Role of bubbling from aquatic sediments in mercury transfer to a benthic invertebrate in the St. Lawrence River, Cornwall, Ontario

by

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Abstract

Benthic uptake of mercury (Hg) governs bioavailability to fish yet there are still large gaps in our knowledge of what mediates this process. Without this information it is difficult to ascertain where Hg accumulation in the foodweb will be greatest. In the St. Lawrence River Area of Concern (AOC) at Cornwall, one contaminated zone (Zone 1) shows elevated Hg in yellow perch (*Perca flavescens*) and their prey items compared to those from other zones in the AOC. Greater availability of Hg to benthos due to unique physical features (large deposition of woodfibre deposits) of Zone 1 is hypothesized to account for this observation. In this study, amphipods (*Gammarus fasciatus* and *Echinogammarus ischnus*) were collected in Zone 1 using artificial substrates between June-September 2007, and Hg concentrations compared to those obtained in sediments and porewaters of surficial sediments, as well as methane gas evasion rates. Methylmercury (MeHg) concentrations in amphipods were significantly related to porewater total Hg (THg) and MeHg concentrations. No parallel relationship was found for sediment Hg concentrations or methane bubbling rates from sediments. Spatial and temporal trends in Hg bioavailability were evident from significant relationships with water column depth and temperature. Water column depth was associated with higher MeHg concentrations in amphipods and porewaters. Concentrations of porewater MeHg were above the detection limit in all of the June samples, the month which also coincided with highest amphipod MeHg concentrations. Finally, sediment organic matter may be influencing patterns of MeHg availability in Zone 1, and displayed a negative relationship to amphipod MeHg. Although bubbling from contaminated sediments did not directly correlate with amphipod Hg uptake, future

studies should look at the influence of bubbling on the redistribution of contaminated sediment particles within the zone.

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Contents

List of Tables

List of Figures

List of Abbreviations, Acronyms and Symbols

AOC	Area of Concern
ANC	Acid neutralizing capacity
AVS	Acid volatile species
BD	Bulk density
CV	Coefficient of variation
DOC	Dissolved organic carbon
d.w.	dry weight
Hg	Mercury
IDW	Inter-distance weighting
LEL	Lowest Effect Level
L.O.I.	Loss on ignition
MeHg	Methylmercury
NRCC	National Research Council of Canada
OM	Organic matter
SEL	Severe Effect Level
SO_4^{-2}	Sulfate
SRB	Sulfate reducing bacteria
SWI	Sediment-water interface
THg	Total mercury
% MeHg	Ratio of MeHg to THg within a given matrix

Chapter 1

General introduction and literature review

Within the Great Lakes-St.Lawrence basin, human activities have resulted in substantial modifications to ecosystem processes. Hydrological changes and large inputs from industrial, agricultural and domestic sources have left many sites incapable of providing 'beneficial uses' to humans and other animals (Environment Canada, 2004). There are currently 41 Areas of Concern (AOCs) dotting the shorelines of lakes and rivers shared by Canada and the U.S. (Environment Canada, 2008). A tremendous effort is being placed by local, municipal, provincial and federal organizations to remediate these sites. Remedial Action Plans (RAPs) outline reasons for the designation and targets for improving the status at each AOC.

The St. Lawrence River at Cornwall, Ontario (Figure 1.1), has been designated an AOC since 1985. Currently, mercury (Hg) found in sediments, water and fish along the waterfront is a reason for the designation (Environment Canada, 2004). This contamination resulted primarily from the discharge of Hg and Hg-tainted products by several plants over nearly a century.

Mercury is a pollutant of concern because of its ability to biomagnify in the food web (Boudou and Ribeyre, 1973) in its methylated form. With each subsequent trophic transfer, biotic concentrations of methylmercury (MeHg) increase, thereby posing a greater risk to animals feeding at higher positions in the food web. Methylmercury produces detrimental neurological and developmental effects in organisms if present in excess concentrations. Such signs have been observed in birds,

fish and mammals. Human cases of MeHg poisoning in Minamata, Japan (Harada, 1995) and the English-Wabigoon River, Canada (Parks and Hamilton, 1987) brought global attention to the possible severity of Hg contamination in the aquatic environment. It is thus of critical importance to understand what influences the uptake of Hg by organisms at the lower trophic levels. Given that sediments are often the main repositories of Hg in freshwater systems (Ullrich et al., 2001), benthos represent an important link between Hg contaminated sediments and top predators.

Sediment contamination remains a key concern in the Cornwall AOC and a sediment management strategy has been developed by Environment Canada and the Ontario Ministry of the Environment to address this issue. Ultimately, the stability of the sediments will largely determine whether the Cornwall AOC will be delisted, creating both economic and social benefits. As stated in the most recent report put forth for the Cornwall Sediment Strategy, 'sediments along the Cornwall waterfront ... are not a major source of mercury to fish in the area through the food chain;' (Environment Canada, 2005). The sediments in question are found in depositional zones along the waterfront, created by the physical structure and patterns of current flow of the river.

Recent data showed that in one zone in particular (Zone 1), Hg concentrations in yellow perch and other fish were higher than at an upstream reference site and a downstream contaminated site (Fowlie et al., 2008). Furthermore, yellow perch from Zone 1 frequently exceeded the provincial consumption guideline of 260 ng/g d.w., and the likelihood of capturing such a fish was highest at Zone 1. Other studies confirm that Zone 1 shows elevated availability of Hg compared to other sites (T. M. Delongchamp, 2006; Yanch, 2007). It is apparent that an investigation into the transfer of Hg from sediments into the food web is needed in Zone 1.

Specifically, knowledge of factors influencing the movement of Hg into the base of the food web is required. In the Cornwall AOC, sediments in the Zone 1 area

experience regular disturbance by methane gas release (Biberhofer and Rukavina, 2002; Golder Associates Ltd., 2004), commonly referred to here as 'bubbling'. This led to the hypothesis that 'older', more contaminated sediments are brought into contact with benthos through disturbance of surficial sediments created by bubbling, thus making Hg more available for uptake. At this time, minimal work exists in the literature which explores the implications that bubbling activity might have on the availability of Hg to benthos. It is imperative that the role of bubbling from Zone 1 sediments be examined as a possible explanation for the patterns of Hg contamination in fish in the Cornwall AOC.

In this study, potential drivers of Hg uptake into the benthic food web in Zone 1 are described. This is achieved by determining the MeHg content of sediment, porewater and a benthic invertebrate species, and comparing these concentrations to relationships with environmental factors such as location, water column depth, and importantly, bubbling rates from sediments.

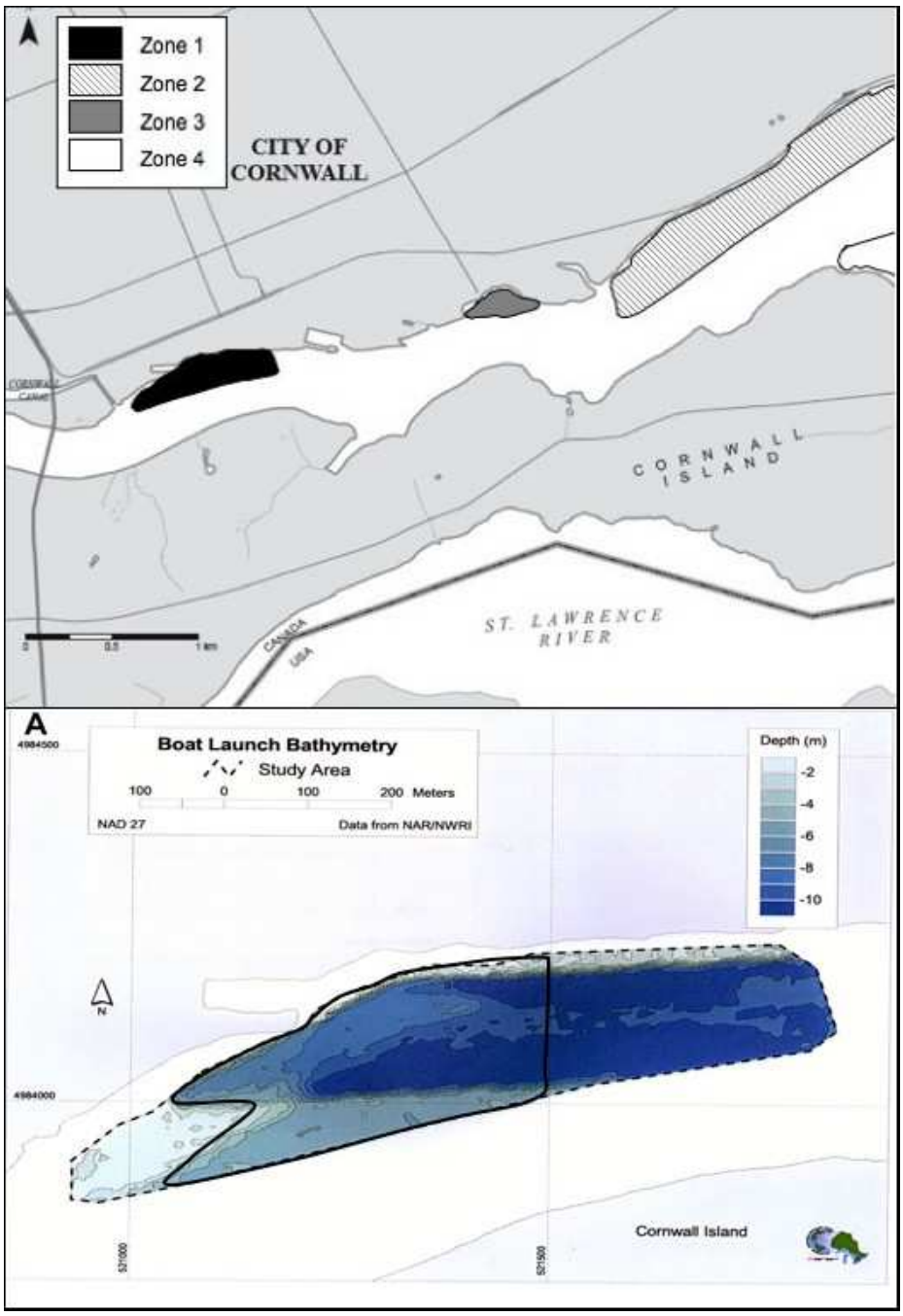

Figure 1.1: Map of contaminated (Zones 1-3) and reference zone (Zone 4) in the St. Lawrence River, Cornwall Area of Concern (AOC). Zone 1 bathymetry is visible in the lower frame with the outline of the sampling area (solid black line) used in this study.

1.1 The Hg cycle

1.1.1 Hg sources

Mercury is a naturally occurring metal that is found in most rock types and in the Earth's upper crust (Parsons and Percival, 2005). It can enter the aquatic environment through weathering of sedimentary rocks or through hydrothermal systems (Rytuba, 2005). Volcanic eruptions also release Hg into the atmosphere, which eventually deposits onto oceans and remote waterbodies (Mason et al., 1994). Currently, considerable anthropogenic inputs of Hg are made to the aquatic environment. Mercury has been widely used in agricultural, medical, industrial and scientific practices due to its unique chemical properties (Parsons and Percival, 2005, Table 1.1). Presently, widespread combustion of fossil fuels and incineration of municipal wastes is increasing the concentrations of Hg in the atmosphere (Pacyna and Pacyna, 2005) with human activity now accounting for sixty percent of global emissions (Seigneur et al., 2004), further increasing the exposure of waterbodies to Hg.

Table 1.1: Chemical and physical properties of Hg (Parsons and Percival, 2005).

Parameter	Value
Atomic number	80
Atomic weight	200.59
Oxidation states	0, +1, +2, +3
Specific gravity	13.5
Melting point	-38.9° C
Boiling point	356.58 ° C
Heat of vaporisation	59.229 kJ/mol
Heat of fusion	2.295 kJ/mol
Number of stable isotopes	7

1.1.2 Hg bioavailability

The bioavailability of Hg to an organism depends on the speciation of Hg in the environment, as well as the physiology of that animal and the animal's interaction with its surroundings. MeHg accumulates over time within an organism, because the rate of excretion is slower than the rate of uptake. MeHg also has a greater potential for toxicity in comparison to inorganic Hg (Eisler, 1987), thus the formation and movement of MeHg through the food web is of primary interest.

1.1.3 Hg methylation

Methylmercury is formed through the process of methylation of inorganic Hg^{2+} to organic MeHg. This occurs with greater frequency and ease in aquatic environments compared to terrestrial ones. Microorganisms, and specifically sulfate reducing bacteria (SRB), are thought responsible for the methylation reaction (Ullrich et al., 2001) through the reduction of sulfate to sulfide (King et al., 2002). Other microorganisms, such as methanogens and iron-reducing bacteria, may also be important in the methylation pathway (Pak and Bartha, 1998). A number of abiotic factors show a negative correlation with the methylating activity of SRB such as pH, dissolved organic carbon (DOC), acid neutralizing capacity (ANC) and sulfate (SO_4^{-2}), decreasing the bioavailability of Hg to food webs (Parkman and Meili, 1993; Ullrich et al., 2001; Chen et al., 2005). Measurements of MeHg in the aquatic environment represent the net methylation in a system (Ullrich et al., 2001), because of the simultaneous production and degradation of MeHg. Photodegradation and bacterial degradation can also influence the processes of demethylation in aquatic sediments (Eckley and Hintelmann, 2006; Lambertson and Nilsson, 2006). Maximal rates of methylation have been recorded at the redox boundary layer, which can experience seasonal fluctuations as it usually coincides with the sediment-water interface (SWI) (Korthals and Winfrey, 1987).

1.1.4 Hg uptake by benthos

In benthic organisms, Hg is bioavailable through direct ingestion or uptake from water. Feeding is believed to an important uptake pathway (Spry and Wiener, 1991). Macroinvertebrate diets comprise a variety of food items, depending on availability and quality. Sediment ingestion can represent a large source of Hg. Many invertebrates also filter-feed on particulates (Langston and Zhou, 1986; King and Davies, 1987; Bryan and Langston, 1992), which are often associated with Hg (Andren and Harriss, 1975; Craig, 1986) given its propensity to adhere to surfaces. Fresh algal matter contain a higher bioavailable fraction of Hg and MeHg, and preferential ingestion of this matter can result in high uptake of Hg (Lawrence et al., 1999). Water transport of Hg and MeHg occurs across the body wall and gills, and experimental evidence suggests this is also an important exposure route (Post et al., 1996; Wang and Wong, 2003). Finally, the extent of metal solubilization during digestion is also an important control, and likely the rate-determing step for accumulation of MeHg in benthic organisms (Lawrence et al., 1999). As all pathways can play a role in Hg transport to benthos, the concentrations in all exposure routes must be considered (Lawrence and Mason, 2001). Determination of factors which affect the availability of Hg, especially MeHg, in these different compartments will also aid in understanding the Hg burden in biota.

1.1.5 Hg complexation

Hg bioavailability is, in part, governed by its speciation in the water and sediments. In solution, dissolved inorganic and organic ligands, colloids and particulate phases represent possible binding sites for Hg. For example, dissolved humic substances are known to bind very strongly to Hg, and show a clear negative influence on the bioavailability of Hg and MeHg to a freshwater *Chaoborus* larvae (Sjoblom et al.,

2000). Organic carbon and sulfide content determine the Hg concentrations found in sediment porewater, as well as in the solid sediment phase (Mason and Lawrence, 1999; Hammerschmidt et al., 2008). The formation of mercury sulfide (HgS_s) removes Hg from solution, making Hg less available for methylation (Winfrey and Rudd, 1990). Redox conditions in sediments are important determinants of complexations, since Hg associates with particulate organic matter in oxic sediments, and with sulfides in anoxic sediments (Gagnon and Fisher, 1997).

1.2 The Cornwall Area of Concern

1.2.1 Physical characteristics of the St. Lawrence River

The St. Lawrence River is considered a major world river, draining the Great Lakes to the Estuary and Gulf of the St. Lawrence. It is fed by Lake Ontario which determines the river's water chemistry (Table 1.2).

Water discharge flow, which averages about 8000 m^3/s, has been regulated since the 1950s with the construction of the Moses-Saunders Dam (Dreier, 2000). Water movement has also been influenced by dredging in the main channel. Below the dam the River splits around Cornwall Island, with about 1/3 of the flow passing along the north shore by Cornwall (Dreier, 2000). River flow is primarily from west to east, with back eddies creating depositional zones in bays along the waterfront.

1.2.2 Sources of Hg to the Cornwall AOC

The Cornwall AOC includes approximately 80 km of the River, and falls under the provincial jurisdiction of Ontario and Quebec, the State of New York (U.S.A.), the federal governments of both Canada and the U.S.A., as well as the Mohawk territory of Akwesasne. Local industrial inputs are identified as the major source of Hg to sediments in the Cornwall AOC (Richman and Dreier, 2001; Grapentine et al., 2003).

Table 1.2: St. Lawrence River water chemistry conditions at Cornwall AOC, adapted from Fowlie (2006).

Parameter	Value
[1]pH	8.4-8.6
[1]Biological oxygen demand (mg O^2/L)	<2
[1]Specific conductivity (μS/cm)	293-296
[1]Dissolved oxygen (mg O^2/L)	8.5-9.7
[2]Alkalinity (mg/L)	87.1-89.5
[3]Water velocity (m/s)	0.11-0.5
[3]Total Kjeldahl nitrogen (mg/L)	0.187-0.265
[3]Total phosphorous (mg/L)	0.012-0.0618
[4]Zooplankton density (zooplankton/L)	0.66-1.88
[5]Suspended particulate matter (mg/L)	1.0 $\pm$ 0.6
[5]Chlorophyll a (mg/g)	0.8 $\pm$ 0.5
[5]Dissolved organic carbon (mg/L)	2.5 $\pm$ 0.5
[5]Particulate organic carbon (mg/g)	295 $\pm$ 262
[5]Dissolved iron (μM)	0.07 $\pm$ 0.04
[5]Particulate iron (mmol/g)	0.64 $\pm$ 0.09
[5]Dissolved manganese (nM)	28 $\pm$ 12
[5]Particulate manganese (μmol/g)	18.9 $\pm$ 7.5

[1] Pers.comm J. Ridal, St. Lawrence River Institute of Environmental Sciences; sampling mid summer 2005.

[2] (Grapentine et al. 2003); sampling October 2001.

[3] (vanHerpen 2006); sampling mid summer 2005.

[4] (Ridal et al., 2006); sampling mid summer 2005.

[5] (Quemarais et al., 1998); sampling in Spring to October 1995-96.

These include Domtar Fine Papers (1881-2006), a pulp and paper company; ICI Forest Products (1935-1995), which included a chlor-alkali plant, and Courtaulds Fibers (1925-1992) a rayon fibre mill. Inputs of Hg from agricultural run-off, storm sewers, combined sewer overflows and atmospheric deposition contribute to local non-point sources of Hg in the AOC (Stage 1 RAP, 1992).

1.2.3 Depositional zones are Hg 'hotspots'

In the depositional zones along the waterfront, reduced water flow allows for the settling of particulate matter (Biberhofer and Rukavina, 2002). Three of these zones (1, 2 and 3) are considered Hg 'hotspots'. Zone 1 is located 1 km downstream from the discharge point used by both the paper mill and the chlor-alkali plant. Approximately 4 kilometres downstream, Zone 2 extends 2 kms downstream from the former location of the effluent outfall of the rayon fibres mill. Zone 3 was later identified at Cornwall Harbour between Zones 1 and 2.

These zones are characterized by a high degree of spatial heterogeneity in sediment type and composition (Biberhofer and Rukavina, 2002). This heterogeneity is mirrored in sediment Hg concentrations. Generally, concentrations of Hg in sediment decrease with increasing distance from the outfalls and with increasing distance from shore. Sampling under such conditions can result in marked differences in Hg concentrations observed in sediments (Yanch, 2007). Zones 1 and 2 were identified as containing the highest sediment Hg concentrations, based on an extensive review of studies conducted since the 1970s (Richman and Dreier, 2001). Spatially-averaged Hg concentrations in Zone 2 are believed to be higher than Zone 1 (Richman, 1999; Grapentine et al., 2003). This is the basis of the 'Zone 1 Paradox': despite the lower concentrations in Zone 1 sediments compared to Zone 2, it is the biota in Zone 1 that have the highest THg concentrations (Yanch, 2007; Fowlie et al., 2008).

