catchments essentially act as sinks for MeHg. It is possible that this relationship between deposition rate and export rate might have a seasonal effect, changing the catchments role from a net sink to a net source over the course of a year and changing the relative importance of the seasons. These dynamics are beyond the scope of this work, and will be addressed in further work.

5.3 Chemical and physical dynamics

Despite great magnitude differences, MeHg, DOC and discharge (but not conductivity) showed a consistent pattern among all streams, illustrating the strong seasonal and environmental dependence.

The most notable result from the chemical dynamics analysis was the strong positive correlation between DOC and MeHg concentration during spring and winter, and the weakening of this relationship during summer and fall. This pattern was consistent among both lakes, and both years sampled.

There are likely several reasons for this seasonal change. A shift in runoff flowpath from superficial to subsurface can cause a change in the amount of MeHg available for binding and also in the speciation between the dissolved and the particulate phases. The seasonal change in the quality of DOC (Peckenham et al. 2007) can also result in changes in the binding properties. It is also possible that during low flow periods the DOC is

supersaturated relative to the MeHg concentration, resulting in a decoupling of the concentrations (but not the transport) of the two variables.

The homogeneity of the seasonal flow might also have an important effect on our ability to understand the relationship between DOC and MeHg. The degree of soil saturation during the spring freshet and winter is relatively stable, probably resulting in a constant relationship between DOC and MeHg. During the fall, and especially during the summer, the forested watershed soil goes through cycles of drying and flushing, and varying physical and chemical conditions. These likely cause great changes in the dynamics of DOC and MeHg, masking the co- transport of the two variables.

The source of the MeHg in spring runoff is not clear. The MeHg yield from snow (calculated based on snow core samples) was an order of magnitude less than the MeHg yield measured during spring freshet, but similar to the MeHg deposition rate measured in St. Anicet during the winter months. This supports the postulation that although the THg in the snowpack may get photoreduced and re-volatilized (as discussed in the introduction), the MeHg does not go through the same chemical transformations, and exits the snowpack with snowmelt. Although the climate data suggests the snow core samples were taken after the onset of snowmelt (hence leading to a gross underestimation of the amount of MeHg in snow), theoretical calculations showed that it is possible that up to 54% of the MeHg in spring runoff originates from direct deposition of spring showers. The almost constant flow of water during the winter, the elevated DOC levels during the early spring as well as other findings reported in the literature, all suggest a terrestrial source of MeHg even during snowmelt period.

To conclude, it seems like terrestrial, direct precipitation during spring and snowmelt all contribute to the MeHg load during snowmelt runoff.

The lack of a consistent pattern in the conductivity dynamics measured in runoff made it difficult use the conductivity to draw conclusions regarding the origin of the DOC and associated MeHg in the runoff, as I had hoped it would. Nonetheless, this does not diminish the importance of the spring freshet contribution to the annual MeHg flux to the lakes. Whatever the source of the MeHg, the springtime runoff is clearly an important event which has major implications on the MeHg load to the lakes studied.

Another surprising finding in this study was that although the lakes differ in the proportion of wetlands, the annual MeHg yield (calculated based on a year long set of weekly samples) did not vary to a great extent: 0.14 $\mu g\ m^{-2}\ year^{-1}$ from Harp drainage basin, and 0.18 $\mu g\ m^{-2}\ year^{-1}$ from Dickie catchment. This illustrates that the MeHg export from a watershed is influenced differently by environmental factors such as the percent wetlands, the origin and quality of DOC as well as the fractionation to dissolved and particulate, and the frequency of precipitation (Grigal, 2002). Moreover, both these export rates were similar to the annual MeHg deposition measured in St. Anicet over the duration of the sampling, (0.19 $\mu g\ m^{-2}\ year^{-1}$).

5.4. Atmospheric deposition

Although the monitoring of THg in precipitation has been part of regular procedures for many environmental agencies for many years (the largest being the NADP for monitoring THg in precipitation across North America-MDN), few measure the deposition of MeHg in precipitation on a regular basis.

Despite the fact that the MeHg deposition rate I found in St. Anicet (0.15-0.19$\mu g\ m^{-2}\ year^{-1}$) was higher than others reported for this region, it still represented only 2.8% of the THg in precipitation, which falls within the normal range previously reported for this region.

The annual MeHg yield from Dickie and Harp sub-catchments varied by over an order of magnitude (0.03-0.43 $\mu g\ m^{-2}\ year^{-1}$). When comparing these numbers to the MeHg deposition rate measured in precipitation (0.19 $\mu g\ m^{-2}\ year^{-1}$), it is clear that the individual sub catchments can act as a net sink or source of MeHg.

Although the photoreduction of THg from the snowpack and subsequent increase in the proportion of MeHg observed in many studies in the arctic and temperate region likely do not change the MeHg deposition rate in precipitation, it is likely that they change the relative contribution of each of the mercury species, making the snowmelt an important source of MeHg to aquatic ecosystems. However, detailed snowpack chemistry dynamics studies could shed more light on the extent of this change and its effect on temperate aquatic ecosystems.

5.5. Further research considerations

As this is one of the few studies to attempt to assess the contribution of actual snowmelt (in contrast to deposition in snow) to temperate aquatic ecosystems, there is much work that needs to be done in this field.

First and foremost there is a need to establish whether the temporal mercury snowpack dynamics influence the MeHg concentration in the snow. In a preliminary study for this thesis I discovered that the THg in the snowpack decreased over time, while the MeHg concentration remained constant or increased in snow deposited to polyethylene boxes on the roof of a university building. The boxes were however open to collect any form of deposition, so these results do not necessarily reflect only snowpack dynamics.

Next, a study of the origin of MeHg in spring freshet runoff would clarify the environmental fate of the MeHg deposited in the snow. This could be done by studying the stable isotope composition of the organic material in snow and runoff, as well as measuring

the fractionation to different media. By using mercury stable isotopes as tracers, it also might be possible to follow the environmental fate of the mercury itself.

Even though I have shown that MeHg in spring runoff has a major contribution to the annual load through runoff to Dickie and Harp Lakes, the relevance to successive bioaccumulation and overall budget of MeHg in lakes needs to be established. In Harp Lake the total amount of MeHg transported to the lake via runoff exceeded the amount exported from the lake, suggesting low in-lake methylation rates and a greater biological relevance of MeHg in runoff. In the partial data for Dickie Lake, I found that the lake exported more data than it received through runoff, suggesting great in-lake methylation rates, and less biological relevance of MeHg in runoff. The methylation rate of lakes reported in the literature varies from 0.5 to about 3 $\mu g\ m^{-2}$ (as reviewed by Rudd. 1995). This offers a variety of models for the relative contribution of MeHg in runoff to the overall budget as a lake.

Finally, one important question has yet to be answered: what is the source of MeHg in the precipitation? Although several researchers have tried to answer this question, so far the answer is not conclusive (as discussed in the introduction). Perhaps an increase in the frequency and intensity of measurements of MeHg deposition rates would offer some insight into this interesting question.

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