1.2.4 Zone 1 characteristics

Zone 1 displays unique features. In addition to showing considerable variation in sediment grain-size, it has a 'windrow' of softwood fibre woodchips, thought to originate from the pulp and paper mill (Stage 1 RAP, 1992). These woodchips have been observed in some areas to be covered by 10 cm of fine grained sediments (Biberhofer and Rukavina, 2002). Furthermore, the decomposition of this organic matter results in Zone 1 being an important area for methane gas production (Biberhofer and Rukavina, 2002). The methane flux is 1.36 times higher than in Zone 2 (T. M. Delongchamp, 2006). This high gas content has implications for sediment erodibility and resuspension.

The highest ratio of MeHg to total Hg (THg) in sediments was found in Zone 1, 5-8% (T. M. Delongchamp, 2006); although lower proportions have been documented (0.3-5.7%, Holmes and Lean (2006), 0.6%, Grapentine et al. (2003)). Generally, MeHg comprises 1-1.5% of THg in freshwater sediments (Craig, 1986), however higher percentages occur (up to 16% in sediments of the Quabbin Reservoir in Massachussetts Gilmour et al. (1992). The higher the ratio of MeHg in sediments, the more likely it will be available for uptake by benthos.

1.2.5 Current status of the Cornwall AOC

The latest published review of sediment contamination in the Cornwall AOC supports the contention that sediment concentrations have decreased substantially since the 1970s (Richman and Dreier, 2001). This conclusion is based on the observation that concentrations in sediments were at the highest ever recorded at that time (Richman and Dreier, 2001). Comparisons of the top 10 cm of a core profile to the lower half revealed considerable reductions (over 70%) in concentrations, implying that cleaner sediments are accumulating on top of older, more contaminated ones (Richman and

Dreier, 2001).

Guidelines set out by the provincial government describe three 'effect' levels of contaminated sediments on benthic biota (Ontario Ministry of the Environment, 1993). These are the: (1) no effect level; (2) the lowest effect level (LEL), i.e., concentrations below which the benthic community is not at risk of impairment; and (3) the severe effect level (SEL), i.e., the concentration above which the benthic community is expected to exhibit adverse effects to the pollutant. In the Cornwall AOC, Hg concentrations exceeded the SEL in the lower portion of 43 of 47 cores (91%) and only 49% of the upper portion of those cores (Richman and Dreier, 2001), further supporting the argument for improved conditions at the site.

However, the bioavailability of Hg does not appear to be the same in all contaminated zones in the AOC. Recent evidence shows that THg in yellow perch over 12 cm in length caught in Zone 1 exceed the guidelines for human consumption (Fowlie et al., 2008). The same is not true for Zone 2. Furthermore, it is unknown how the large gas production and evasion in Zone 1 affects the stability of sediments and the distribution of Hg in surface sediments and porewaters. Recommendations for special focus on Zone 1 have been made previously (Poissant et al., 2007; Yanch, 2007). Understanding how the unique characteristics of Zone 1 may affect Hg uptake into the food web is needed.

1.3 Bubbling in aquatic environments

Zone 1 exhibits extensive ebullition. This is the process of formation and release of gas bubbles from sediments. Oxygen-poor and organic-rich sediments create ideal conditions for anaerobic bacterial decomposition of organic matter. Gas bubbles form once the partial pressures of the dissolved gases are above the hydrostatic pressure of the sediment (Chanton and Dacey, 1991). Bubbles are most often comprised of

methane, nitrogen, carbon dioxide, hydrogen and carbon monoxide gases (Chau et al., 1977). In the Cornwall AOC, conditions are amenable to bubble formation, especially in the more eutrophic Zone 1 where sediments are most anaerobic and therefore capable of degrading organic matter (Poissant et al., 2007).

1.3.1 Sediment type affects bubbling activity

Cornwall sediments are highly heterogeneous, and differences in sediment type can affect bubbling activity. This is because bubbles take on different shapes given the type of sediment they are formed in. Muddy sediments have disk shaped bubbles that grow by fracturing the sediment or reopening prexisting fractures, and sandy sediments create spherical shaped bubbles, thereby acting as a fluid in response to growth stress (Boudreau et al., 2005). The type of sediment also determines the support and maintenance of bubble tubes (Kelley et al., 1990). These can enhance the diffusion of gases and solutes up to a 3 times across the SWI (Klump and Martens, 1981), since the surface area of the SWI increases from a 2-dimensional to a 3-dimensional structure (Martens and Klump, 1980; Chanton et al., 1987).

Percent water content is important in sediments because it affects the bulk density and therefore the % gas. Sediment bulk density impacts the movement of gas bubbles. Less compaction at depths of less than 1 meter in sediments makes sediments more permeable and allows for gas and/or dissolved gas to move more rapidly through the medium (Telmer et al., 2005). A gas fraction of 25-37% was found to create sediment bulk density below that of water, the threshold which allows for the release of gas (vanKessel and van Kesteren, 2002).

1.3.2 Seasonal influence

Increased microbial activity is expected with rising temperatures, a phenomena also noted for sediment methanogenesis (Zeikus and Winfrey, 1976). However, bubbling

rate did not show seasonal variations over the summer in some lake studies (Huttunen et al., 2001; Bussmann, 2005), although other studies show that it had in a river estuary (Chanton and Martens, 1988). Highest rates recorded in September in one study (Huttunen et al., 2001) were attributed to increased sedimentation at that time of year. Kelly and Chynoweth (1981) showed that fairly stagnant temperatures during summer stratification mean that microbial activity of methanogens is largely governed by the rate of organic input, especially at the SWI. Therefore, in absence of rapid temperature changes, bubbling rates will be greatly influenced by inputs of organic materials.

1.3.3 Bubbling contributes to resuspension

Bubbling (Yuan et al., 2007), as well as movement in the benthos (Reynoldson, 1987) and dredging activities (Schafer et al., 2006), contribute to suspended load in the water column in freshwater areas. Disturbances of sediments from wave action, storm events and wave-current interactions are important in coastal areas. Resuspension occurs when particles become eroded and remain in suspension resulting from flow conditions having passed a critical threshold (Dyer, 1986). Resuspension is the only way that metals bound in the solid phase can get into the water column. Since sediments represent the largest repository of metals in the aquatic environment, it is important to understand what occurs in terms of speciation changes and quantity of released contaminants during such an event (Kalnejais et al., 2007).

1.3.4 Resuspension and contaminant flux

Sediment resuspension has been shown in the lab to enhance the flux of organic pollutants, such as PAHs and PCBs (Latimer et al., 1999) and trace metals, such as manganese, iron, zinc, copper and cadmium into overlying water (Calvo et al., 1991; Petersen et al., 1997; Laima et al., 1998). A study of resuspension caused by

ebullition on the release of dichloromethane, chloroform and polynuclear aromatic hydrocarons from Hamilton Harbour, found gas bubbles from sediment to be an important pathway of release for these chemicals (Fendinger et al., 1992). The flux of sediment contaminant was a function of the gas ebullition rate, Henry's Law constant and porewater concentrations (Fendinger et al., 1992). The desorption, partitioning, bacterial degradation, and oxidation of organic contaminants as a result of resuspension events induced by dredging has also been demonstrated (Latimer et al., 1999; Rice and White, 1987). Very little is known about the fate of Hg following a resuspension event. Kim et al. (2004) found that mimicking tidal resuspension caused increased concentrations of THg and MeHg particulates in the water column, though no dissociation of Hg occurred.

Evidence that bubbles can act as a vector for Hg transport was recorded at Kejimkujik National Park (Telmer et al., 2005) and in the St. Lawrence River (Poissant et al., 2007). At Kejimkujik, methane gas in sediment was documented below 1 m depth, suggesting microbial decay of organic matter and release of Hg associated with the organic matter (Telmer et al., 2005). At the redox conditions under which methanogenesis occurs, the only species that are stable are HgS and Hg(0). Hg(0) migrated with the gas bubbles through the sediment. Since no methane was recorded at depths shallower than 1 m, Telmer et al. (2005) concluded that gas bubbles moved quickly through these shallow depths due to the higher permeability of sediments, carrying Hg(0) to the surface. Evidence of Hg diffusion was found in an upward-decreasing gradient of dissolved Hg in porewaters, although the gradient was low (Telmer et al., 2005). This could result from the slow conversion of Hg from sediments into porewaters, or the rapid diffusion of Hg(0) through porewaters. Spiked peepers (porewater samplers) gave a preliminary indication that rapid diffusion was driving the gradient at this site (Telmer et al., 2005).

1.3.5 Resuspension and sediment chemistry

In addition to mechanical disturbance, contaminant flux is also largely dependent on sediment chemistry. A positive change in redox occurs following disturbance events by allowing dissolved oxygen to enter the sediments (Eggleton and Thomas, 2004). The oxidation of anoxic sediments allows for heightened activity of bacteria. Lower pH results from the oxidation of sulphides, although the extent to which this occurs is contingent on the initial concentration of sulphides present in the sediments. Negligible release of metals can be expected if the change in redox and pH is not great (Salomons and Forstner, 1988).

After anoxic sediment resuspension, the desorption rates depend on the rate of dissociation of each metal from the sulphides, for example, that of Hg was found to be higher than that of zinc (Caille et al., 2003). Within the oxic layer, it is not likely that metals tightly bound to sulphides (such as HgS) will readily desorb (DiToro et al., 1990; Allen et al., 1993). However, a negative relationship observed between acid volatile species (AVS) and CH_3-^{199}Hg indicates that resuspension can alter the association of Hg with binding phases (Kim et al., 2006).

It appears that resuspension may affect methylation rates in sediments. Sunderland et al. (2004) found that in well-mixed marine sediments, classical sediment Hg profiles were not visible. Instead, an enlarged active sediment layer was seen, approximately 15 cm thick, where Hg was being converted to MeHg in organic rich pockets. This well-mixed model was able to account for the high %MeHg found in integrated surface samples (0-10 cm), and the higher THg and MeHg concentrations in porewaters of surface sediments (Sunderland et al., 2004). Mass balance calculations in a mesocosm study showed an increase in MeHg production in tanks mimicking tidal resuspension (Kim et al., 2004) Heyes et al. (2004) also confirmed that methylation was increased by a secondary effect of resuspension. Additionally, it had been hypothesized that sediment resuspension can enhance methylation by decreasing sul-

fide levels (Kim et al., 2006); however, it was also possible to decrease methylation if too much aeration created oxic environments in which the SRB cannot function. Indeed, a long-term aeration study found resuspension of Hg from anoxic sediments to be very low, although Hg was released in the early stages of the experiment (Caille et al., 2003).

1.3.6 Bubbling effects on contaminant bioavailability

Resuspension has been linked to enhanced bioavailability of organic pollutants in field studies using fathead minnow and mussels (Rice and White, 1987; Voie et al., 2002) and of certain metals such as cadmium and iron in experimental studies using mussels (Vale et al., 1998). The release of PCBs to the benthic food chain in the NW Mediteranean (Charles et al., 2005) was linked to resuspension caused by storm events. However, some field studies failed to find significant increases in PCB concentrations after sediment disturbance during scrap metal removal (Miller et al., 2000). The fate of contaminants subjected to disturbances remains poorly understood, and knowledge about the bioavailability of Hg due to ebullition and resuspension even more unresolved due to the paucity of studies on this subject (Eggleton and Thomas, 2004).

One study showed preliminary evidence that polychaetes in the field from well-mixed sediments display significantly higher THg than those collected from undisturbed sites (Sunderland et al., 2004). Mixing may act as a vector of MeHg transport to the water column and to animals feeding at the SWI. Core profiles show MeHg production occurs throughout the core as well as at the SWI, whereas the unmixed sediments have an oxic sediment layer (Sunderland et al., 2004) which acts to prevent the diffusion of MeHg to the water column by precipitating out the iron and manganese hydroxides (Gagnon et al., 1996).

A recent mesocosm study by Kim et al. (2006) investigated the effects of resuspen-

sion on sediment dynamics, MeHg production and bioavailability. Tidal resuspension was mimicked and THg and MeHg were measured in zooplankton and clams. No treatment effect was found (Kim et al., 2006).

Gagnon and Fisher (1997) tested the assimilation efficiencies of inorganic and organic Hg associated with suspended sediments to a marine benthivore. Uptake through both dissolved and particulate pathways occurred, and the dissolved phase found to be an important vector to marine mussels. Methylmercury assimilation from ingested particles with organic coatings increased uptake in suspension feeders (Gagnon and Fisher, 1997). Furthermore, assimilation of dissolved species is very high for both inorganic and organic Hg. Turbid waters favor the association of MeHg with suspended particles, and once these particles sink they remove the MeHg from water As a result the particulate phase can play an important role in Hg transfer to mussels.

1.4 Amphipods as biomonitoring species

Amphipods are crustaceans found in abundance in freshwater and marine environments. They are benthic omnivores that live at the SWI and can be found living on macrophytes. Amphipods (2 dominant species are common in the AOC: *Gammarus fasciatus* and *Echinogammarus ischnus*) represent an appropriate biomonitoring tool at my study site because they are a common prey item of a popular local sport fish, the yellow perch (*Perca flavescens*). Amphipods were found to make up a major part of yellow perch diet in all the contaminated zones in the Cornwall AOC (Yanch, 2007). Amphipods are frequently used in biomonitoring studies because they are abundant, easy to collect and to identify, and represent conditions on a localized scale (Amyot et al., 1996). At my study site, amphipods were easily collected using artificial substrates on a short time scale, and were relatively hardy in the collection

process. Others (vanHerpen, 2006; Yanch, 2007) also showed that prey items of yellow perch in Zone 1 are contaminated to the same extent as the yellow perch. Amphipods were therefore chosen as the test species in this study to represent the Hg burden of benthos in Zone 1.

Rufugia are well documented to be an important habitat consideration for amphipods. Leaf litter provides ideal dark microhabitats from which the amphipods can hide from visual predators during the day. They filter feed on suspended particulates, as well as ingest detritus and sediment (Covich and Thorp, 2001). They are also classified as predators since they display intraguild predation and cannibalism (Covich and Thorp, 2001). Since they exploit such a wide range of feeding and habitat types, they are exposed to all possible vectors of Hg through sediments, porewaters, overlying waters and suspended particulate matter (Lawrence and Mason, 2001).

Females of most amphipods only produce a single brood during their life cycle (Smith, 2001), although *Hyella azteca* produces a series of broods during the breeding months. The life cycle of *Crangonyx aberrans* is used to infer the life cycle of other amphipod species (Smith, 2001). Females and males mature and breed in the spring. Eggs are deposited between early-April to mid-May in the marsupium, and after hatch larvae remain with the parent for a few molts. The young disperse from late-May to mid-June. Growth is arrested during periods of low water levels or during the winter months. Molting is variable, occurring every 3 to 40 days, depending on local food and temperature conditions and species type. Most amphipods complete their life cycle in a year or less (Smith, 2001).

Amphipods are commonly used as toxicity test species for metals and organic pollutants (DeWitt et al., 1992) because of their sensitivity to sediment-bound contaminants (Schlekat et al., 1992; Schlekat et al., 2000). With increasing metal exposure, *Hyella azteca* accumulated Hg with highest non-toxic and lowest toxic tissue doses reported to be 56 and 90 μg Hg/g d.w., respectively (Borgmann et al., 1993).

1.5 Study objective

The greater accumulation of Hg by fish in Zone 1 as compared to Zone 2 suggests either an alternative source of Hg, or enhanced transfer of Hg from sediments. The objective of this study was to determine whether Hg concentrations observed in Zone 1 biota were explained by the bubbling of methane gas from historically Hg enriched sediments.

Using amphipods as bioindicators of Hg contamination in the benthos of Zone 1, the relationship between Hg exposure and bubbling rates was assessed. Artificial substrates were used to collect amphipods and gas ebullition from sediments quantified. The relationship between bubbling rates and possible exposure pathways of Hg to amphipods was investigated by sampling sediments and porewaters in the same locations where biota were collected.

A strong association between ebullition and Hg concentrations in tissues of amphipods would indicate that bubbling increased the exposure of these organisms to Hg either by augmenting the flux of contaminated porewaters and particulates, or increasing methylation activity in surficial sediments. A relationship between porewater and sediment Hg concentrations and bubbling would suggest that this was the mode of Hg transport. Alternatively, no association would suggest that bubbling was not an important vector of Hg. Possible indirect effects of bubbling on the Hg distribution in Zone 1 were also considered.

The following hypotheses were tested in Zone 1:

$\mathbf{H}_o1$: Amphipod abundance is not significantly different among sites in Zone 1 as a result of bubbling rate or location.

$\mathbf{H}_o2$: Amphipod Hg burden is not significantly different among sites in Zone 1 as a result of bubbling rate, sediment Hg concentration, porewater Hg concentration, abundance or location.

$\mathbf{H}_o3$: There is no significant difference in Hg concentrations in porewater and sedi-

ments among sites in Zone 1 as a result of bubbling rate or location.

$\mathbf{H}_o4$: The effects of location, bubbling rate and Hg in sediments and porewaters is not modified by temperature or bulk sediment characteristics.

Chapter 2

Materials and methods

2.1 Sample collection

Zone 1 was divided into a grid of 100 8x8 meter squares. Ten different grid squares were randomly selected before every sampling event which occurred four times over the 2007 field season (June 14-26, July 17- 31, August 9-22 and September 9-22; Figure 2.1). A random sampling design was chosen due to the high degree of spatial variability in sediment types (Biberhofer and Rukavina, 2002). Study sites were characterized by location, depth, bubbling rate, amphipod density and water temperature.

2.1.1 Amphipods

Gravel rock baskets, as described by van Herpen (2006), were used as artificial substrates to collect amphipods. Two replicate baskets were deployed at each site, with a combined area free for entry of 0.4 m^2. A cement block was used as an anchor to keep the baskets from getting displaced refcollector. Amphipods readily colonized baskets that were set out for a two-week period to ensure that sufficient biomass was collected for tissue Hg analyses. Previously, basket materials were tested by leaving them in tubs of water for half an hour and collecting water for analyses using the clean hands/dirty hands method (J. Ridal, pers. comm, St. Lawrence River Institute of Environmental Sciences, Appendix G). Compared to the THg in Zone 1 surface water of 1.5 ng/L (value quoted in Fowlie (2006); no Hg leaching was found (average

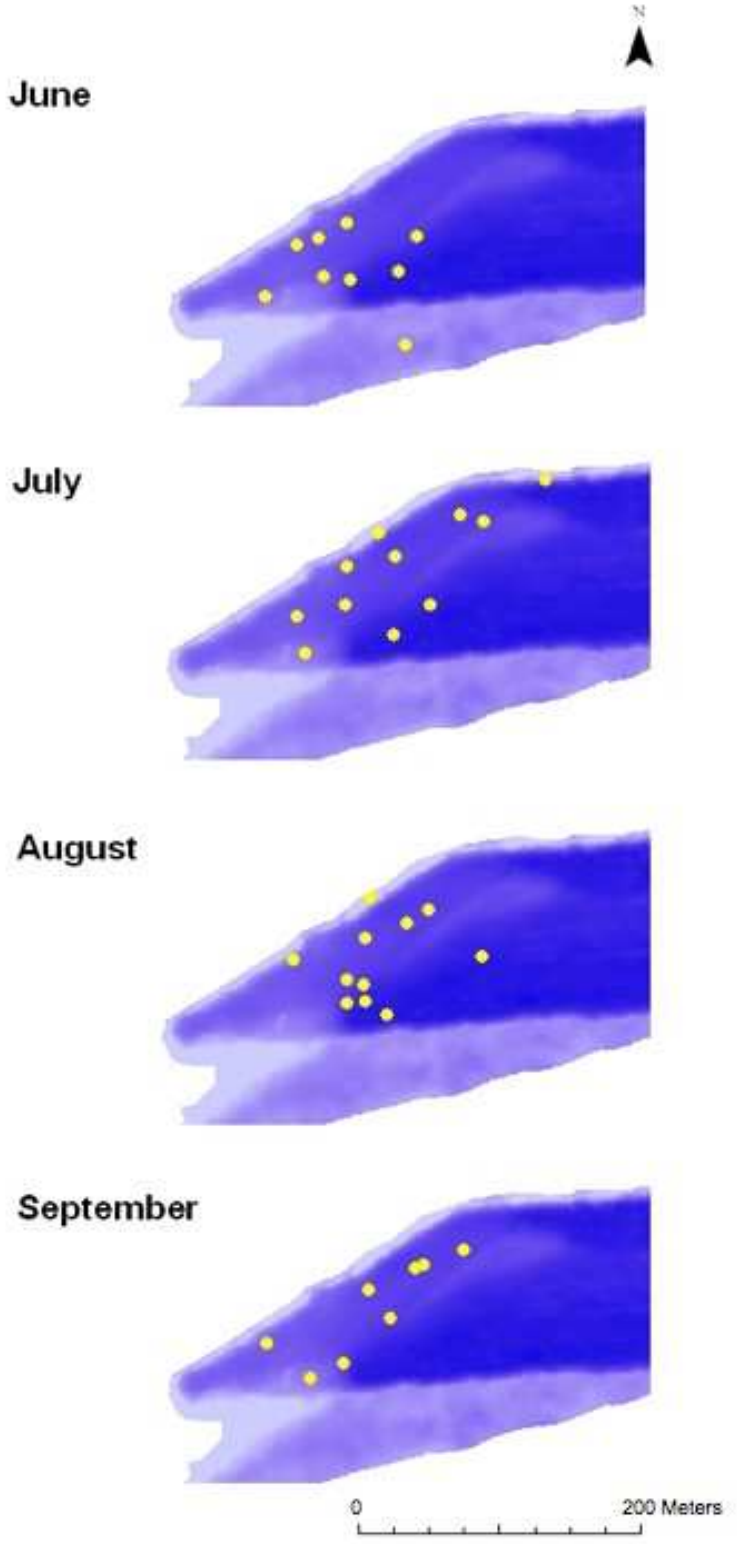

Figure 2.1: Sampling locations in Zone 1 from June-September 2007.

THg from baskets without rocks: 0.52 ng/L; with rocks from the River Institute: 0.7 ng/L; with rocks from the quarry: 1.1 ng/L). On one occasion divers were asked to place the baskets in a net to see if any amphipods could fall out during the retrieval process; none were lost. Baskets were retrieved by pulling them up to the surface and placing them in tubs with enough water to immerse 1/3 of the baskets. Tubs with baskets were brought to shore and sorted immediately for amphipods by emptying the gravel into the tub and checking each rock. As soon as an amphipod was found it was placed in tin foil kept over ice. Water left in the tubs was sieved through 35 mm mesh sieves and amphipods were enumerated. The sample was then placed in the freezer for subsequent Hg analyses.

2.1.2 Gas collection and analysis

The gas collector design was adapted from that of Huttunen et al. (2001). An 80 cm polyvinylchloride (PVC) pipe of 2.5 cm diameter (3/4) overlapped the narrow end of a 30 cm diameter plastic, down-facing funnel collector. A 2 kg weight was attached to the funnel to maintain the collector in an upright position underwater. A 60 mL Luer Lok syringe was fitted to the other end of the PVC pipe with an attached Luer 2-way stopcock, allowing for gas measurement of volume collected. The collector was suspended about 1 meter above the sediment surface. Gas readings were taken several times over the course of the 2-week deployment period. From July to September, 5 ml of gas were taken whenever sufficient volume was available. These samples were taken back to the lab and analyzed by gas chromatography (GC Varian 3300, stainless steel column packed with Haysep Q Mesh). One ml of sample was used for each run, blanked after each duplicate and a standard gas (1.99% CO_2; 38% N_2 and 60.01% CH_4) run every 10 samples.

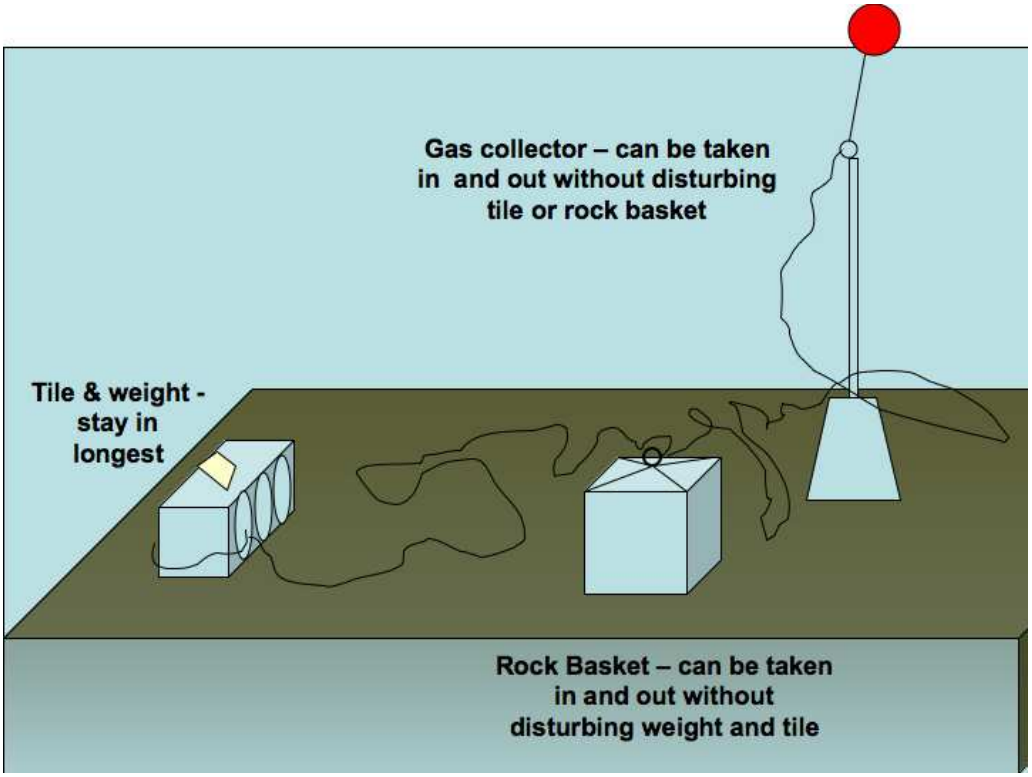

Figure 2.2: Collector set-up. Approximately 10 meters of line were used to connect each device. The gas collector hovered approximately 1 meter above the rock baskets. Note: figure not to scale.

2.1.3 Sediment and porewaters

Triplicate sediment cores were taken using a gravity corer at each site to collect sediments (Telmer et al., 2005). The boat was anchored at the front and back to prevent drifting and two ropes were used to facilitate the lowering and raising of the corer and to keep it in an upright position. The surficial sediments of each core were sectioned by placing a clear Lexan tube with a mark at the 5 cm line over the top of the core and pushing the tube down and slicing at the mark (D. Lean, pers. comm., University of Ottawa). Sediments were placed in a single bag that had been purged with nitrogen and the sediments were manually mixed. All subsequent handling of sediments and porewaters were done under nitrogen atmosphere in a sealed glove box. Subsamples were taken from the bag using Falcon tubes which were then centrifuged for 15 minutes at 3500 rpm to separate the solid and aqueous phases. The solid phase was preserved immediately by freezing. The porewater extract (aqueous phase) was then centrifuged at 3500 rpm for 5 minutes before passing through a Whatman syringe filter (25 mm GD/X, PES membrane, 0.45 um pore size) using a purged syringe under nitrogen atmosphere into a new Falcon tube. Sufficient volume was collected for duplicates. Five ml of porewater were preserved for THg analyses using 300 μg/L BrCl and 35 ml of deionized water. Ten ml of porewater were preserved for MeHg using 50 μg/L HCl. All samples were kept in the refrigerator until further analyses. All equipment (including the core tube for slicing) was thoroughly cleaned before the next core was sectioned.

Bulk sediment analyses were also carried out to determine the bulk density (g/cm^3), percent organic matter (loss-on-ignition) as well as the percent water content of sediments. The latter two variables were determined following standard protocols (in Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005). Methods designed to deal with unconsolidated sediments at the sediment-water interface (Telmer et al. 2005) were used to determine bulk density.

2.2 Hg analyses

2.2.1 Hg in amphipods

Frozen amphipods were dried at 50 ^{o}C for 18-24 hours. Dry samples were ground into a homogeneous powder using an agate mortar and pestle, and placed into new aluminum foil wrap. Small sample mass prevented the use of a mechanical grinding method. All equipment was washed with detergent and water, rinsed with distilled water and rinsed again with Millipore water between samples. Amphipods were analysed in duplicate for Hg (ng THg per g dry weight d.w.). Approximately 8 amphipods was the minimum number needed for duplicate runs. Measurements were made using a Nippon Automated Mercury Analyser SP-3D (Nippon Instruments Corporation, Osaka, Japan) with a detection limit of 0.01 ng. Amphipod samples had an average coefficient of variation (CV) or precision of 15.9% (n=39). The accuracy of THg in amphipods was estimated by analyses of procedural blanks and spiked samples. Following 10 runs, a check standard was preformed, and blanks were completed after highly contaminated samples to ensure the removal of any trapped Hg residues. After each analytical session, a certified reference material (CRM) (DOLT-3 from the National Research Council of Canada) was analysed. The average THg results of DOLT-3 samples were 3.33 $\pm$ 0.64 μg/g (n=6) close to the expected 3.37 $\pm$ 0.14 μg/g (98.7% recovery). MeHg analyses in amphipods followed methods described by Cai et al. (1997) using capillary gas chromatography coupled with atomic flurorescence spectrometry (GC-AFS; GC model number HP 6890 series with autosampler model number 7683 series) with a detection limit of 0.02 ng. Fifty mg of dry mass sample was required for a single run, which represented approximately 100 amphipods. The average MeHg and standard deviation of DOLT-3 was 1.49 $\pm$ 0.58 (n=5) close to the expected 1.59 $\pm$ 0.12 μg/g (93.7 % recovery).

2.2.2 Hg in sediments

Sediments were freeze-dried and homogenized using mortar and pestle. THg analyses were conducted using the SP-3D Hg analyzer (Nippon Instruments Corporation, Osaka, Japan) with a detection limit of 0.01 ng. Samples ground by hand had a CV of 20.4% (n=35). Given the high variance, sediments were ground mechanically, and CV improved to 6.9% (n=35). There appeared to be an increase in mean THg concentrations by mechanically grinding sediments (mean of all samples increased from 3.8 to 5.0 μg/g after grinding), but the difference was not statistically significant. This reflects the high heterogeneity of the substrate and the need, therefore, to properly homogenize the samples. The CRM (MESS-3) recovered was 91 $\pm$13 (n=19) close to the expected 91$\pm$9 μg/g (99% recovery).

Methylmercury in sediments was extracted and measured by GC-AFS (Cai et al., 1997), with a detection limit of 0.02 ng. Precision for MeHg in sediments was found to average 12.1% (n=23 pairs). Accuracy was ensured in sediment analyses by running procedural blanks and spiked samples. Recovery of spiked samples was 91.3 % for MeHg using IAEA-405 (estuarine sediment) certified reference material (n=5), and 105.3 % using ERM-CC580 (n=4).

2.2.3 Hg in porewaters

Porewater THg was analyzed by pre-oxidation with BrCl, $SnCl_2$ reduction, and preconcentration by two-stage gold amalgamation. Cold vapour atomic fluorescence spectroscopy (CV-AFS) was used for THg detection by the Tekran 2600 system following the US EPA Method 1631 guideline for Hg analysis. Analysis of MeHg in porewater followed Cai et al. (1997) using GC-AFS. Detection limits for both methods was 0.02 ng/L. Procedural blanks revealed no contamination during THg or MeHg extraction or analysis. The mean recovery of spiked samples was always above 95%.

2.3 Statistical analyses

Data were analysed using the statistical package JMP 7.0 (SAS Institute, Cary, North Carolina, USA). Correlation analyses were performed to look for covariation among all environmental variables measured. Log transformations were used to ensure normality of residuals, and a Shapiro-Wilks test employed to confirm the residuals were from the Normal distribution. Regression statistics were reported, and null hypotheses rejected at the 0.05 alpha level. Of 91 comparisons, the chance of a false positive was approximately 5. Correlations were reported for comparisons in which residuals are not normally distributed (Appendix F).

Two outliers were removed. These sites were in shallow areas where the water column depth did not exceed 3 m, and they were considerably different from the rest of the locations in deeper parts of the zone because of the presence of dense beds of vegetation. These outliers were removed from all regressions analyses.

2.3.1 Seasonal trends

The sampling design was chosen to quantify the greatest amount of heterogeneity in Zone 1, and sites were not resampled in order to eliminate pseudoreplication. However, this implies that differences among months cannot be teased apart from differences among sites. As a result, conclusions about seasonal influences are drawn from observations and require validation in future studies.

2.4 Surface representation and analysis

2.4.1 Interpolation

To predict what the pattern of Hg contamination may be in the biotic and abiotic compartments across my study area, an interpolation technique known as Inverse

Distance Weighting (IDW) was used. This technique creates a spatial surface using the data points that were measured to estimate the values at unsampled locations. IDW calculates a local mean by giving more weight to control points that are near than those that are further away, assuming that proximity is a guage of similarity (Tobler, 1970). An inverse-distance-squared-weighting was selected. The reciprocal function $1/d^2$ is most commonly employed, where d represents the distance between a nearby point and the point to be estimated:

$$Z(x_j) = \frac{\sum_{i=1}^{n} Z(x_j) \cdot d_{ij}^{-2}}{\sum_{i=1}^{n} d_{ij}^{-2}} \tag{2.1}$$

and where x_j is the point at which the surface is to be interpolated.

IDW is a useful screening technique because of its low computational complexity and ease of implementation (Reed et al., 2004), although it does not provide estimates of interpolation error (O'Sullivan and Unwin, 2003). Since the sample size is small, obtaining only a rough contour map of Hg concentrations at the study site was possible, and therefore this technique was appropriate for my purposes. Contour lines were added onto maps to indicate the patterns of concentrations. It is important to recognize that where there were fewer lines, and especially where lines cross, corresponded to a large degree of uncertainty either because there were no data available or a single data point influenced the outcome at that point.

2.4.2 Trend surface analysis

To assess whether the data contained any major feature or trend, a technique called trend surface analysis was used. A trend is a large-scale systematic change occurring predictably from one end of the study site to the other (O'Sullivan and Unwin, 2003). Trend surface analysis generates a surface based on a polynomial expansion using locational coordinates (X, Y) as the independent variables. The coefficients of the polynomial function were calculated by SPSS (SPSS Inc., Chicago, Illinois, USA)

and used to determine the height (Z) of the surface, or the dependent variable, as follows:

$$Z(X,Y) = \sum_{r+s<=p} (b_{rs} \cdot X^r \cdot Y^s) \tag{2.2}$$

where r and s are the polynomial coefficients, p is the order of the trend surface and b_{rs} is the constant. This technique has merit mostly as an exploratory tool (O'Sullivan and Unwin, 2003), and will provide a rough generalization about the shape of the field.

Chapter 3

Results

3.1 Bubbling distribution in Zone 1

Bubbling rates ranged from <1 to approximately 2800 ml/m^2/day, with median and mean rates of 658.3 and 769.6 ml/m^2/day, respectively. There were no significant differences among sampling months, though highest bubbling rates were recorded in September. The distribution of the records did not follow a Gaussian distribution: 33 of the 38 records were below 1500 ml/m^2/day and nearly half (48 %) of those were below 500 ml/m^2/day. Bubbling patterns follow a Generalized Pareto distribution, characteristic of extreme event data, which is commonly over-represented in the tail of the distribution curve (Ramos et al., 2006). Therefore I applied a log transformation, deemed appropriate for this type of distribution, given the exponential term in the distribution equation (D.J. Thomson pers.comm., Queen's University).

Percent CH_4 in gas ranged from 29 to 84% over the season. There were no significant differences in mean % CH_4 in gas among sampling months, though an apparent increase from July to September was observed. At locations of higher bubbling activity, the % CH_4 in gas was significantly higher than at lower bubbling rate sites ($p<0.0001$, Table 3.1, Figure 3.1). Methane flux also increased with decreasing water column depth (hereafter referred to as depth; $p=0.018$, Table 3.1), although 2 data points heavily influence this relationship and, therefore, I am hesitant to conclude that there is an effect with depth without further data.

3.2 Amphipod distribution in Zone 1

Between June and September 2007, amphipod abundance between the pair of collectors ranged from a minimum of 9 to a maximum of 816 amphipods, with a median and mean of 54 and 107 individuals, respectively. Standardizing this to individuals/m^2 (sampling area of two rock baskets = 0.4 m^2, therefore multiply by 2.5 to get 1 m^2) for comparative purposes with literature values gives 23-2,040 individuals/m^2 with a mean of 268 individuals/m^2.

Log amphipod abundance increased significantly with increasing depth and temperature, although the relationships were weak (p=0.015 and p=0.012, respectively; Table 3.1). Low temperatures in June supported fewer amphipods than in the warmer months of July and August. In September abundance decreased again with the decreasing temperatures.

Log amphipod abundance and log bubbling rate were significantly, and negatively related (p<0.0001; Table 3.1, Figure 3.2). A similar negative relationship existed with % CH_4 in gas, though with more variation (p=0.035; Table 3.1, Figure 3.3). Figure 3.4 shows the spatial relationship between abundance and bubbling rate. Areas of high amphipod abundance do not overlap with areas of high bubbling rates.

3.3 Hg burden of Zone 1 amphipods

Amphipod THg concentrations ranged from 60.2 to 596.1 ng/g d.w., with a median and mean concentration of 140.0 and 192.4 ng/g d.w., respectively. Amphipod MeHg concentrations ranged from a minimum of 27.6 to and a maximum of 146.9 ng/g d.w. with a median and mean concentration of 56.9 and 65.4 ng/g d.w., respectively.

Neither bubbling rate, nor sediment Hg concentrations (both total and inorganic) were related to amphipod Hg concentrations (Table 3.1).

With increasing porewater THg and MeHg concentrations, amphipods showed

a significant increase in MeHg concentrations (p=0.019 and p=0.011, respectively; Table 3.1, Figure 3.5 and Figure 3.6). Note, however, that the latter relationship is based on a small sample size (n=8) due to all of the porewater MeHg samples in July and 80% of those in August being below detection limits.

Log amphipod THg concentrations and depth did not co-vary (Table 3.1). The opposite was true for log amphipod MeHg concentrations and depth, where a strong and significant relationship was found (p=0.004; Table 3.1, Figure 3.7).

Amphipod THg concentrations did not significantly predict amphipod MeHg concentrations (Table 3.1). Percent MeHg was highly variable in Zone 1, ranging from 9.6% to 85.1%, with a median and mean of 35.7 and 39.1 %, respectively. Temperature had the same significant effect on the MeHg concentrations and the % MeHg in amphipods, specifically, at higher temperatures, lower concentrations and ratios were observed (p=0.002 and p=0.048, respectively; Table 3.1). The percent MeHg in amphipods increased with percent MeHg present in both porewaters and sediments (Table 3.1).

Only one significant relationship between a bulk sediment characteristic and amphipod Hg concentrations was observed. Namely, log amphipod MeHg concentrations decreased with log L.O.I. (p=0.035; Table 3.2, Figure 3.8).

Figure 3.9 shows amphipod THg and MeHg concentrations compared to the spatial distribution of bubbling in Zone 1. Amphipod THg concentrations and bubbling patterns were not comparable, as the majority of areas of highest amphipod THg concentrations are located north of the high bubbling sites. Patterns of amphipod THg concentrations and amphipod MeHg concentrations showed little overlap.

3.4 Hg sources in Zone 1

3.4.1 Core description

Variability was observed in sediment cores throughout Zone 1. Generally, I found two types of sediments: one very black, viscous, with only fine wood fibre debris; these sites were very easy to core. The other type of sediments contained considerably more bark, found in chip form as opposed to a fine fibre. There was no consistent depth at which bark layers were found, with bark deposits ranging from a defined layer to the entire length of the core. The sediment layer that had accumulated on top of the bark also varied, from 1-2 mm to 10 cm. Gas pockets were visible in both types of cores. Benthic invertebrates were not seen in the top 5 cms of all cores.

3.4.2 Factors affecting sediment Hg

Sediment THg concentrations ranged from 768 ng/g d.w. to 17 911 ng/g d.w., with a mean of 5 338 ± 4 560 ng/g d.w (n=36). Sediment MeHg concentrations ranged from 2.7 to 18.8 ng/g d.w.; the mean concentration was 8.1 ± 4.8 ng/g d.w. The %MeHg in sediments was always below 1%, with a mean of 0.2 % and a minimum of 0.04 and a maximum of 0.64 %.

Temperature and log sediment THg concentrations showed a significant positive relationship (p=0.0083; Table 3.1); however, no ecological or physicochemical explanation can be made for this and therefore it is believed to be a Type I error. Neither bubbling rate, depth nor bulk sediment characteristics displayed any relationships with sediment THg concentrations (Table 3.1).

An increase in sediment THg concentrations corresponded to a significant increase in sediment MeHg concentrations (p=0.0016; Table 3.1, ; Figure 3.10). No other significant relationships for sediment MeHg concentrations were found (Table 3.1). However, higher bubbling rates did appear to correspond to lower MeHg concentrations

and %MeHg in sediments (Table 3.1,Table 3.2).

Extrapolated sediment concentrations compared to bubbling rates in my study area do not show much overlap between high sediment Hg concentrations and bubbling rates (Figure 3.11).

3.4.3 Factors affecting porewater Hg

Porewater THg concentrations ranged from 4.1 to 944.1 μg/L, with a median and mean concentration of 31.6 and 72.5 μg/L, respectively. Porewater MeHg concentrations varied from 2.6 to 22.9 μg/L; median and mean concentrations were 5.9 and 9.3 μg/L, respectively.

There were no clear linear relationships capable of accounting for observed porewater THg concentrations. However, log porewater MeHg concentrations was significantly and negatively related to depth (p=0.025; Table 3.1, Figure 3.12). No comparison could be made between porewater MeHg concentrations and L.O.I., because the latter was not collected in the month of June.

Several trends were observed with porewater MeHg concentrations. First, as mentioned previously, porewater MeHg concentrations were below detection limits in July and August samples. This resulted in the negative trend between log porewater MeHg concentrations and temperature (p=0.075, Table 3.1). Porewater samples for September were not analyzed because amphipod MeHg concentrations were not available for comparison due to low biomass collected in that month. Second, porewater MeHg concentrations appeared to increase with increasing sediment and porewater THg concentrations, although the relationships were not significant (p=0.36 and p=0.16; Table 3.1). Finally, porewater MeHg concentrations appeared to increase with % MeHg in sediments, although the relationship was not significant (p=0.06, Table 3.1).

As with sediment Hg, extrapolated porewater Hg did not show a similar distribution compared to bubbling rate (Figure 3.13). However, the highest concentrations

for both Hg in amphipods and Hg in porewaters were highest in the south-west part of my study site; compare Figure 3.9 and Figure 3.13.

3.5 Trend surface analysis results

Many of the trends observed with porewater and amphipods Hg were confirmed using linear trend surface analyses. For instance, 53 % of the variation in amphipod MeHg concentrations was explained by the location variables in the linear trend surface equation (Table 3.3). Variation in porewater Hg (both THg and MeHg concentrations) was also explained by the equation (38 and 93%, respectively). The trend surface shows a decrease in MeHg concentrations in amphipods and porewaters, in the north-east direction (Table 3.3a,c). A decrease in porewater THg concentrations was observed following an east gradient only. These patterns may be a reflection of the bathymetry of Zone 1; variance in water column depth was also significantly explained by the linear trend surface equation (Table 3.3d). The sampling sites towards the eastern part of the study area were deeper than in the locations where the Hg hotspots in amphipods and porewaters were observed. No other variables showed the same spatial patterns as those observed for amphipod MeHg, porewater Hg and water column depth.

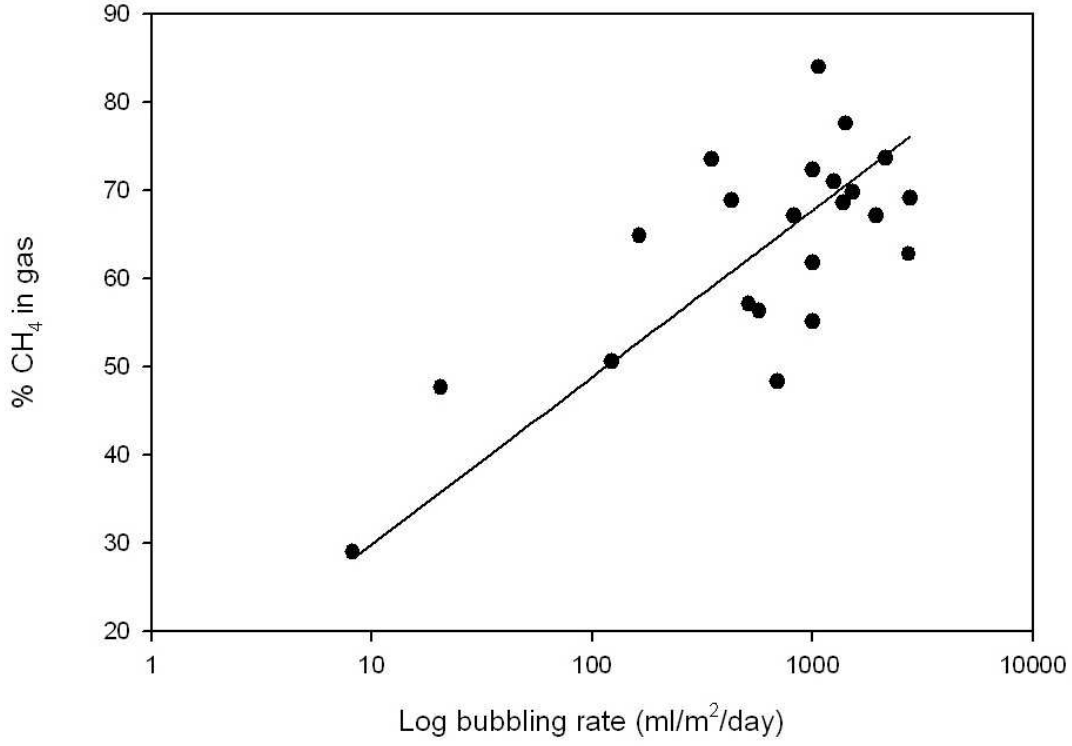

Figure 3.1: Percent methane (CH_4) in gas versus log bubbling rate (r=0.73, p<0.0001, n=22).

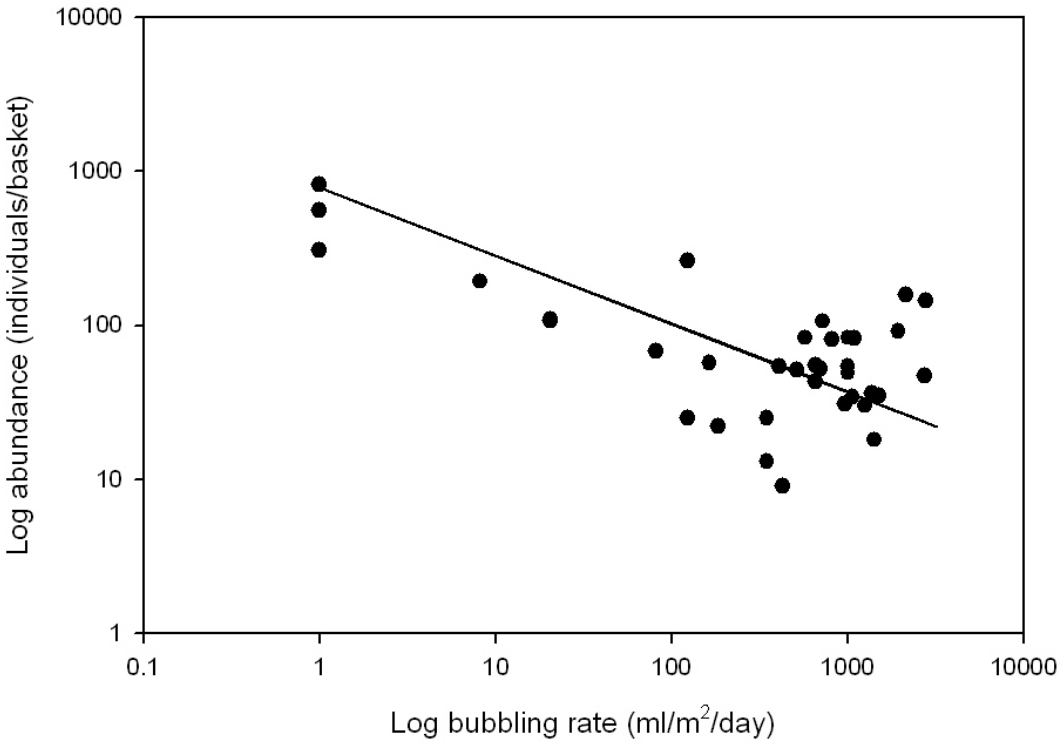

Figure 3.2: Log amphipod abundance versus log bubbling rate (r=0.62, p<0.0001, n=36).

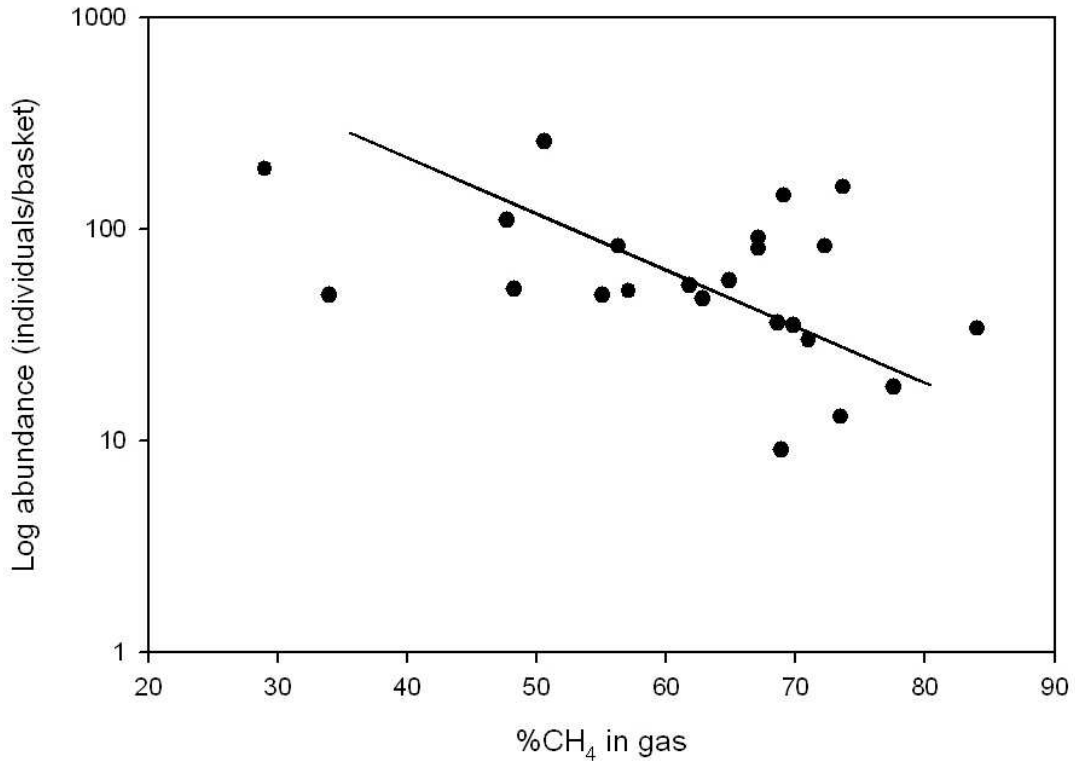

Figure 3.3: Log amphipod abundance versus percent methane (% CH_4) in gas (r=0.45, p=0.03, n=23).

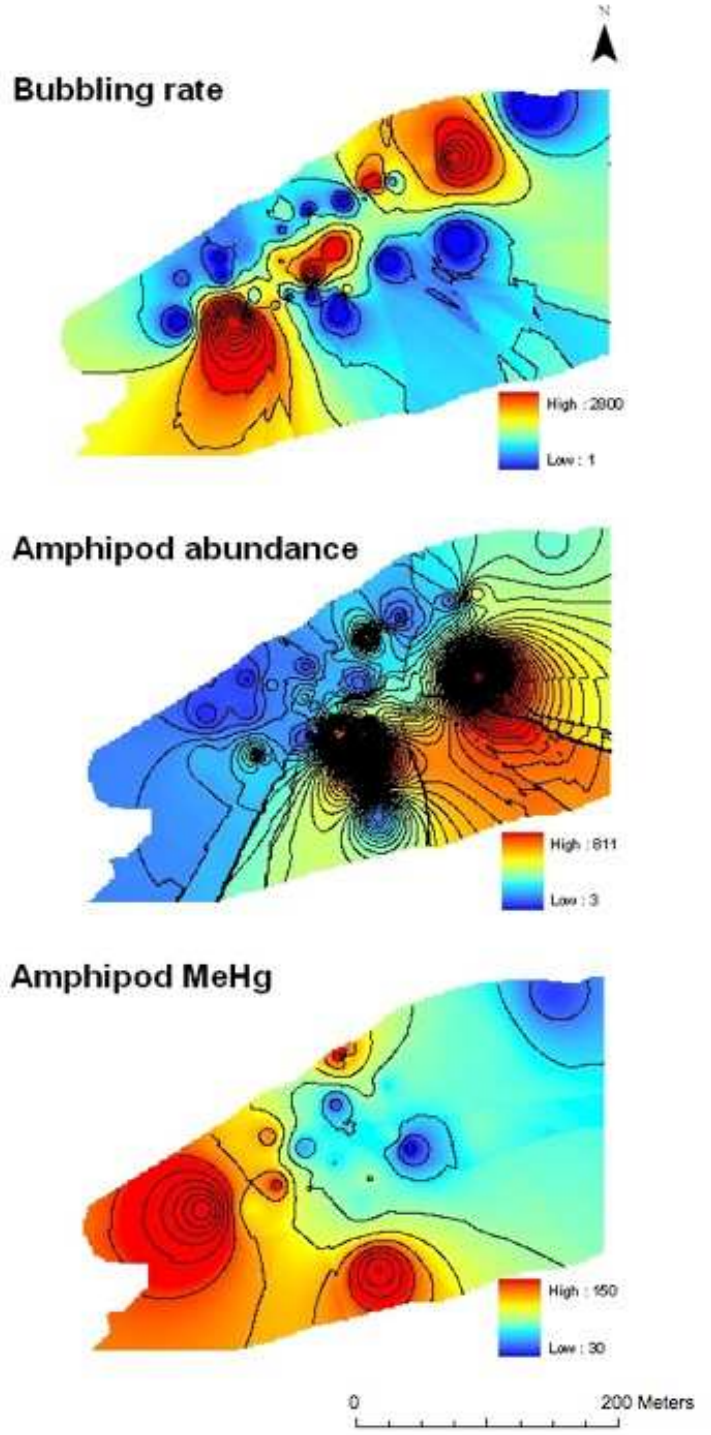

Figure 3.4: Surface representation of bubbling rates (ml/m^2/day) and amphipod abundance (individuals/basket).

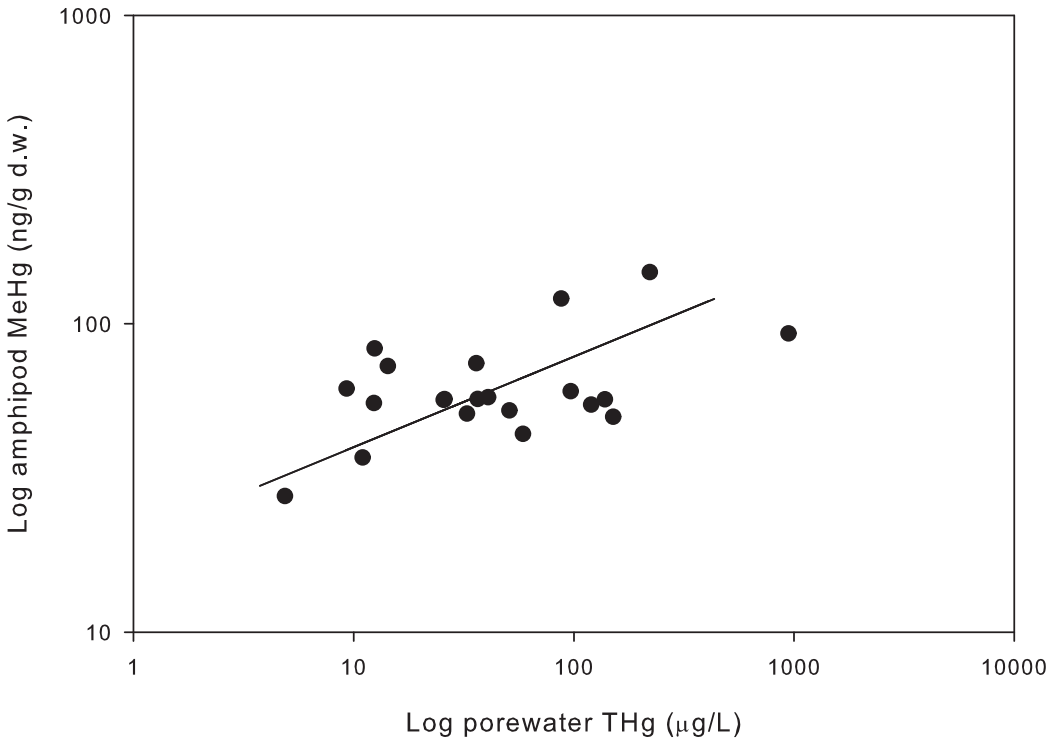

Figure 3.5: Log amphipod methylmercury concentration (MeHg) versus porewater total mercury concentration (THg) (r=0.51, p=0.019, n=21).

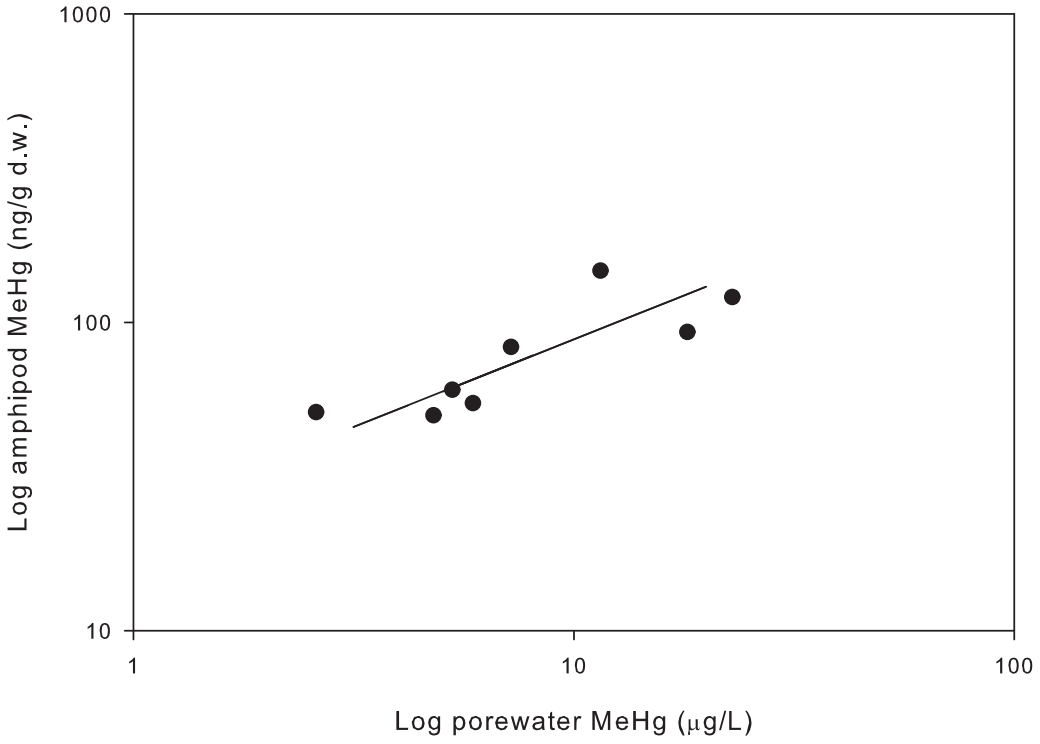

Figure 3.6: Log amphipod methylmercury concentration (MeHg) versus log porewater MeHg (r=0.82, p=0.011, n=8).

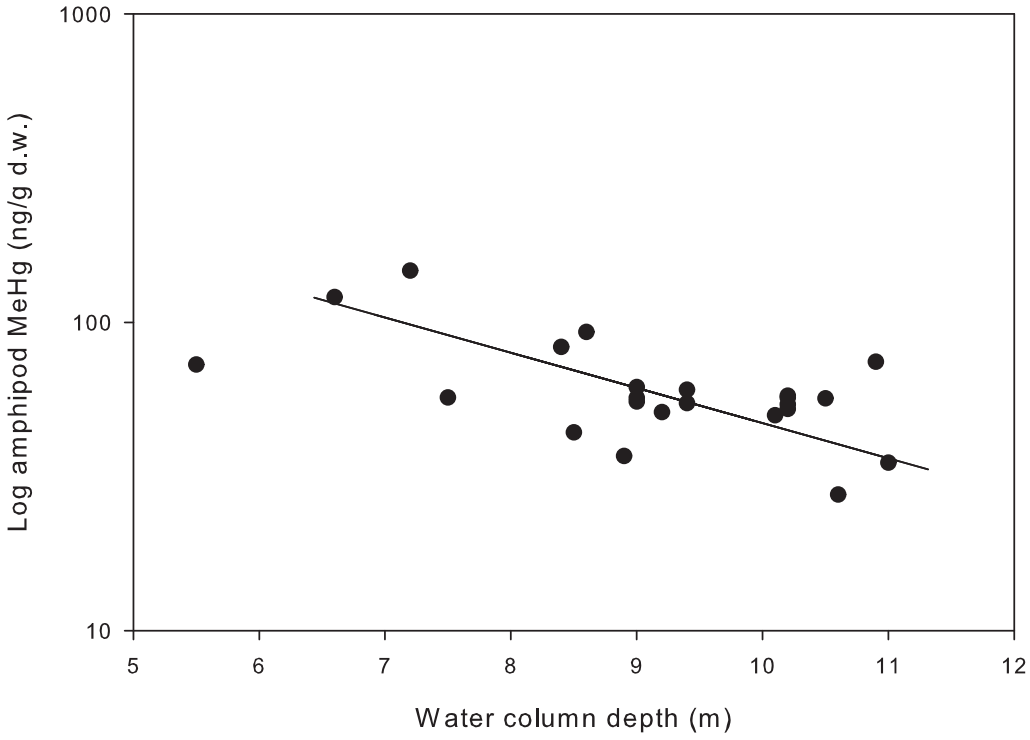

Figure 3.7: Log amphipod methylmercury concentration (MeHg) versus water column depth (r=0.58, p=0.004, n=23).

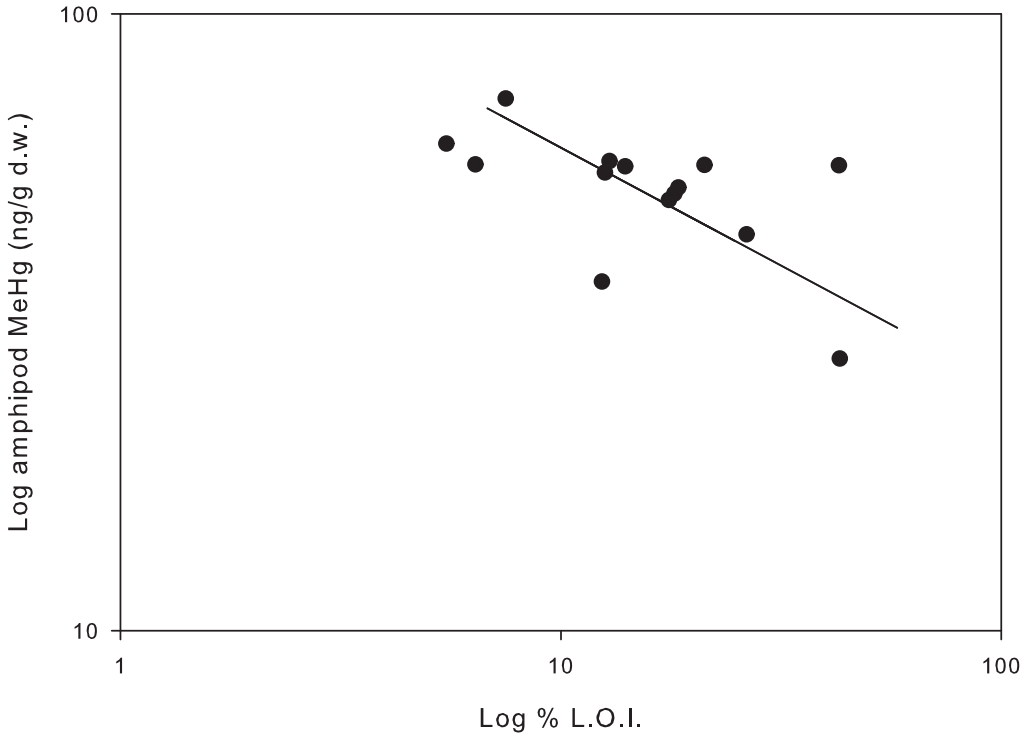

Figure 3.8: Log amphipod methylmercury concentration (MeHg) versus log loss on ignition (L.O.I.) (r=0.57, p=0.035, n=14).

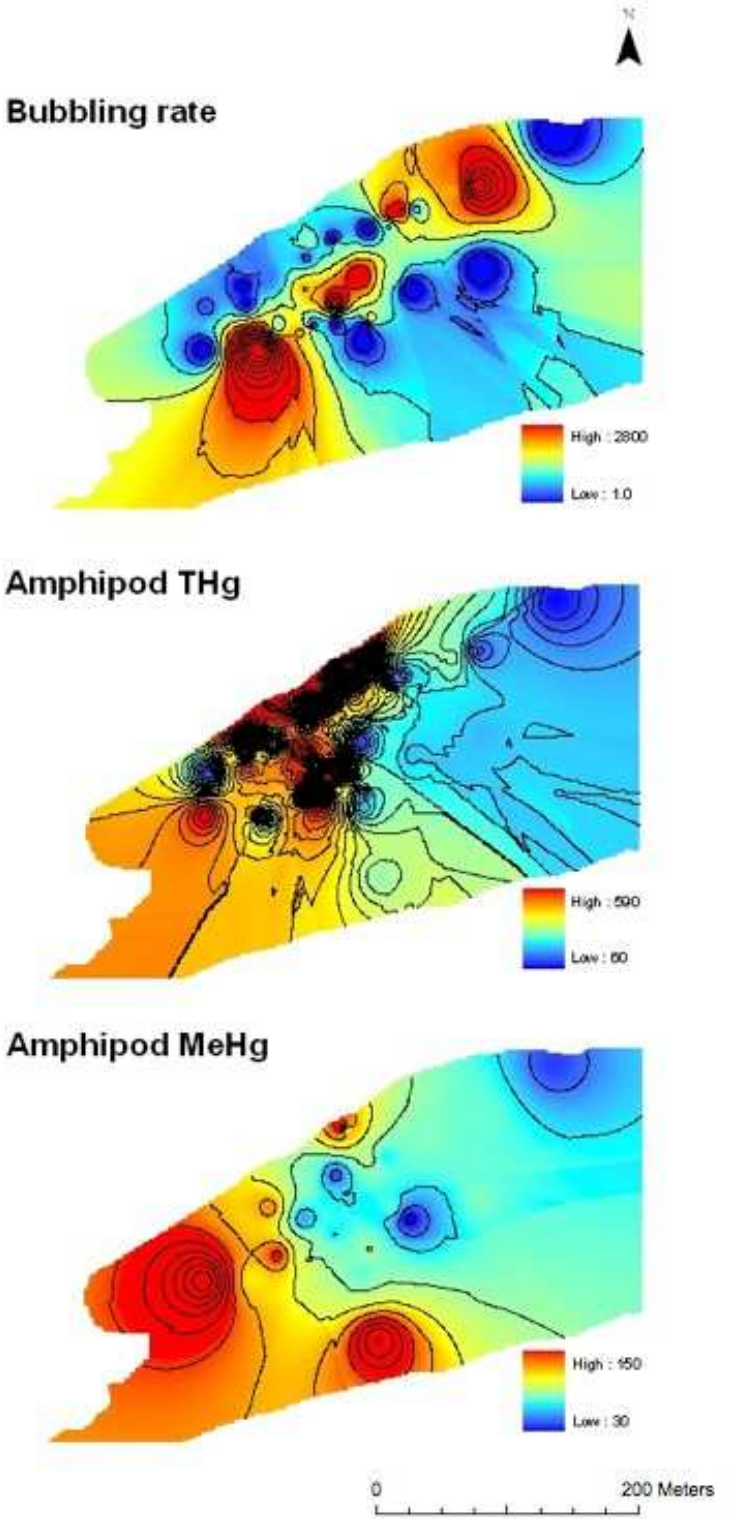

Figure 3.9: Surface representation of bubbling rates (ml/m^2/day) and amphipod total mercury (THg) and methylmercury (MeHg) concentrations.

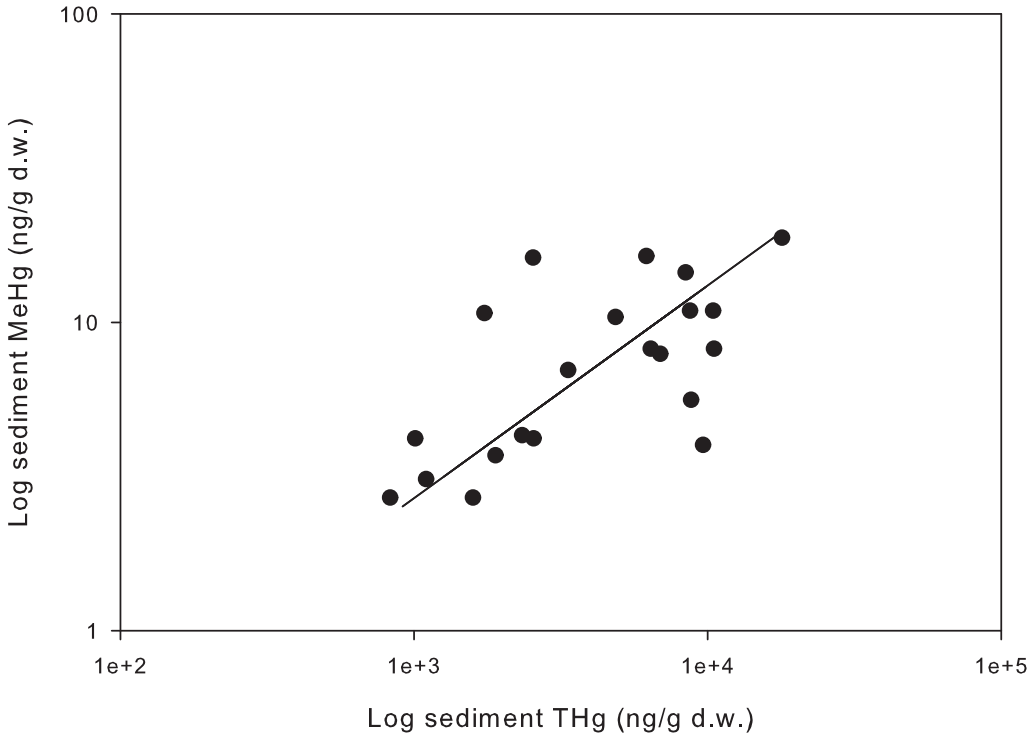

Figure 3.10: Log sediment methylmercury concentration (MeHg) versus log sediment total mercury (THg) (r=0.65, p=0.0016, n=21).

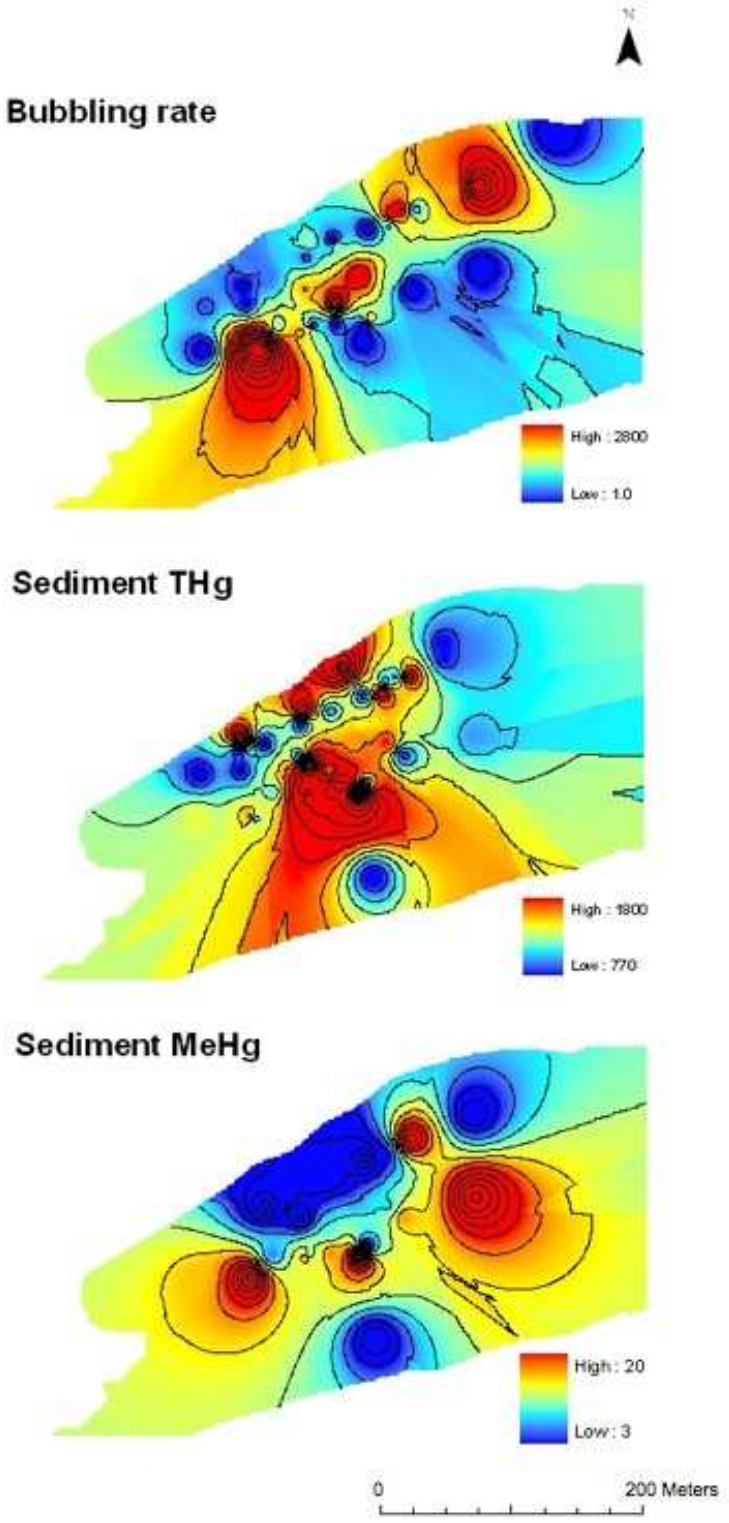

Figure 3.11: Surface representation of bubbling rates (ml/m^2/day) and sediment total mercury (THg) and methylmercury (MeHg) concentrations (ng/g d.w.).

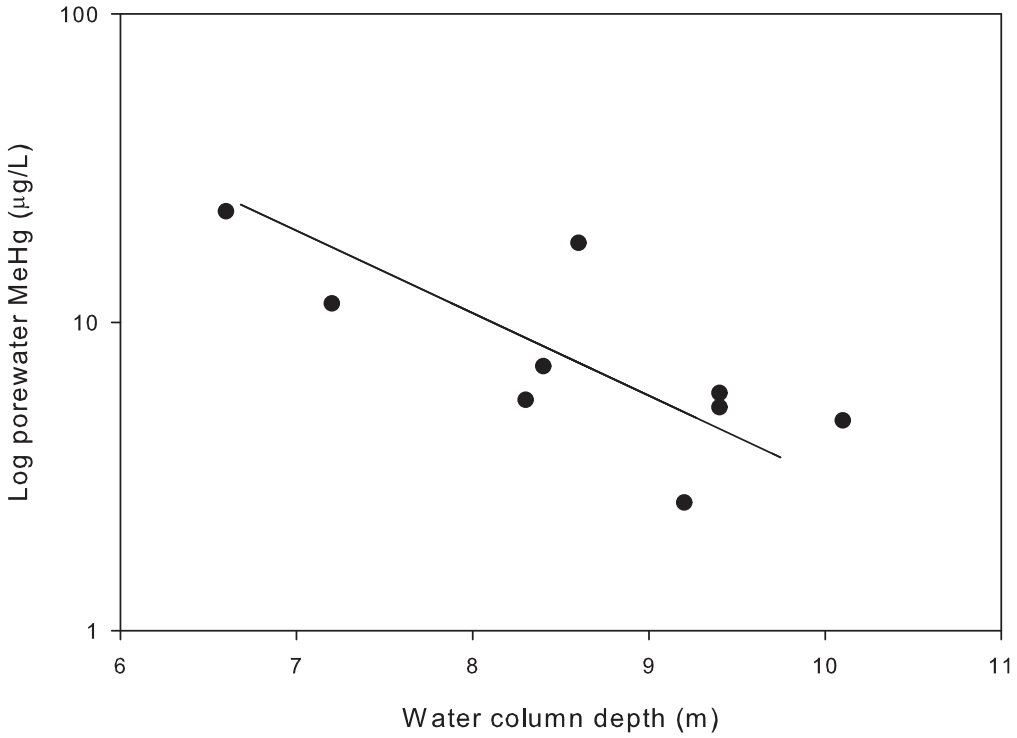

Figure 3.12: Log porewater methylmercury (MeHg) versus water column depth (r=0.73, p=0.025, n=9).

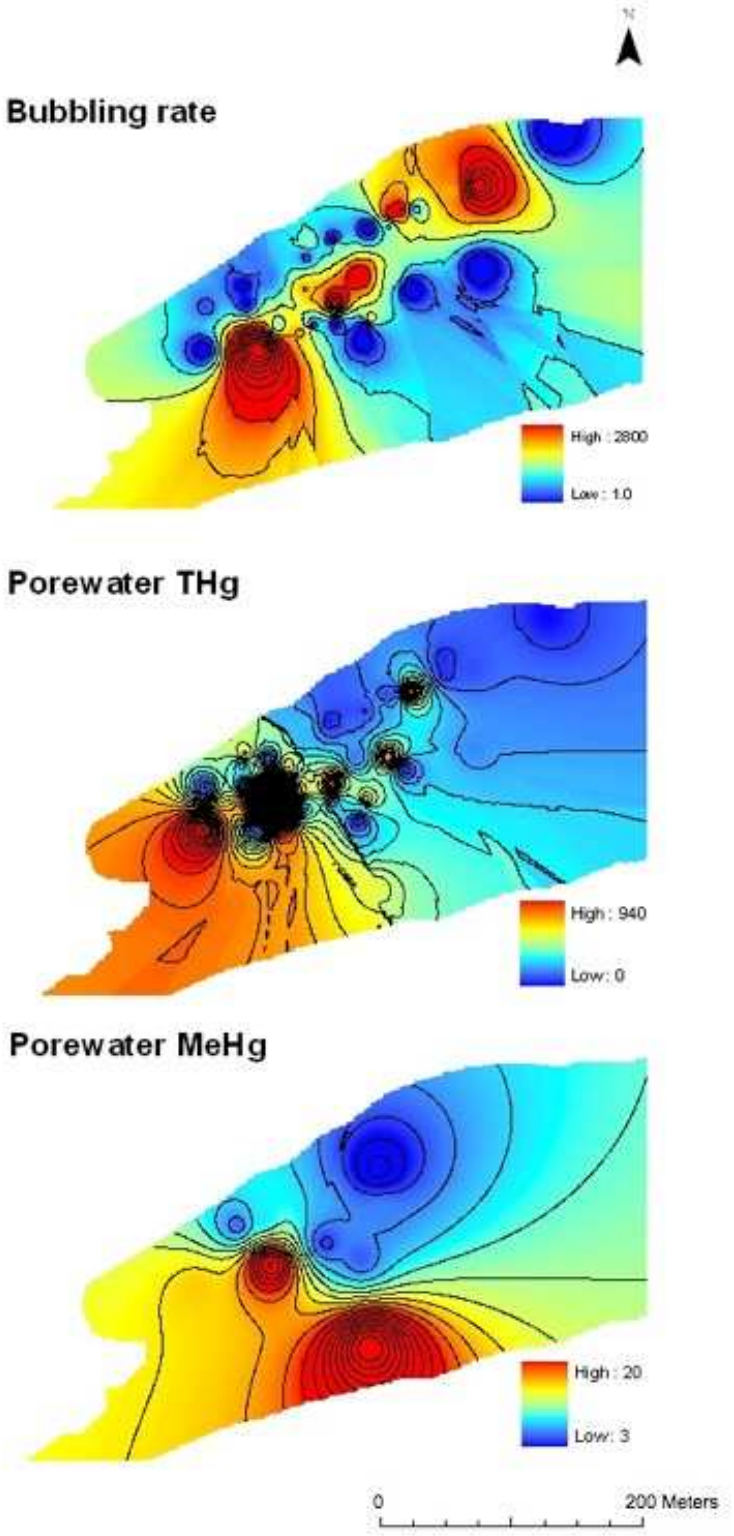

Figure 3.13: Surface representation of bubbling rates (ml/m^2/day) and porewater total mercury (THg) and methylmercury (MeHg) concentrations (μg/L).

Table 3.1: Summary of correlation coefficients. Comparisons with residuals that did not follow a normal distribution were not included here (see Appendix F). Significant p-values are highlighted in bold.

Variable		r	p	n
$\%CH_4$ in gas	Depth	0.49	**0.018**	23
	Bubbling rate	0.73	**0.0001**	22
Amphipod abundance	Depth	0.40	**0.015**	37
	Temperature	0.41	**0.012**	37
	Bubbling rate	0.62	**< 0.0001**	36
	$\%CH_4$ in gas	0.45	**0.035**	23
Amphipod [THg]	Depth	0.20	0.23	38
	Temperature	0.22	0.16	38
	Bubbling rate	0.14	0.44	37
	Sediment [THg]	0.32	0.066	34
	Sediment [MeHg]	0.10	0.62	21
	%Sediment MeHg	0.47	**0.031**	21
	Porewater [MeHg]	0.00	0.92	9
	%MeHg porewater	0.51	0.16	9
Amphipod [MeHg]	Depth	0.58	**0.004**	23
	Temperature	0.62	**0.002**	23
	Bubbling rate	0.17	0.45	23
	$\%CH_4$ in gas	0.24	0.45	12
	Amphipod [THg]	0.20	0.39	23
	Porewater [THg]	0.51	**0.019**	21
	Porewater [MeHg]	0.82	**0.011**	8
	%MeHg porewater	0.24	0.57	8
	Sediment [THg]	0.10	0.71	21
	Sediment [MeHg]	0.00	0.95	21
	%MeHg sediment	0.00	0.86	21
%MeHg amphipods	Depth	0.14	0.57	23
	Temperature	0.41	**0.048**	23
	Bubbling rate	0.24	0.25	23
	%CH4 in gas	0.10	0.59	22
	Porewater [THg]	0.10	0.60	21
	Porewater [MeHg]	0.70	**0.052**	8
	%MeHg porewater	0.65	0.08	8
	Sediment [THg]	0.36	0.10	21
	Sediment [MeHg]	0.00	0.99	21
	%MeHg/THg sediment	0.36	0.11	21
Porewater [THg]	Depth	0.00	0.92	34
	Temperature	0.14	0.38	34
	Bubbling rate	0.00	0.86	34
	%MeHg sediment	0.26	0.25	21
Porewater [MeHg]	Depth	0.73	**0.025**	9
	Temperature	0.62	0.075	9
	Bubbling rate	0.17	0.68	9
	Sediment [THg]	0.35	0.36	9
	Sediment [MeHg]	0.00	0.91	8
	%MeHg sediment	0.69	0.06	8
	Porewater [THg]	0.51	0.16	9
%MeHg porewater	Sediment [THg]	0.65	0.06	9
	Sediment MeHg	0.70	**0.055**	8
	%MeHg sediment	0.60	0.12	8
Sediment [THg]	Temperature	0.45	**0.0083**	34
	Bubbling rate	0.00	0.84	34
	$\%CH_4$ in gas	0.20	0.39	22
Sediment [MeHg]	Depth	0.22	0.33	21
	Temperature	0.26	0.25	21
	Bubbling rate	0.36	0.11	21
	$\%CH_4$ in gas	0.14	0.62	12
	Porewater [THg]	0.14	0.57	21
	Sediment [THg]	0.65	**0.0016**	21
%MeHg sediment	Bubbling rate	0.37	0.09	21
	$\%CH_4$ in gas	0.10	0.75	12

Table 3.2: Summary of correlation coefficients for bulk sediment characteristics. BD and L.O.I. denote bulk density and loss on ignition, respectively. Comparisons with residuals that did not follow a normal distribution were not included here (see Appendix F).

Variable	Sediment characteristic	r	p	n
Amphipod [THg]	BD	0.00	0.71	23
	L.O.I.	0.22	0.29	25
	%water	0.00	0.83	26
Amphipod [MeHg]	**L.O.I.**	**0.57**	**0.035**	**14**
Porewater [THg]	BD	0.24	0.26	22
	L.O.I.	0.24	0.23	25
	%water	0.24	0.22	25
Sediment [THg]	L.O.I.	0.14	0.48	25
	%water	0.32	0.13	25
Sediment [MeHg]	BD	0.36	0.27	11
	L.O.I.	0.35	0.23	14
	%water	0.32	0.28	14
Amphipod abundance	BD	0.00	0.90	23
	L.O.I.	0.00	0.74	25
	%water	0.00	0.96	26

Table 3.3: Summary of regression models using geographic location (Easting, Northing) as independent predictor variables. Tables with coefficients provided below.

Regression	R^2	SS	df	Mean square	F	Significance level	Standard error
MeHg amphipod[a]	.53	8314.255	2	4157.128	11.116	.001	19.338
THg porewater[b]	.38	329095.113	2	164547.557	9.758	.000	131.817
MeHg porewater[c]	.93	351.931	2	175.966	40.445	.000	2.086
Depth[d]	.39	21.702	2	10.851	11.220	.000	0.9834

a.

Model	B	Standard error	Significance level
(Constant)	-63189.02	55332.860	0.267
Easting	-0.202	0.052	0.001
Northing	0.034	0.010	0.004

b.

Model	B	Standard error	Significance level
(Constant)	550804.817	363521.248	0.140
Easting	-1.492	0.338	0.000
Northing	0.046	0.070	0.520

c.

Model	B	Standard error	Significance level
(Constant)	-23437.630	6305.706	0.010
Easting	-0.050	0.008	0.001
Northing	0.010	0.001	0.000

d.

Model	B	Standard error	Significance level
(Constant)	2415.606884	2706.519	0.378
Easting	0.010	0.002	0.000
Northing	-0.001	0.001	0.008

Chapter 4

Discussion

4.1 Hg in abiotic and biotic compartments in Zone 1

Of the factors I investigated, bubbling rate and sediment Hg appear to have little direct effect on amphipod Hg burden. In contrast, it appears that porewater transport is an important uptake pathway. Also, sediment organic matter likely mediates the fraction of Hg that is in bioavailable form. Indirect pathways through sediment resuspension, and other food sources require further investigation. I have thus identified potentially important drivers of Hg to a benthic species at my study site. These findings will aid the design of future research investigating causes of elevated Hg in biota of Zone 1.

Numerous confounding factors exist at my study site. Differences in Hg content (both THg and MeHg) in sediments and porewaters, depth, substrate type, wood fibre deposits (location and type), bubbling rates, current direction and speed, vegetation and human use are prevalent. Seasonal differences occur in both the abiotic and biotic matrices, adding further complexity. Obviously interactions occur among these environmental variables. Therefore, despite my conclusion that Hg in porewaters appears to be the most efficient transport route, amphipod Hg burden is not independent from all other factors. For example, I observed that the concentration of MeHg in sediments was related to the THg content. In turn, the ratio of MeHg/THg in sediments possibly affected the presence of MeHg in the sediment porewater. Therefore,

although I observed no direct relationship between sediment and amphipod Hg, the former is still involved in the process of Hg transfer to biota. I consider these kinds of interactions within this discussion because they are important in the cycling of Hg *in situ*.

4.1.1 Sediment Hg is not the limiting factor in benthic uptake

The Zone 1 paradox may result from a sampling artifact. The findings reveal THg concentrations in surficial sediments of Zone 1 higher than expected. However, it is apparent that a larger sampling effort was undertaken at Zone 2 compared to Zone 1 since studies began in the 1970s (Table 4.1). Similarly, in both of the most recent studies, sediment concentrations in Zone 1 (Grapentine et al., 2003; T. M. Delongchamp, 2006, Table 4.1) were also based on small sample sizes due to the nature of the question they were addressing (comparing amongst zones in the AOC). I was able to gather a comparatively larger sample size since I needed to characterize the bubbling rates in the highly heterogeneous sediments of Zone 1. The findings support the idea that differences between Zone 1 and 2 are not a result of differences in THg concentrations in sediments.

In addition to the number of samples collected, the amount of sediment may be an important determinant of the final concentrations obtained. For instance, I measured a larger range of MeHg concentrations in sediments than those measured previously by Grapentine et al. (2003) within Zone 1, although % MeHg in sediments was comparable (Table 4.2). However, MeHg concentrations have been recorded at nearly 2.5 times my highest concentration, resulting in very large ratios of MeHg in sediments (T. M. Delongchamp, 2006, Table 4.2). The difference observed in all three studies is likely due to the layers of sediments that were measured. The very high concentrations recorded in the top layer (0-1 cm) by Delongchamp (2006) suggests

that MeHg production is highest directly at the SWI in Zone 1. The latter study also concluded that MeHg production was highest in Zone 1. This was likely not evident before because the quantification of MeHg in bulk surface layers (i.e. 0-5 or 0-10 cms, Table 4.1) may have diluted the high concentrations at the SWI. Characterization of the SWI (between 1-2 cms of the surface sediment) is required to fully understand uptake patterns of MeHg in Zone 1 biota.

It is believed that chemical and biological cycling at the SWI mediates the flux of MeHg (Gill et al., 1999). MeHg is produced by SRB in surficial sediments (Korthals and Winfrey, 1987). The SWI is often found to coincide with the redox boundary layer, where highest rates of methylation are recorded (Korthals and Winfrey, 1987; Ullrich et al., 2001). Furthermore, MeHg production was observed to increase 2-3 fold after a decrease in pH at the SWI under aerobic conditions (Miskimmin, 1991). The SWI also receives input from particulates in the water column which can act as substrates for bacteria. Finally, benthos live at the SWI, as deeper sediments become too anoxic to support invertebrate life. These reasons further highlight the potential for MeHg availability to be higher within the top surface sediment layer.

The extent of THg contamination in Zone 1 surficial sediments remains significant, and equivalent to Zone 2. This finding supports a new formulation of the Zone 1 paradox: why, despite similar sediment THg concentrations in Zone 1 and 2, are Hg concentrations in biota greater in Zone 1? The answer to explain the greater bioavailability of Hg in Zone 1 may lie in elevated production of MeHg at the SWI in Zone 1. Future research should focus on determining differences of MeHg production at the SWI between Zone 1 and 2.

4.1.2 Porewater Hg is highly bioavailable

The concentrations of MeHg in porewaters were also high in Zone 1, confirming other recent findings (T. M. Delongchamp, 2006; Canario et al., 2008). My mean

concentrations were higher than recorded by Delongchamp (2006), but likely because I found a larger range due to the larger sample size. Nevertheless, both of our studies found ratios of MeHg in porewaters up to 60%. Similarly, observations of nearly 80 %MeHg have been made in porewaters in May at Lavaca Bay, Texas (Gill et al., 1999). These high concentrations have important implications for benthic organisms.

Hg can enter aquatic organisms in the aqueous phase via passive (diffusion) or energy dependent methods. It is known that Hg binds strongly to gills (Klink et al., 2005). In water with low DOC, observations of significant direct accumulation of Hg and MeHg from the aqueous phase were made in fish (Pickhardt et al., 2006). Although the latter study found that ultimately diet was the primary contributor of Hg, emphasis was placed on consideration of both factors. Furthermore, MeHg in the aqueous phase can be passively taken up by dead organic matter (Lock, 1975), a food item of detrivores such as the amphipod. Therefore, I expect elevated bioavailable Hg in porewater will be an important vector of Hg uptake to benthos in Zone 1.

4.1.3 Amphipod MeHg is more explanatory than amphipod THg

Concentrations of THg in amphipods were similar to those recorded previously in the AOC (Grapentine et al., 2003; Yanch, 2007, Table 4.3). Yanch (2007), however, observed a higher mean THg concentrations in amphipods collected in Zone 1. The difference may be due to the collection method: amphipods I measured were from the wild and had not yet passed through the digestive tract of the fish. It is also possible that fish are feeding in certain habitats which correspond to higher Hg availability sites, such as the littoral zone, where periphyton is abundant on macrophyte beds or on rocks. This material has been found recently to be an important source of MeHg (Desrosiers et al., 2006). In fact, the highest concentrations of Hg recorded in amphipods along the waterfront were found by Filion and Morin (2000) in am-

phipods living in macrophyte beds in shallow areas of Zone 1. THg concentrations in amphipods were not related to environmental variables measured in my study.

The lack of clear relationships between amphipod THg and other environmental variables could result from sediment particles remaining in the guts of the amphipods. This would cause a misrepresentation of the actual body burden of THg. For example, MeHg concentrations in amphipods were not related to their THg concentrations (Table 3.1). Depuration of amphipods prior to analyses can change the concentrations obtained (Martin, 2008). In my collection devices, it is feasible that amphipods, once separated from sediments, were excreting ingested sediment particles; thus collection baskets would be acting as depuration devices. Rock baskets were observed underwater by divers to collect plant debris. Since amphipods are known to exploit a range of food sources, this plant material could be important in determining the Hg burden of the amphipods. The exposure to Hg may differ depending on the preferred food source of the animals (sediments vs. plant material). The accumulation of suspended particulates and growth of periphyton on rock baskets could increase the availability of MeHg. It is feasible that amphipods collected using rock baskets are therefore less exposed to sediment THg than those that were collected by other means, altering correlations I might see with its environment.

In contrast, I found several correlations between environmental variables and amphipod MeHg burden. This is likely because this form is more readily assimilated in animal tissues (Huckabee et al., 1979; Pickhardt et al., 2006), thereby more accurately reflecting exposure. Since toxicological problems with Hg arise from MeHg, it is recommended that effort be placed in monitoring this chemical form (Wiener et al., 2007). I therefore focus on the MeHg burden in amphipods for the remainder of the discussion.

In Zone 1, amphipods represent an important vector of Hg to fish because of their high MeHg content. A wide range of ratios of MeHg in amphipods were found

(10-85%), suggesting they are exploiting many different functional feeding groups. For instance, (Tremblay et al., 1996) found MeHg/THg ratios were 20-25 % in detritivores, 30-40% in grazers and 60-85% in grazer-predators. I recorded a maximum ratio of 85%, much higher than was seen before (Table 4.3). This also suggests that Zone 1 amphipods are exposed to highly bioavailable Hg, as %MeHg/THg ratios in amphipods have been previously recorded between 35-70 % in the Idrijca River, Slovenia, one of the most highly contaminated waterways in the world (Žižek et al., 2007). These high ratios highlight the need to understand factors leading to such elevated body burdens.

In summary, concentrations of Hg in abiotic and biotic compartments of Zone 1 remain elevated. These concentrations are not static or homogenous, however, as temporal and spatial variations are also at play. This is especially true of the availability of MeHg, as production by methylating bacteria is largely mediated by changes in temperature. Thus, space and time are important considerations of MeHg availability to benthos.

4.2 Amphipod Hg uptake is related to spatial and temporal determinants of Hg availability in Zone 1

The environmental factors I investigated were chosen because sediments and porewaters represent sources of Hg to the aquatic environment. Bubbling was hypothesized to enhance the availability of contaminated dissolved and particulate compounds to benthos, such as amphipods. The Hg body burdens of the amphipod should be a reflection of their location within the zone and their exposure to these sources.

4.2.1 Bubbling may be structuring amphipod habitat

Bubbling may have an indirect effect on Hg burden, given the strong negative correlation I saw between amphipod abundance and bubbling distribution. By structuring the habitat, bubbling could influence possible exposure to Hg. Alternatively, this unexpected result may be confounded by sediment bottom type. Amphipods avoid bare substrate (Starry et al., 1998), and seek out interstitial spaces among zebra mussels (Duggan and Francoeur, 2007) and rocks (Dermott et al., 1998). Amphipods show improved growth under these conditions, given that they are sheltered from predation and abiotic factors such as flow (Franken et al., 2006). Furthermore, certain sediment size particles, such as sand, cause increased activity and consumption of oxygen in amphipods. This results in greater feeding rates that often do not make up for the higher metabolic costs of living in sand (Franken et al., 2006). Since the majority of Zone 1 is believed to be covered by hard bottom type (%76), it is possible that bubbling was higher in areas that are already avoided by amphipods, or that higher amphipod densities exist in the narrower range of locations with softer bottom substrate. It is also possible, however, that amphipods avoid conditions which are conducive to high bubbling activity, namely anaerobic sediments. The production and release of gas itself may make the habitat unfavorable to amphipods. These hypotheses need further validation in field or laboratory studies. At present, I will assume that amphipods are distributing in the Zone as they would irrespective of bubbling, supposing bare bottom sites would be avoided in preference of protected habitats. Therefore, I conclude that patterns of Hg uptake in amphipods are independent of the distribution of bubbling until further studies are conducted.

4.2.2 MeHg uptake/exposure is greater in shallower areas of Zone 1

Amphipod MeHg was positively related to spatial and temporal variations in concentrations of porewater Hg. Spatial evidence indicates a possible Hg hotspot for porewater and amphipods (Figure 3.9 and Figure 3.13), confirmed by surface trend analyses (Table 3.3). Amphipod MeHg did not correlate with bubbling rate or sediment Hg. Thus, I believe porewater MeHg is an important driver in transfering MeHg in the Zone 1 food web.

Porewater is not generally thought to be an important uptake route of Hg to aquatic biota (Hall et al., 1997; Lawrence and Mason, 2001). Field experiments show uptake from the aqueous phase is approximately 15% (Hall et al., 1997). Concentrations of MeHg in the water column used in that study were chosen to mimic those found in natural waters (0.8-2.1 ng/L; Hall et al. (1997). In contrast, the concentrations of MeHg I measured in porewaters were between 2-23 ng/L, suggesting that the availability of MeHg at my site is elevated, and the potential for uptake across gills probably higher in amphipods. Using Hg concentrations closer to the ones I observed in the porewaters of Zone 1, Pickhardt et al. (2006) showed considerable uptake of inorganic Hg from the aqueous phase. Mason and Lawrence (1999) also calculated that the accumulation of MeHg from the water column was an important contributor to the food chain in the Chesapeake Bay. Although the dominant contributor of MeHg to aquatic organisms is still through the diet, contributions from water should not be ignored (Post et al., 1996; Pickhardt et al., 2006). The similar patterns in porewater and amphipod Hg indicate a probable dependence on a similar factor.

The OM content of sediments may be responsible for the spatial patterns observed. Increasing organic content with depth may explain patterns of MeHg uptake in amphipods, since neither bubbling nor any other sediment characteristic I mea-

sured showed a trend with depth. Furthermore, the organic content in Zone 1 shows a large range of concentrations, reaching very high levels. Studies have confirmed that high OM content in sediments decreases bioavailability of Hg. For example, the transfer of MeHg was greater from sediments to biota in a lake with low OM content relative to a reservoir with high OM content (Tremblay et al., 1996).

Organic matter content can also influence the methylation potential of sediments. Korthals and Winfrey (1987) found that methylation/demethylation (M/D) ratios in sediments varied with water column depth. For example, in surficial sediments (0-7 cm) they found an M/D ratio of 5.3 at a water depth of 7.5 m, compared to an M/D ratio of 1.4 at a water depth of 10.5 m. The difference in ratios was attributed to greater demethylation, which was significantly and positively related to % carbon (Korthals and Winfrey, 1987). Recent evidence shows that organic matter controls the availability of Hg by regulating the partitioning of Hg(II) between particle and dissolved phases (Hammerschmidt and Fitzgerald, 2004). Potential gross rates of Hg methylation, assayed by experimental addition of ^{200}Hg to intact cores, showed that when the proportion of Hg(II) was greater in the porewater phase, ^{200}Hg methylation was enhanced (Hammerschmidt and Fitzgerald, 2004). Thus, sediments with less OM in Zone 1 should have proportionally more Hg (II) in the aqueous phase, enabling more MeHg to be produced.

In summary, porewater MeHg availability appears important to amphipod Hg uptake. In addition, Zone 1 displays high OM content in sediments. Bioaccumulation factors for invertebrates were found to be best explained in terms of sediment organic content (Mason and Lawrence, 1999). Once sediment particles are in the gut, those with high OM content prevent the release of MeHg, thus limiting the bioaccumulation from sediment bound particles (Lawrence et al., 1999). Therefore the spatial distribution of areas in Zone 1 with low OM may also correspond to the sites with greatest bioavailability, since these sites may allow for greater MeHg production, and

greater retention of MeHg by the benthos.

4.2.3 MeHg uptake/exposure is linked to temperature

Similar temporal trends were evident between porewater and amphipod MeHg concentrations, further supporting a relationship between the two variables. The concentration of MeHg and %MeHg in amphipods was significantly and negatively related to temperature, with highest concentrations of MeHg in June samples. In the case of porewater, I did not measure detectable levels of MeHg in the warmest summer months. Goulet et al. (2007) found that % MeHg was higher in porewaters where sulfate was consumed. It is possible that the availability of sulfate for methylation was limited in the later summer months or that sulfide levels had become limiting. Hammerschmidt and Fitzgerald (2004) suggested that different microbial communities can account for the lack of methylation activity under otherwise suitable conditions (fresh OM input, increased temperatures) for the process. It is possible that bacterial communities other than SRB dominate in the later summer months in Zone 1. I acknowledge that these observations are made on small sample sizes. However, ignoring these trends would risk missing important clues which aid in deciphering patterns in this complex interaction of environmental variables. Future studies should control specifically for seasonal differences in Zone 1.

4.3 Effect of bubbling in Zone 1

If direct correlations existed between bubbling and Hg content in both sediments, porewaters and amphipod Hg, I could conclude that bubbling activity was having an effect on Hg cycling in Zone 1. However, no significant regressions were found between amphipod Hg and bubbling, nor between any possible vector of Hg, such as sediments or porewaters. Therefore, my data support my null hypothesis that bubbling is not

creating differences in Hg concentrations in amphipods, sediments or porewaters.

4.3.1 Variability in bubbling rates

The inconsistency I observed in bubbling rate could obscure relationships with other variables. The range of recorded rates should have improved my chances of seeing an effect, and yet none were apparent. This was despite the relatively large data set I accrued within a small spatial scale.

Variable rates can originate from several sources. Different grain sizes and bottom types in Zone 1 are well documented by previous studies (Biberhofer and Rukavina, 2002). Furthermore, visual inspection confirmed differences in the quantity and size of bark chips even within replicate cores at the same site. This observation is supported by a large range of sediment organic matter found at my study site (5-43%). In addition, the lack of a clear relationship between bubbling rate and organic matter content in the surficial sediments illustrates that the material being degraded is not always found in the upper 5 cm of sediments. Also, the quantity of accumulated sediment on top of the bark was not always consistent. This is in contrast to earlier reports stating that bark chips were covered by 10 cm of cleaner sediments (Biberhofer and Rukavina, 2002). The variation I observed suggests that there are different rates of sedimentation within Zone 1, so that older, more contaminated sediments are not always out of reach of surface-dwelling animals. Finally, different redox conditions in the surficial sediments also exist. The positive relationship between $\%CH_4$ gas and bubbling rate illustrates that there are some areas in Zone 1 that have more reduced sediments, which facilitates greater production of gas.

The difficulty with having such variability in rates is that the identification of general areas exhibiting high and low bubbling rates is not easy, which would otherwise facilitate a test in the field of uptake rates from these two different areas. Future studies may try comparing known locations of high bubbling in Zone 1 to equally

contaminated but low bubbling locations in Zone 2.

4.3.2 Bubbling does not play a major role in Hg availability in Zone 1

No trends were detected between THg and MeHg in porewater or amphipods and bubbling rates. A small trend of decreasing MeHg in sediments and bubbling rate is also likely not an important influence on the availability of MeHg to biota. However, subtle trends in the data with bubbling warrant closer examination, given that I know little about what to expect in terms of magnitude of an effect. I found very small trends of decreasing MeHg concentrations and %MeHg in sediments with bubbling activity (Table 4.1). The latter ratio is used to infer the pool of inorganic Hg that is bioavailable to the process of methylation, since methylation rate constants are linked with % MeHg in sediments (Sunderland et al., 2004; Krabbenhoft et al., 2007). This suggests that higher bubbling sites are not associated with the production of MeHg. Methanogens are responsible for the production of the methane gas, but are also capable of reductive demethylation in freshwater sediments under anaerobic conditions (Oremland et al., 1991; Marvin-Dipasquale et al., 2000). I observed greater methane release at higher bubbling sites, suggesting greater methanogenic activity in these areas. Methanogens and SRB are also capable of oxidative demethylation, a process that occurs primarily in surficial sediments. Bubbling creates vents that allow for the influx of overlying water into the sediment surrounding these structures (O'Hara et al., 1995). This could result in oxygen entering sediments and facilitating the oxidative degradation of MeHg. Either of these demethylation pathways could account for the lower ratio of MeHg in sediments observed at my study site with higher bubbling rates. Furthermore, there is experimental evidence that the activity of methanogens is important to the net methylation in Zone 1 sediments, as the inhibition of methanogens resulted in increases in MeHg production (L. Avramescu,

pers. comm., University of Ottawa). Overall, however, the change in % MeHg as a result of bubbling is small, since proportions are all below 1%. This is likely the result of high OM content in sediments. Therefore, I believe changes in Hg availability as a result of bubbling activity are negligible. Although in-place sediments are ingested by amphipods, I further support the conclusion that differences made by bubbling on sediment concentrations are minor, based on evidence that sediments are not the most important vector of Hg to amphipods (see discussion below). This highlights the importance of considering feeding in the uptake of Hg by amphipods. I maintain that bubbling is having minimal direct impact on the observed concentrations of Hg in amphipods.

4.3.3 Bubbling may have an indirect role in the Hg cycle through sediment resuspension

Instead, bubbling activity may be acting through indirect effects. Discounting the bubbling hypothesis may be premature without having first explored the movement and quantity of resuspended materials as a result of this activity. This is because amphipods are also filter feeders, thus the concentrations of Hg in this material represents a possible exposure route. Indeed my spatial results showing a possible hotspot of Hg in the southwest of my study site could be interpreted as follows: patterns of water flow (back eddies) may bring resuspended particles to shallower parts of the zone, depositing contaminated particulates or dissolved species in these areas. Other studies showed how the importance of the movement of resuspended particles can influence the MeHg content in surficial sediments. He et al. (2007) observed significant relationships between water column depth and sediment MeHg concentrations, as well as surficial porewater THg and MeHg concentrations. This was attributed to sediment focusing in their study sites, a phenomenon common to lake systems. It is the process of redistribution of sediments to deeper parts of the lake by the resuspen-

sion of particulates from wind and wave action (Haekanson, 1983). The data cannot decipher if such an indirect influence is occurring at my study site. I acknowledge that this in an important gap that must be addressed in future studies of Zone 1.

In contrast to bubbling rates, I saw that other environmental factors were significantly correlated with amphipod MeHg availability. Therefore, I believe that factors other than bubbling are exerting a greater influence on the cycling of Hg in Zone 1.

4.4 Conceptual model

I present a conceptual model (Figure 4.1) to show influences on the cycling of Hg in Zone 1. The model likely represents what is occurring in spring. As the summer progresses, activity of the SRB increases and as a result, so do concentrations of sulphide in sediments. This produces charged disulfide complexes which are less bioavailable, limiting MeHg production (Benoit et al., 1999).

Bioavailability of Hg to amphipods is influenced by the dissolved fraction over the particulate in my study. Indeed, recent observations that up to 90 % of Hg in the surface sediments is quickly remobilized into porewaters was made in the Cornwall AOC (Canario et al., 2008). Clearly, bathymetry is also an important factor in the presence of MeHg. I saw relationships with depth and amphipod and porewater MeHg, as well as with sediment OM. These spatial relationships are likely dependent on OM, as studies indicate that it is an important determinant of speciation of Hg between the dissolved and particulate phases. Thus I model porewater in greater proportions in shallower areas than in deeper parts of the site. At present, I do not know what influences the distribution of OM in the surficial layers of the sediments. I cannot rule out the possibility that bubbling activity may be involved through release of resuspended material. Currents in Zone 1 could also be playing a role in this redistribution, or these factors could be acting in tandem. A thorough investigation

of the role of porewater transport and OM distribution is therefore warranted in Zone 1.

Inorganic Hg is not a limiting factor because of elevated concentrations observed in surficial sediments throughout my study site. Instead, it appears that the bioavailability of Hg in Zone 1 to amphipods is regulated by physical and temporal characteristics of the zone.

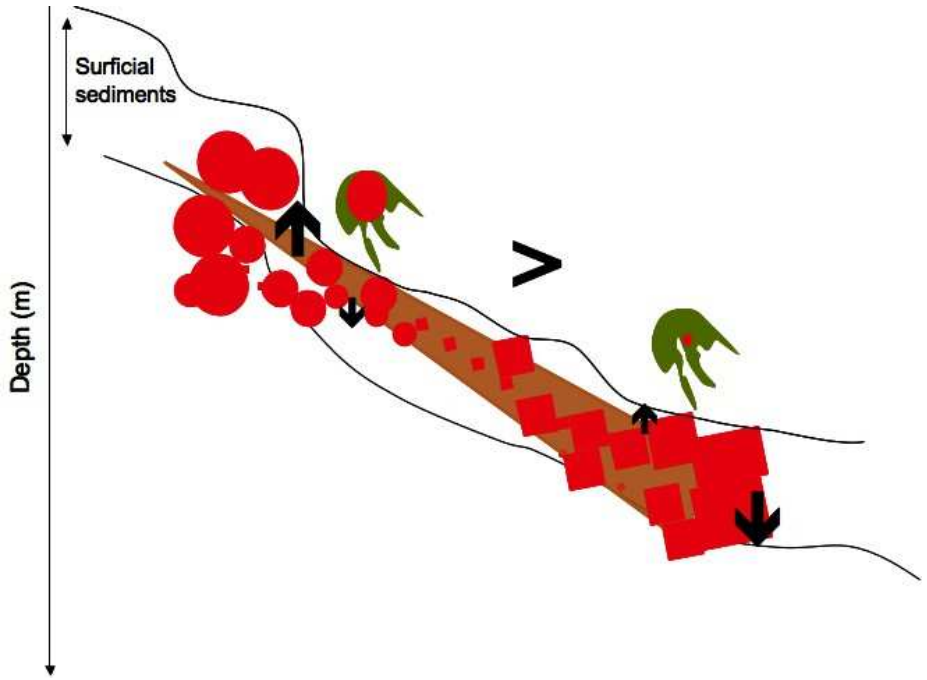

Figure 4.1: Conceptual model for Hg uptake in amphipods in Zone 1. Depth refers to water column depth. Circles represent Hg in porewaters, squares represent Hg in sediments. Scale of dots on amphipods represents the relative body burden of Hg for amphipods collected at different depths within the Zone. Extent of brown cone in the surficial sediments represents the organic matter content. As the organic matter content of sediments increases in the surficial sediments (top 5 cms) of Zone 1, is hypothesized that less MeHg is available in porewater. Instead, it is present in the particulate phase, thereby less bioavailable to amphipods at those locations.

Table 4.1: Minimum and maximum concentrations (mean and standard deviation provided if $n > 2$) of THg concentrations in sediments (μg/g dry weight). Note that the concentrations obtained in this study were from the combination of the top 5 cms of 3 separate cores (Table adapted from Richman 2001).

Study	Sampling year	n	Zone 1	n	Zone 2	Method
MOE (1979)	1970	6	0.85-14.5 (4.70± 5.37)	14	1.24-23.9 (9.07± 6.67)	7 cm surficial grab
MOE (1979)	1975	5	0.85-18.2 (6.91± 7.50)	36	0.55-44.0 (8.72± 9.28)	3 cm surficial grab
Kauss et al. (1988)	1979	4	1.5-19.8 (4.5)	6	0.13-18.0 (5.4)	3 cm surficial grab
Anderson (1990)	1985	2	0.63-0.90	6	0.25-4.40 (1.23± 1.60)	3 cm surficial grab
Richman (1994)	1991	1	3.26	6	0.98-3.13 (1.88± 1.29)	3 cm surficial grab
Richman (1996)	1994	-		63	0.01-13.8 (3.32± 3.47)	10 cm core sample
Richman (1999)	1997	3	0.79-1.71 (1.23± 0.46)	14	0.44-19.5 (4.84± 5.09)	10 cm core sample
Grapentine et al. (2003)	2001	4	0.38-1.65 (0.80± 0.6)	10	0.42-5.57 (2.25± 1.66)	10 cm mini-box core sample
Delongchamp (2006)	2004/5	3	0.56-0.73 (0.63± 0.09)	4	0.44-0.78 (0.57± 0.15)	1 cm core sample
This study	2007	36	0.77-17.9 (5.33± 4.56)	-	-	5 cm core sample

Table 4.2: MeHg concentrations in sediments (ng/g d.w.) in Zones 1 and 2 along the Cornwall waterfront.

		Grapentine et al. (2003)	Delongchamp (2006)	This study
Zone	Method	10 cm mini-box core	1 cm core sample	5 cm core sample
1	Sample size	4	3	23
2		10	4	-
1	[MeHg] range	1.28-5.35	34.49-45.47	2.7-18.8
2		0.72-4.81	9.41-18.58	-
1	[MeHg] mean	2.49 ± 1.92	39.7 ± 5.5	8.1± 4.8
2		2.64 ± 1.37	13.91 ± 3.87	-
1	% MeHg range	0.3-0.4	5-8	0.04-0.64
2		0.06-0.8	2-3	-
1	% MeHg mean	0.4	6.3	0.2
2		0.2	2.3	-

Table 4.3: Mean THg concentrations in amphipods (ng/g d.w.) in Zones 1 and 2 along the Cornwall waterfront. Mean of % MeHg also provided.

		Grapentine et al. (2003)	Yanch (2007)	This study
Zone	Collection method	Grab sample	Grey perch stomach	Artificial substrate
1	Sample size	1	19	40
2		5	5	-
1	[THg]	239	287±158	192±145
2		287	80 ± 45	-
1	%MeHg/THg	7.4	-	9.6-85.1
2		4.2-30.4	-	-

Chapter 5

Conclusions

5.1 Research question and approach

The observation of a paradox in sediment, fish and invertebrate Hg concentrations in Zone 1 motivated this study. Despite spatially averaged sediment THg concentrations in Zone 1 lower than those in Zone 2, fish and their prey items were significantly more contaminated in Zone 1 (Yanch, 2007; Fowlie et al., 2008). This could not be accounted for by differences in food chain length or rates of biomagnification between zones (Yanch, 2007). However, the presence of twice the amount of THg at the base of the Zone 1 food web suggested the availability of Hg is heightened in this Zone. Yanch (2007) proposed 2 causes for this observation: the greater presence of submerged aquatic vegetation and/or the significant methane ebullition from sediments.

This study investigated the role that gas bubbling has on the availability of MeHg to a benthic invertebrate in Zone 1. I also described the effect of bubbling on the concentrations of Hg in surficial sediments and associated porewaters, two known exposure routes to benthic invertebrates.

5.2 Summary of results

The following observations were made in this study:

1. Variability in bubbling rates was high, as was expected given the heterogeneity of sediment type, grain size, bark chip deposit, current direction, redox conditions and bathymetry in Zone 1;

2. Greater methanogenic activity exists at high bubbling sites as evidenced by the larger proportion of CH_4 in gas;

3. A large range of % MeHg was observed in amphipods, meaning that Hg availability within Zone 1 differs markedly, and that transfer of Hg to upper trophic levels through these organisms is substantial;

4. Bubbling activity was not significantly related to amphipod THg or MeHg burden. Therefore the effect of bubbling on amphipod Hg vectors I measured must be minimal;

5. The correlation between amphipod THg and sediment THg was non-significant, indicating that sediments are not a significant food source for amphipods, and/or that the high OM content in sediments hinders bioavailability of Hg to amphipods;

6. Significant regressions and spatial relationships between amphipod MeHg and porewater THg and MeHg concentrations highlight the importance of porewater as an exposure route to amphipods;

7. OM content of sediments likely plays an important role in the cycling of MeHg in Zone 1, based on evidence from the literature and the increasing trend with depth;

8. Decreases in porewater and amphipod MeHg throughout the summer season suggest that temporal fluctuations are important to consider.

I did not find that amphipod Hg uptake was related to bubbling activity in Zone 1, although, as discussed in the previous chapter, I cannot rule out bubbling until the effect of this disturbance on all the possible exposure routes is known. Nevertheless, my study found indications of other variables that have an important effect on amphipod Hg uptake. The following summary will address what needs to be done to further elucidate the complex relationship between the numerous biological, physical and chemical factors that ultimately influence invertebrate Hg uptake.

5.3 Future research

This study highlights the importance of large sample sizes even within a small area, especially when the variability in sediments is so high. Sediment characteristics, such as OM content, that are known to control Hg speciation, should always be assessed when studying Hg bioavailability. Furthermore, the extent of the active layer of methylation should be well characterized before sampling, in order to properly quantify the transfer of Hg to benthos. Important questions remain about the movement of resuspended material, seasonal effects and the importance of the littoral area to the Hg cycle of Zone 1.

5.3.1 Bubbling and Hg availability

I cannot rule out the possibility that Hg cycling in Zone 1 is influenced by bubbling activity, without assessing the effect on resuspension of particulates. The latter are a known food source to filter feeding invertebrates (Lawrence and Mason, 2001). Bubbling increased the particulate flux of THg in the water column of a mesocosm experiment (Kim et al., 2004). However, Hg release from these resuspended particles was minimal. Furthermore, the particulate flux of MeHg to the water column was lower compared to the control which experienced no resuspension, and dissolved concentrations did not change in tandem with changes in particulate flux (Kim et al., 2004). Nevertheless, the movement of resuspended particulates was offered as a way to explain spatial trends in surficial sediment and porewater Hg elsewhere (He et al., 2007). Resuspended material that is freshly deposited can be used as a substrate for methylation at the sediment-water interface. Future research should test the hypothesis that the movement of particulates via currents is creating hotspots for MeHg uptake within Zone 1.

5.3.2 Temporal variations

Temporal variations are important to the Hg cycle. The effect of temperature on Hg speciation and bioaccumulation is mainly attributed to its effect on microbial activity, thus controlling the rates of methylation and demethylation in aquatic systems (Ullrich et al., 2001). Usually maximum temperatures in mid-summer parallel highest MeHg production in aquatic systems. However, I observed a spring maximum in amphipod and porewater MeHg concentrations. This has been observed in other systems (Bloom et al., 1999), and was attributed to a spring methylation peak, with subsequent degradation of MeHg back to soluble Hg (II) throughout the summer months. The rate of decomposition of organic matter, and by extension the rate of bubbling, should vary with microbial activity. Future research should test explicitly for differences in Hg uptake at the same locations following a time series, to assess the impact of seasonal changes in Zone 1 Hg availability.

5.3.3 Alternate exposure sources

In light of the absence of a direct correlation between bubbling and amphipod Hg, other unique features of Zone 1 deserve closer attention. Specifically, the importance of submerged aquatic vegetation and periphyton/biofilm should be assessed as highlighted by Yanch (2007) in her concluding remarks. The significance of these biological components in Zone 1 is further supported by the observation that yellow perch become increasingly reliant on littoral food webs by mid-summer (Yanch 2007). A salient observation of Hg concentrations ten times higher than expected at a single site in Zone 1 sediments and a parallel observation of elevated uptake in macroinvertebrates taken from shallow littoral areas (0.5-1.1m; (Filion and Morin, 2000), reinforces the idea that these areas may represent important sites of MeHg production. Indeed, periphyton associated with macrophyte beds can be large repositories

of Hg (Desrosiers et al., 2006) and aquatic plants are capable of efficient uptake of Hg from water (Skinner et al., 2007). It is imperative that the question of how the plant community influences Hg cycling in Zone 1 be addressed.

5.4 Study implications for the Cornwall AOC

5.4.1 Zone 1 'paradox'

A review of 30 years of sediment concentrations in the Cornwall AOC concluded that higher spatially averaged THg concentrations existed in Zone 2 compared to Zone 1 (Richman and Dreier, 2001). Therefore, a similar pattern was expected from the biota. Surprisingly, the pattern that emerged was the opposite; Zone 1 fish and their prey items were significantly more contaminated than other zones in the AOC (Yanch, 2007; Fowlie et al., 2008).

This study found THg concentrations in surficial sediments that have not been recorded in Zone 1 since the late 1970s. I suggested that this is most likely an artifact of sampling effort, and that concentrations of THg are in fact alike in Zone 1 and 2. If this is the case, the paradox still remains, though slightly modified: why, despite similar concentrations of THg in surficial sediments, is increased bioavailability of Hg observed in Zone 1? I have identified porewater as a possible driver of Hg availability in Zone 1. Similar data needs to be collected in Zone 2 to determine what differences exist in porewater MeHg production between the two zones. This study was the first to examine the effect of bubbling rate on amphipod Hg uptake. I did not find a direct correlation. However, it would be premature to discount the hypothesis without further study into other possible interactions of bubbling as discussed above. The alternative hypothesis that the macrophyte community in Zone 1 is increasing the availability of MeHg must also be assessed. In any case, the likelihood of catching a yellow perch above the consumption guidelines remains highest in Zone 1 in all of

the Cornwall AOC (Fowlie et al., 2008). Furthermore, year round use of this spot for fishing by residents and visitors of the Cornwall area increases the concern about exposure to Hg in fish. Special research focus on Zone 1 should continue before decisions to delist are made.

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Appendix A

Amphipod Hg concentrations

Table A.1: Amphipod mercury (Hg) concentrations (ng/g d.w.) in Zone 1 collected between June and September 2007.

Sample ID	Total Hg			Methyl Hg			%MeHg
	Average	SD	% CV	Average	SD	% CV	
2007-JUN-1-RB1	154.2	74.8	48.5	-	-	-	-
2007-JUN-1-RB2	126.8	16	12.6	54.6	-	-	43.1
2007-JUN-1-RB3	141.7	47.8	33.7	120.6	-	-	85.1
2007-JUN-1-RB4	255.3	25.4	9.9	146.9	6.6	4.5	57.5
2007-JUN-1-RB5	109.1	44.1	40.4	-	-	-	-
2007-JUN-1-RB7	260.3	95	36.5	74.4	6.2	8.3	28.6
2007-JUN-1-RB8	200	69	34.5	92.9	28	30.1	46.5
2007-JUN-1-RB9	135.2	12	8.9	60.4	-	-	44.7
2007-JUN-1-RB10	116.6	11.2	9.6	83.1	-	-	71.3
2007-JUL-1-RB1	94.1	13	13.8	57.7	4	6.9	61.3
2007-JUL-1-RB2	515	135	26.2	57	-	-	11.1
2007-JUL-1-RB3	60.2	1.5	2.5	35	3.3	9.4	58.1
2007-JUL-1-RB4	531.5	101.1	19	71	-	-	13.4
2007-JUL-1-RB5	138.2	-	-	-	-	-	-
2007-JUL-1-RB6	192	29.7	15.5	61.6	1.8	2.9	32.1
2007-JUL-1-RB7	77.8	1.5	1.9	55.3	5.7	10.3	71.1
2007-JUL-1-RB9	105.3	6.6	6.3	27.6	-	-	26.2
2007-JUL-1-RB10	247	15.6	6.3	72.9	-	-	29.5
2007-JUL-1-RB11	235.1	-	-	-	-	-	-
2007-JUL-1-RB12	284.7	116.2	40.8	43.9	-	-	15.4
2007-AUG-1-RB1	174.3	46.4	26.6	51.1	-	-	29.3
2007-AUG-1-RB2	544.4	77	14.1	52.3	-	-	9.6
2007-AUG-1-RB3	596.1	28.5	4.8	105.4	-	-	17.7
2007-AUG-1-RB5	214.6	16.3	7.6	36.8	0.5	1.4	17.1
2007-AUG-1-RB6	112.6	27.3	24.2	56.8	-	-	50.4
2007-AUG-1-RB8	100.9	-	-	54.1	10.9	20.1	53.6
2007-AUG-1-RB9	335.1	40	11.9	49.9	3.4	6.8	14.9
2007-AUG-1-RB10	147.2	35.5	24.1	-	-	-	-
2007-AUG-1-RB11	159.2	33.1	20.8	56.9	-	-	35.7
2007-AUG-1-RB16	444.5	-	-	-	-	-	-
2007-AUG-1-RB17	103.9	4.6	4.4	56.6	2.1	3.7	54.5
2007-SEPT-1-RB2	97.2	2.4	2.5	-	-	-	-
2007-SEPT-1-RB3	144.3	16.3	11.3	-	-	-	-
2007-SEPT-1-RB4	71.2	11.4	16	-	-	-	-
2007-SEPT-1-RB5	76	12	15.8	-	-	-	-
2007-SEPT-1-RB6	69.8	2.8	4	-	-	-	-
2007-SEPT-1-RB8	84.4	2.3	2.7	-	-	-	-
2007-SEPT-1-RB9	73.4	2.3	3.1	-	-	-	-
2007-SEPT-1-RB11	86.5	3.2	3.7	-	-	-	-
2007-SEPT-1-RB17	82.1	5.2	6.3	-	-	-	-

Appendix B
Sediment Hg concentrations

Table B.1: Sediment mercury (Hg) concentrations (ng/g d.w.) in Zone 1 collected between June and September 2007.

Sample ID	Total Hg			Methyl Hg			% MeHg
	Average	SD	% CV	Average	SD	% CV	
2007-JUN-1-RB1	1201.1	127.8	10.6	-	-	-	-
2007-JUN-1-RB2	6899.1	494.4	7.2	7.9	0.3	3.8	0.11
2007-JUN-1-RB3	1009.1	20.3	2.0	4.2	0.8	19.0	0.42
2007-JUN-1-RB4	4855	481.2	9.9	10.4	0.1	1.0	0.21
2007-JUN-1-RB5	953.1	44.3	4.6	-	-	-	-
2007-JUN-1-RB7	8715	565.3	6.5	10.9	0.5	4.6	0.13
2007-JUN-1-RB8	3347.6	262.3	7.8	7	0.4	5.7	0.21
2007-JUN-1-RB9	1099.15	58.4	5.3	3.1	0.3	9.7	0.28
2007-JUN-1-RB10	829.8	21.4	2.6	2.7	0	0.0	0.33
2007-JUL-1-RB1	17911.1	327.3	1.8	18.8	1	5.3	0.1
2007-JUL-1-RB2	9650	1139.2	11.8	4	0.3	7.5	0.04
2007-JUL-1-RB3	-	-	-	-	-	-	-
2007-JUL-1-RB4	13090.1	1829	14.0	5.8	0.1	1.7	0.04
2007-JUL-1-RB5	1065.3	36.6	3.4	-	-	-	-
2007-JUL-1-RB6	1587.8	193.9	12.2	2.7	0.4	14.8	0.17
2007-JUL-1-RB7	2334.7	294.1	12.6	4.3	0.4	9.3	0.18
2007-JUL-1-RB9	1738.2	160.7	9.2	10.7	0.1	0.9	0.62
2007-JUL-1-RB10	6187	49.3	0.8	16.4	0.2	1.2	0.27
2007-JUL-1-RB11	868.9	8.4	1.0	-	-	-	-
2007-JUL-1-RB12	1894.7	238	12.6	3.7	0	0.0	0.2
2007-AUG-1-RB1	8787.2	228.7	2.6	5.6	0.4	7.1	0.06
2007-AUG-1-RB2	10505.6	496.6	4.7	8.2	0.5	6.1	0.08
2007-AUG-1-RB3	9069.2	613.8	6.8	6.1	0.4	6.6	0.07
2007-AUG-1-RB5	2556.1	211.7	8.3	4.2	1.5	35.7	0.16
2007-AUG-1-RB6	8415.4	34	0.4	14.5	0.1	0.7	0.17
2007-AUG-1-RB8	-	-	-	-	-	-	-
2007-AUG-1-RB9	6398.7	270.9	4.2	8.2	0.6	7.3	0.13
2007-AUG-1-RB10	14171.5	1897.6	13.4	-	-	-	-
2007-AUG-1-RB11	10434.9	1455.1	13.9	10.9	0.4	3.7	0.1
2007-AUG-1-RB16	11302.3	-	-	-	-	-	-
2007-AUG-1-RB17	2545	13.9	0.5	16.2	7.7	47.5	0.64
2007-SEPT-1-RB2	-	-	-	-	-	-	-
2007-SEPT-1-RB3	1365.2	185	13.6	-	-	-	-
2007-SEPT-1-RB4	766.7	93.5	12.2	-	-	-	-
2007-SEPT-1-RB5	3590.7	145.5	4.1	-	-	-	-
2007-SEPT-1-RB6	9012.9	478.7	5.3	-	-	-	-
2007-SEPT-1-RB8	2497.8	123.1	4.9	-	-	-	-
2007-SEPT-1-RB9	2687	225.2	8.4	-	-	-	-
2007-SEPT-1-RB11	-	-	-	-	-	-	-
2007-SEPT-1-RB17	2836.5	68.4	2.4	-	-	-	-

Appendix C
Porewater Hg concentrations

Table C.1: Porewater mercury (Hg) concentrations (μg/L) in Zone 1 collected between June and September 2007

Sample ID	Total Hg	Methyl Hg	% MeHg
	Average	Average	
2007-JUN-1-RB1	34.03	-	-
2007-JUN-1-RB2	119.92	5.9	4.9
2007-JUN-1-RB3	87.6	22.9	26.1
2007-JUN-1-RB4	221.24	11.5	5.2
2007-JUN-1-RB5	34.68	5.6	16.1
2007-JUN-1-RB7	36.08	-	-
2007-JUN-1-RB8	944.13	18.1	1.9
2007-JUN-1-RB9	96.87	5.3	5.5
2007-JUN-1-RB10	12.46	7.2	57.8
2007-JUL-1-RB1	40.83	-	-
2007-JUL-1-RB2	36.6	-	-
2007-JUL-1-RB3	-	-	-
2007-JUL-1-RB4	16.51	-	-
2007-JUL-1-RB5	4.61	-	-
2007-JUL-1-RB6	9.29	-	-
2007-JUL-1-RB7	12.37	-	-
2007-JUL-1-RB9	4.88	-	-
2007-JUL-1-RB10	14.3	-	-
2007-JUL-1-RB11	4.13	-	-
2007-JUL-1-RB12	58.8	-	-
2007-AUG-1-RB1	32.74	2.6	7.9
2007-AUG-1-RB2	51.04	-	-
2007-AUG-1-RB3	16.44	-	-
2007-AUG-1-RB5	11	-	-
2007-AUG-1-RB6	138.39	-	-
2007-AUG-1-RB8	-	-	-
2007-AUG-1-RB9	150.97	4.8	3.2
2007-AUG-1-RB10	77.5	-	-
2007-AUG-1-RB11	25.9	-	-
2007-AUG-1-RB16	92.06	-	-
2007-AUG-1-RB17	25.67	-	-
2007-SEPT-1-RB2	-	-	-
2007-SEPT-1-RB3	5.63	-	-
2007-SEPT-1-RB4	9.16	-	-
2007-SEPT-1-RB5	10.75	-	-
2007-SEPT-1-RB6	30.38	-	-
2007-SEPT-1-RB8	9.79	-	-
2007-SEPT-1-RB9	11.99	-	-
2007-SEPT-1-RB11	-	-	-
2007-SEPT-1-RB17	8.35	-	-

Appendix D
Sampling sites

Table D.1: Sampling site descriptions. Amphipod abundance is measured in units of individuals per paired rock basket.

Sample ID	Easting	Northing	Depth (m)	Amphipod abundance
2007-JUN-1-RB1	18521237	4984308	8.4	25
2007-JUN-1-RB2	18521303	4984294	9.4	106
2007-JUN-1-RB3	18521293	4984191	6.6	43
2007-JUN-1-RB4	18521158	4984237	7.2	68
2007-JUN-1-RB5	18521189	4984287	8.3	25
2007-JUN-1-RB7	18521240	4984254	10.9	-
2007-JUN-1-RB8	18521215	4984256	8.6	55
2007-JUN-1-RB9	18521286	4984261	9.4	31
2007-JUN-1-RB10	18521209	4984293	8.4	54
2007-JUL-1-RB1	18521282	4984255	10.2	307
2007-JUL-1-RB2	18521239	4984320	7.5	52
2007-JUL-1-RB3	18521428	4984403	11	107
2007-JUL-1-RB4	18521268	4984353	3	78
2007-JUL-1-RB5	18521347	4984370	9	82
2007-JUL-1-RB6	18521285	4984330	9	193
2007-JUL-1-RB7	18521369	4984364	9	158
2007-JUL-1-RB9	18521317	4984284	10.6	110
2007-JUL-1-RB10	18521198	4984238	5.5	144
2007-JUL-1-RB11	18521191	4984273	8	22
2007-JUL-1-RB12	18521236	4984284	8.5	83
2007-AUG-1-RB1	18521300	4984332	9.2	83
2007-AUG-1-RB2	18521242	4984256	10.2	57
2007-AUG-1-RB3	18521265	4984355	3	51
2007-AUG-1-RB5	18521260	4984318	8.9	81
2007-AUG-1-RB6	18521321	4984345	9	51
2007-AUG-1-RB8	18521280	4984244	10.2	816
2007-AUG-1-RB9	18521259	4984273	10.1	91
2007-AUG-1-RB10	18521243	4984277	9.5	54
2007-AUG-1-RB11	18521260	4984257	10.2	260
2007-AUG-1-RB16	18521191	4984297	7.8	9
2007-AUG-1-RB17	18521371	4984300	10.5	556
2007-SEPT-1-RB2	18521233	4984251	8.5	34
2007-SEPT-1-RB3	18521348	4984359	9.2	49
2007-SEPT-1-RB4	18521160	4984270	8	13
2007-SEPT-1-RB5	18521202	4984236	6.5	47
2007-SEPT-1-RB6	18521278	4984294	9.5	30
2007-SEPT-1-RB8	18521302	4984342	9.2	36
2007-SEPT-1-RB9	18521278	4984294	9.5	35
2007-SEPT-1-RB11	18521258	4984321	9	49
2007-SEPT-1-RB17	18521310	4984345	9.2	18

Appendix E
Sediment bulk characteristics

Table E.1: Sediment bulk characteristics. L.O.I. refers to loss on ignition.

Sample ID	Bulk density (g/cm^3)	% water content	% L.O.I.	Temp. (°C)
2007-JUN-1-RB1	-	-	-	18
2007-JUN-1-RB2	-	-	-	18
2007-JUN-1-RB3	-	-	-	18
2007-JUN-1-RB4	-	-	-	18
2007-JUN-1-RB5	-	-	-	18
2007-JUN-1-RB7	-	-	-	18
2007-JUN-1-RB8	-	-	-	18
2007-JUN-1-RB9	-	-	-	18
2007-JUN-1-RB10	-	-	-	18
2007-JUL-1-RB1	0.46	76.8	12.9	21.2
2007-JUL-1-RB2	1.22	72	6.4	21.2
2007-JUL-1-RB3	0.96	46.4	-	21.2
2007-JUL-1-RB4	0.85	75.3	15.1	21.2
2007-JUL-1-RB5	1.97	53.4	7.6	21.2
2007-JUL-1-RB6	1.65	44.3	5.5	21.2
2007-JUL-1-RB7	-	61.2	12.6	21.2
2007-JUL-1-RB9	-	79.1	43	21.2
2007-JUL-1-RB10	-	69.3	7.5	21.2
2007-JUL-1-RB11	0.9	48.3	16.1	21.2
2007-JUL-1-RB12	0.81	75.4	26.4	21.2
2007-AUG-1-RB1	1.42	58	18.1	22.7
2007-AUG-1-RB2	1.12	53.2	18.5	22.7
2007-AUG-1-RB3	1.23	74.2	14.4	22.7
2007-AUG-1-RB5	1.74	52.6	12.4	22.7
2007-AUG-1-RB6	0.5	74	42.8	22.7
2007-AUG-1-RB8	-	-	-	22.7
2007-AUG-1-RB9	1.73	49.9	17.6	22.7
2007-AUG-1-RB10	1.21	57.4	18.5	22.7
2007-AUG-1-RB11	2.31	71.9	21.2	22.7
2007-AUG-1-RB16	1.5	67.6	8.2	22.7
2007-AUG-1-RB17	1.65	46.6	14	22.7
2007-SEPT-1-RB2	-	-	-	19.8
2007-SEPT-1-RB3	1.82	41.6	9.3	19.8
2007-SEPT-1-RB4	1.44	72.9	9.4	19.8
2007-SEPT-1-RB5	0.67	80.3	33.2	19.8
2007-SEPT-1-RB6	2.55	53.8	14.6	19.8
2007-SEPT-1-RB8	1.51	57.6	12.5	19.8
2007-SEPT-1-RB9	1.41	47.8	14.6	19.8
2007-SEPT-1-RB11	-	-	-	19.8
2007-SEPT-1-RB17	1.2	50.5	12.5	19.8

Appendix F
Summary of comparisons that did not meet assumptions of normality

Table F.1: Summary of correlation coefficients that did not meet the assumption of normal distribution of the residuals. Significant p-values are highlighted in bold.

Variable		r	p	n
%CH_4 in gas	Depth	0.49	**0.018**	23
	Bubbling rate	0.73	**0.0001**	22
Bubbling rate	Depth	0.42	**0.009**	37
	Temperature	0.07	0.35	37
Amphipod [THg]	Porewater [THg]	0.36	**0.039**	34
Amphipod [MeHg]	Bulk density	0.00	0.91	12
	%water	0.00	0.99	15
Porewater [THg]	Sediment [THg]	0.42	**0.011**	34
%MeHg porewater	Depth	0.35	0.37	9
	Temperature	0.28	0.47	9
	Bubbling ratet	0.14	0.72	9
Sediment [THg]	Depth	0.22	0.189	34
	Bulk density	0.20	0.40	22
%MeHg sediment	Depth	0.00	0.93	21
	Temperature	0.26	0.25	21

Appendix G
Protocol for the Clean Hands/Dirty Hands method for water sampling

Designate one Clean Hands person and one Dirty Hands person prior to sampling. The Clean Hands person has the only contact with the sample bottle, while the Dirty Hands person operates anything which may contaminate the sample.

1. 3 CLEAN white buckets:

a. Clean with soap and water

b. Soak 10% conc. HCl for 20 minutes

c. Rinse with Reverse Osmosis (RO) water

d. Rinse with site water (x3)

e. Fill all 3 buckets with site water

2. Fill 3 different baskets 1 without rocks, 1 with institute rocks and 1 with quarry rocks. Then place each basket in a prepared bucket outdoors.

3. Wait 30 mins.

4. 6 CLEAN centrifuge tubes:

a. If already clean, soak in 10% HCl for 20 minutes

b. Rinse with RO water

c. Fill with RO water

d. Place in double-bagged Ziploc

e. Move outdoors

f. Empty RO water when ready to collect sample

g. Dip and ditch and dip sample with Clean Hands

h. Place in first Ziploc bag with Clean Hands, then place in second Ziplock with Dirty Hands

5. Place samples in a clean garbage bag with Dirty Hands and place in the cooler for transportation to the lab.

6. Bring to lab within 24 hours.